

THERMAL PROPERTIES AND FLAMABILITY BEHAVIOR OF AUTOMOTIVE POLYMERS

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ABSTRACT

The work described in this presentation is being conducted under the "flammability of materials" project which is part of the fire safety research program of March, 1995 General Motors/U.S. Department of Transportation Settlement Agreement. For this report twenty two components, consisting of seventy one polymeric parts used on a 1996 model year passenger van were studied.

A high resolution thermal gravimetric analysis (TGA) was used to determine thermal decomposition temperatures, and rates of decomposition. TGA runs were conducted in nitrogen and air atmospheres. For the different polymers investigated the ranges of decomposition temperatures were between 223°C and 552°C in nitrogen, and 240°C to 565°C in air.

Correlation was made between the thermal properties and the flammability characteristics quantified in this study. Ignition temperatures estimated from the Critical Heat Flux (CHF) values were about 14% higher than the decomposition temperatures from the thermal properties measurements. The experimental Thermal Response Parameter (TRP) values were about 28% higher than the TRP values calculated from thermal analysis. A rigorous correlation between the thermal properties and flammability characteristics of the plastics in components and parts of vehicles will be sought.

INTRODUCTION

Several complementary research projects for studying different aspects of the flammability characteristics of polymeric materials used in passenger vehicles and light trucks are being conducted at the National Institute for Science and Technology (NIST), Factory Mutual Research Corporation, and at the GM Global R&D Operations. Four segment leader vehicles were chosen for the investigation; namely: a passenger van, a utility sport vehicle, a front wheel drive vehicle and a rear wheel drive vehicle. This particular study deals with the investigation of thermal characteristics and flammability behavior of twenty two polymeric components used on a 1996 model year passenger van.

EXPERIMENTAL

Polymer Composition Analysis

The compositions of most of the polymeric parts chosen for this investigation were not known. A Nicole magnum-IR.550 Fourier transform infrared spectrometer (FTIR) was used to identify the nature of the polymer and in some cases identify the type of additive used. The amount of inorganic filler used in the polymer compositions was determined using thermal gravimetric analysis.

Qualitative and semi-quantitative elemental analysis of fillers was conducted by X-ray fluorescence spectroscopy. In some instances the crystalline structure of the filler, determined by X-ray diffraction, was used for identifying the filler type.

Thermal Gravimetric Analysis (TGA) was conducted using a TA 2100 controller (TA Instruments, Inc.). 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. All samples were heated from room temperature to 980°C. For each sample, decomposition temperatures and the maximum rates of decomposition were determined.

Modulated Differential Scanning Calorimetry (MDSC) was conducted using a TA 2920. Measurements were made at temperatures of -62°C to 270°C. The heating rate was set at 5°C/minute. The degree of modulation was set at $\pm 0.531^\circ\text{C}$, every 40 seconds. Glass transition temperatures, melting points, heats of fusion, and heat capacity values were all determined from these measurements.

Specific gravity values of all solid samples except foams were determined from weight in air and weight in water. For sponge samples the density was determined from measurements of weight and volume of uniform cylinders cut from these samples.

The Flammability Apparatus used in the study is shown in Figure 2.* The Apparatus consists of a lower and an upper section. The lower section is used to measure: time-to-ignition and mass-loss rate, as well as, visual observations of flame heights, smoke color, and fire propagation. The upper section, consisting of sampling duct and an exhaust pump, is used for measuring gas temperature, optical transmission through the product-air mixture flowing through the sampling duct, and concentrations of CO, CO₂, O₂, and total hydrocarbons.

The ignition tests were performed to determine Critical Heat Flux (CHF), defined as the externally imposed heat flux at or below which sustained piloted ignition does not occur, and the Thermal Response Parameter (TRP) which is an indicator of ignition time delay and relates the time-to-ignition to the net heat flux.

Ignition tests were performed in air under natural flow, with an external heat flux in the range of 20 to 60 kW/m². The sample was placed horizontally in the flammability apparatus. The time-to-ignition was taken as the time at which a self-sustained flame was observed. At the completion of the ignition test series, data for the time to ignition versus external heat flux were used to determine the CHF and TRP.

The combustion tests were performed in normal air under co-flow condition at a fixed external heat flux value of 50 kW/m². The inlet flow rate of air was 3.3 x 10⁻³ m³/s. The combustion tests were performed to determine the chemical heat release rate, generation rates of CO, CO₂, total hydrocarbons, smoke density, consumption rate of oxygen, chemical heat of combustion, and yields of products.

RESULTS & DISCUSSION

Location of Polymeric Parts on the Vehicle

The locations of the selected polymeric components on the van are schematically shown in Figure 1. Table 1 lists the components along with the name and part numbers of all polymeric parts that make up these components, and the type of polymer used to make the parts. Weights of most of the components and some of the parts are also shown in the table.

* Chu, F., and Tewarson, A., "Standard Method of Test for Material Properties Using the FMRC Flammability Apparatus", Technical Report FMRC J.I. OBOJ4.BU. Factory Mutual Research Corporation, Norwood, MA 02062, February 1997.

Composition of Polymers

Automotive polymers are commodity polymers that are easily processable and have good aging resistance to withstand severe automotive environments. Table 2 lists the most highly used polymers arranged in a descending order with respect to the amount used per 1996 model average car. * Typical applications for each of the polymers are also shown in the table. The top ten most widely used polymer types are polyurethane (PU) including both foam used in seats and reaction injection molded polyurethanes used for body panels, followed by polypropylene (PP), polyvinyl chloride (PVC), polyethylene (PE), nylon (polyamide (PA)), poly(acrylonitrile/butadiene/styrene(ABS), sheet molding composites (SMC/BMC), polycarbonate (PC), polyesters (PET & PBT), and styrene/polyphenylene oxide blends (PS/PPO). Other large volume automotive polymers are phenolics, styrene-maleic anhydride copolymer, acrylic polymers, acetals, and epoxy compounds.

The polymers selected for the flammability investigation are shown in Table 1. For few of the parts a label showed the type of polymer used. However, for most of these parts identification was carried out using infrared spectroscopy. A great majority of the parts are made of polyolefins (i.e., polypropylene, polyethylene, and polypropylene/polyethylene blends and copolymers including cross linked elastomers and thermoplastic elastomers). Other polymers used in these parts include polyurethanes polyvinyl chloride, nylons, ABS, polycarbonate, SMC, polyethylene terephthalate polyester, polyacetal, polyimide, polyether copolyester thermoplastic elastomer, and natural rubber and acrylonitrile-butadiene elastomers. Some of the polymer parts contained no filler while others contained as high as 53% filler. Glass, talc calcium carbonate, kaolin, clay, silica, barium sulfate, and carbon black are some of the typical fillers used. Density values for the different polymer composites ranged between 0.075 g/cc for a foamed seal used in the heating/ventilation/air conditioning (HVAC) housing (part number 4734370) to 2.10 g/cc for a very highly talc filled part used as a unit seal in the HVAC system (4734067B).

* Automotive Plastics Newsletter, April, 1996, Market Search, Inc.

For some samples, such as polyethylene obtained from the fuel tank, a simple decomposition pattern was observed. In nitrogen atmosphere the polymer shows no sign of degradation as it is heated up until the temperature approaches 440°C (Figure 3). A one step degradation is observed at that temperature with a decomposition rate of 16.79% per °C. The rate was calculated with respect to temperature rather than time because of the variable heating rate programmed into the instrument to give a higher resolution of decomposition peaks. The high density and high molecular weight polyethylene used for making the fuel tank is essentially filler free. The 0.3% residue that remains after heating to 900°C is probably the carbon black used in the resin for coloring.

When the same polymer is degraded in air, different degradation mechanisms are observed as seen in Figure 4. Decomposition starts at a lower temperature of 290°C. The main decomposition peak occurs at 418°C, and has a lower decomposition rate (5.88%/°C) than when the sample was degraded in nitrogen (16.79%/°C). Apparently, oxidation reactions taking place at lower temperatures slow down the decomposition of the polymer at higher temperatures either by increasing the formation of cross links or the formation of char and forcing the pyrolysis to occur over a wider temperature range, thus leading to lower rates of decomposition.

In the case of rubbers, which are molecularly cross linked polymers, we find that the decomposition rates are lower both in nitrogen and in air than for comparable thermoplastic uncross linked polymers. For example, the maximum decomposition rates of ethylene-propylene (EPDM) rubber, taken from the grommet used for the wire harness entry into the passenger compartment (part number 3009), are lower in nitrogen (1.54%/°C) and in air (1.29%/°C), than the rates observed for the two polymers that make up the rubber, namely polyethylene (16.79 & 5.88%/°C) and polypropylene (15.12 & 1.82%/°C).

Most foams used in the car are also thermoset cross linked polymers. Hence, their rates of degradation are lower than rates measured for thermoplastics.

For most polymeric compositions, decomposition starts at higher temperatures in nitrogen as compared to air, but the rate of decomposition is lower in air. One exception is the polyacetal (polyoxymethylene), used in the headlight. This is a polyether which upon heating unzips very fast via a free radical mechanism to yield the monomer. The decomposition of this polymer occurs at

lower temperatures (252°C versus 310°C) and at a faster rate (71.0 vs 3.3%/°C) in the presence of oxygen.

Modulated Differential Scanning Calorimetry (MDSC)

Heat absorption or evolution measurements are conducted in a nitrogen atmosphere at programmed heating rates of 5°C per minute with a modulation in rate of $\pm 0.531^\circ\text{C}$ every 40 seconds. The technique is capable of identifying reversible and non-reversible transitions that are measured during the heating run. The reversible transitions measured are first order transitions such as heats of fusion or heats of recrystallization, and second order transitions such as glass transitions. Non-reversible transitions are those associated with an entrapped unstable polymeric morphology that upon heating would relax to a more thermodynamically stable structure.

Crystalline polymers such as high density polyethylene (HDPE) show very well defined melting peaks and large values for the heat of fusion (128°C and 161 Joules/gram, respectively, for HDPE).

For amorphous polymers melting does not take place, instead the polymer undergoes softening at the glass transition temperature. This is the temperature at which a polymer goes from a stiff glassy state to a soft rubbery state. At the glass transition, polymers have enough free volume to allow the chains to suddenly become free to move resulting in a sharp increase of heat capacity. The rate of change in the value of heat capacity with temperature is lower in the rubbery state (0.00251 J/g.°C.°C) than in the glassy state (0.00364 J/g.°C.°C) as in the case of polycarbonate. For a crystalline polymer (polyethylene terephthalate, used in the door lock), heat capacity increases in a uniform manner as the sample is heated from -60°C to melting. A large peak in heat absorption is observed at melting. As in the case of amorphous polymers, the slope or the rate of increase in heat capacity with temperature is lower for the liquid state (0.000946 J/g.°C.°C) than for the solid polymer (0.00200 J/g.°C.°C)

Ignition

The measured thickness versus the thermal penetration depth governs the ignition behavior of the samples.* In these studies, the thermal penetration depth was calculated from the thermal diffusivity values and measured times-to-ignition.** The calculated values show that beyond about 30 kW/m², the thermal penetration depth is less than the actual thickness of the samples and thus time to ignition is expected to follow the relationship:

$$\sqrt{l/t_{ig}} = \left(\dot{q}_e'' - \dot{q}_{cr}'' \right) / \Delta T_{ig} \sqrt{(\pi/4)(k_v \rho_v c_v)}$$

where \dot{q}_e'' = external heat flux

\dot{q}_{cr}'' = critical heat flux

and $\Delta T_{ig} \sqrt{(\pi/4)(k_v \rho_v c_v)}$ is the Thermal Response Parameter (TRP) of the plastic (kW-2^{1/2}/m²). k_v , ρ_v , and c_v are the thermal conductivity, density and specific heat of the sample, respectively. Figure 5 shows a typical example of the ignition time versus heat flux for plastic part VAC #870. The experimental TRP value is obtained from the slope of the line in this figure. The calculated TRP value is determined from the ignition temperature, thermal conductivity and specific heat value obtained from the thermal analysis study. Good correlation is observed as seen in Figure 6.

The ignition temperature calculated from critical heat flux values (\dot{q}_{cr}'') by the relationship

$$T_{ig} \approx [(\dot{q}_{cr}'')^{0.25} \times 364]$$

* Protection Delichatsios, M. A. Panagiotou, Th.P., and Kiley, F., "The use of time to ignition data for characterization of the thermal inertia and minimum energy for ignition or pyrolysis", *Combustion and Flame*, 84, 223, 1991.

** Murty Kanuary, A., "Flaming Ignition of Solid Fuels", *The SFPE Handbook of Fire Protection Engineering*, Section 2, Chapter 13, pp. 2-190 to 2-204. The National Fire Production Association Press, Quincy, MA, 1995.

** Quintiere, J. G., "Surface Flame Spread", *The SFPE Handbook of Fire Protection Engineering*, Section 2, Chapter 14, 2-205 to 2-216. The National Fire Association Press, Quincy, MA, 1995.

is compared in Figure 7 with the decomposition temperature (T_d) obtained from thermal gravimetric analysis. As expected for most samples T_{ig} values fall above the perfect correction line with respect to T_d values.

Combustion

After ignition combustion of the polymer starts. During combustion the variables measured include mass loss rate, generation rates of combustion products, such as CO and CO₂, and the depletion of oxygen. In addition, the chemical heat release rate (\dot{Q}_{ch}'') is calculated. \dot{Q}_{ch}'' is in turn used to calculate a Fire Propagation Index (FPI) by the following semi-empirical relationship,

$$FPI = 1000 (0.42 \dot{Q}_{ch}'')^{1/3} / TRP$$

Comparisons with large-scale fire tests indicate that the rate of fire propagation increases with increase in the FPI value. The estimated FPI values for some of the plastic parts used on the van are listed in Table 3. Three parts, namely, polyethylene fuel tank (VAC #201), polycarbonate headlight lens (VAC #798), and SMC windshield wiper structure (VAC #967) with FPI values less than 10 are expected to have decelerating fire propagation, whereas the other 12 plastic parts shown in the table are expected to have steady or accelerating fire propagation beyond the ignition zone.

In summary, thermal properties of plastic parts used on a 1996 passenger van were determined. High resolution thermal gravimetric analysis (TGA), and modulated differential scanning calorimetry were the two techniques employed. Thermal analysis results were compared with flammability parameters obtained using a flammability apparatus capable of measuring ignition, combustion and heat release variables.

Good agreement was observed between measured flammability parameters, such as ignition temperature, critical, heat flux and thermal response parameter and the thermal analysis results such as specific heat, thermal conductivity and a decomposition temperatures.

Table 1.
Mass of Selected Polymeric Components and Parts

Component Number	Part Number	Part Description	Polymer Identification	Mass kg	
743	GJ42SK4A	headliner, backing - top layer, structural support	polyethylene terephthalate (PET)	2.61	
	GJ42SK4B	headliner, high density foam - layer 3	polyether urethane (PPO + MDI)		
	GJ42SK4C	headliner, low density foam - layer 2	polyester urethane with Surfyn film		
	GJ42SK4D	headliner, fabric - exposed surface, bottom layer	nylon 6		
	GJ42SK4E	headliner, center - structural support	PET Binder on glass		
654	JF48SK5A	instrument panel, foam - between structure and cover	polyether urethane (PPO + MDI)	3.61	
	JF48SK5B	instrument panel, cover - exposed surface	polyvinylchloride (PVC)		
	JF48SK5C	instrument panel, structure	polycarbonate (PC)		
611	PL98SX8A	instrument panel shelf, main panel	PC	2.75	
	PL98SX8B	instrument panel shelf, foam - small seals	polyether urethane		
256	4612512A	resonator, structure	polypropylene (PP)	0.71	
	4612512B	resonator, intake tube	ethylene propylene diene monomer (EPDM) elastomer	0.29	
	4612512C	resonator, effluent tube	EPDM	0.14	
		Whole system		1.14	
788	4674711A	kick panel insulation, foam	polyether urethane	4.82	
	4674711B	kick panel insulation, backing	PVC		
		Whole system			
732	4678345A	air ducts, small ducts	polyethylene (PE)	4.28	
	4678345B	air ducts, large ducts	PP		
		Whole system			
673	4680250A	Steering column boot, inner interior boot	natural rubber (NR)	0.04	
	4680250B	Steering column boot, cotton shoddy	mixture of cotton, polyester and other fibers	0.02	
	4680152C	Steering column boot, outer interior boot	polyether copolyester elastomer	0.10	
		Whole system		0.17	
736	4683264A	brake fluid reservoir, reservoir	PP	0.67	
	4683264B	brake fluid reservoir, cap	PP	0.07	
		Whole system			
3008	4707580	wire harness tube,	PE	0.07	
1019	4707808A	door lock contact, wire coating			
	4707808B	door lock contact, wire mesh - groups wires together			
	4707743C	door lock contact, structure	poly(acrylonitrile-butadiene-styrene) ABS		
		Whole system			
967	4716051	windshield wiper tray, structure	sheet moulding compound (SMC)	3.40	
868	4716345A	fender insulation, low density foam - sound reduction	polystyrene (PS)	0.11	
	4716345B	fender insulation, high density foam - sound reduction	PS		
		Whole system			
870	4716832A	hood liner, insulation (back)	PET, cellulose and epoxy	1.00	
	4716832B	hood liner, face	PET		
		Whole system			
208	4716895	wheel well cover, fuel tank shield	PP	0.56	
676	4734025	HVAC unit, door - foam covering		0.29	
	4734033	HVAC unit, door - for thermostat	PVC	0.08	
	4734039A	HVAC unit, door - structure	nylon 66	0.23	
	4734039B	HVAC unit, door - rubber seal	thermoplastic polyolefin (TPR)		
			Whole system		
	4734041A	HVAC unit, door - structure	nylon 66	0.11	
	4734041B	HVAC unit, door - rubber seal	TPR		
			Whole system		
	4734042A	HVAC unit, door - structure	nylon 66	0.10	
	4734042B	HVAC unit, door - rubber seal	TPR		
			Whole system		0.13
	4734063	HVAC unit, cover	PP	0.13	
	4734067A	HVAC unit seal, foam - heating coil entrance	acrylonitrile-butadiene rubber and PVC blend	0.05	
	4734067B	HVAC unit seal, backing - heating coil entrance	ethylene vinyl acetate		
			Whole system		0.87
	4734071	HVAC unit, top main housing - contains coils, doors and fan	PP		1.61
4734072	HVAC unit, bottom main housing - contains coils, doors and fan	PP		0.29	
4734073	HVAC unit, fan top cover	PP		0.11	
4734074	HVAC unit, fan bottom cover	PP			

Table 1 (cont'd).
Mass of Selected Polymeric Components and Parts

Component Number	Part Number	Part Description	Polymer Identification	Mass kg
	4734080	HVAC unit, cover - for directional control	PP	
	4734081	HVAC unit, deflector - for air flow	PP	0.09
	4734225	HVAC unit, actuator - casing	PP	0.15
	4734367	HVAC unit, housing	PP	0.25
	4734370	HVAC unit, Seals - both large and small	acrylonitrile-butadiene rubber and PVC blend	0.04
	4734396	HVAC unit, seal		0.00
	4734650	HVAC unit, seal		0.02
	4734651	HVAC unit, seal		0.01
	4734724	HVAC unit, defogger tube	TPR	0.03
201	4883140A	fuel tank, tank	PE	
	4883140B	fuel tank, hoses	nylon 12	
	4883140C	fuel tank, threads/seal - for fuel pump	PE	
		Whole system		8.48
788	4857041A	headlight, lens	PC	
	4857041B	headlight, backing	PC	
	4857041C	headlight, retainer	polyacetal (polyoxymethylene)	
	4857041D	headlight, bulb support structure - halogen	polyimide	
	4857041E	headlight, leveling mechanism	PC	
		Whole system		1.70
222	4364944A	battery casing, top	PE/PP blend	
	4364944B	battery casing, sides & bottom	PE/PP blend	
		Whole system		17.30
230	5235267	battery cover,	PP	0.36
971	4675359A	hood to cowl weather stripping, foam	EPDM	
	4675359B	hood to cowl weather stripping, rubber base	EPDM	
		Whole system		0.44
959	4716896A	Bulkhead insulation engine side, exterior/face	mixed fibers: cotton, nylon 66 and glass	
	4716896B	Bulkhead insulation engine side, insides	PVC coating over glass	
	4716896C	Bulkhead insulation engine side, support structure	PVC-hydrocarbon elastomer	
		Whole system		2.38
3009		grommet, wire harness cap for 3008	EPDM	

Table 2.
Polymers Most Used in Cars and Light Trucks

Polymer Type	Average Weight lb./1996 Vehicle	Typical Applications in Vehicles
Polyurethane PU	44 (RIM & Foam)	Body panel, fender, roof panel, bumpers, headliner, seat, upholstery
Polypropylene PP	40	HVAC, fan & shroud, battery tray, console, radiator, cowl vent, air duct, instrument panel, package shelf
Polyvinyl Chloride PVC	21	Bumper trim, electrical wiring, boots, bellows, seat cover, steering wheel, floor
Polyethylene PE	20	Gas tank, bumper, electrical wire, reservoir, fuel filler pipe
Nylon(Polyamide) PA	18	Fuel system, fuel line, gas cap, canister, grille head lamp support, brake, radiator end tank, engine cover, intake manifold, lamp housing
Acrylonitrile/styrene/ butadiene ABS	16	Bumper beam, console, cowl vent, engine cover, fascia, head liner, duct
Thermoset Polyester (SMC/BMC)	16	Door lift gate, fenders, hood, quarter panels, rear deck, spoiler, body panel
Polycarbonate & ABS/PC	9	Bumper trim, electrical, grille, lamp support, lens, lamp, instrument panel, console, door fender, instrument panel
Thermoplastic Polyester PET/PBT	8	Body panel, hood, connector, door, fuse junction, HVAC components, fuel rail
Styrene/polypheylene oxide PS/PPO	7	Connectors, console, engine air cleaner, instrument panel
Styrene Maleic Anhydride Polymer SMA	4	Console, head liner, instrument panel
Phenolic	4	Brake system, engine pulley, ash tray, transmission component
Acrylic Polymers	3	Emblems, lamp and instrument panel lenses
Polycetals	2	Radiator fan, door handle, carburetor, fuel pump, fuel filler neck.
Epoxy Resins	0.3	Electrical, fuel tank(filament wound), adhesives

Table 3
 Estimated Fire Propagation Index Values for the Plastics
 in Parts of the 1996 Passenger Van Examined in this Study

VAC#	Dodge Part #	Description	Plastics	FPI
201	4883140A	Fuel Tank	PE	8
208	4716895	Wheel well cover, fuel tank shield	PP	13
230	5235267	Battery cover	PP	12
256	4612512A	Resonator structure	PP	14
611	PL98SX8A	Instrument panel shelf, main panel	PC	11
654	JF48SK5B	Instrument panel cover, exposed surface	PVC	15
676	4734071	HVAC unit, top main housing, outer top	PP	12
	4734370	HVAC unit, seals-both large and small	ABS-PVC	57
732	4678345B	Air ducts, large ducts	PP	11
743	GJ42SK4D	Headliner, fabric-exposed surface	Nylon 6	26
788	4674711B	Kick panel insulation backing (silencer?)	PVC	18
798	485041A	headlight lens	PC	9
868	4716345B	Fender sound reduction foam	PS	27
870	4716832B	Hood liner face	PET	23
967	4716051	Windshield wiper structure	SMC	8

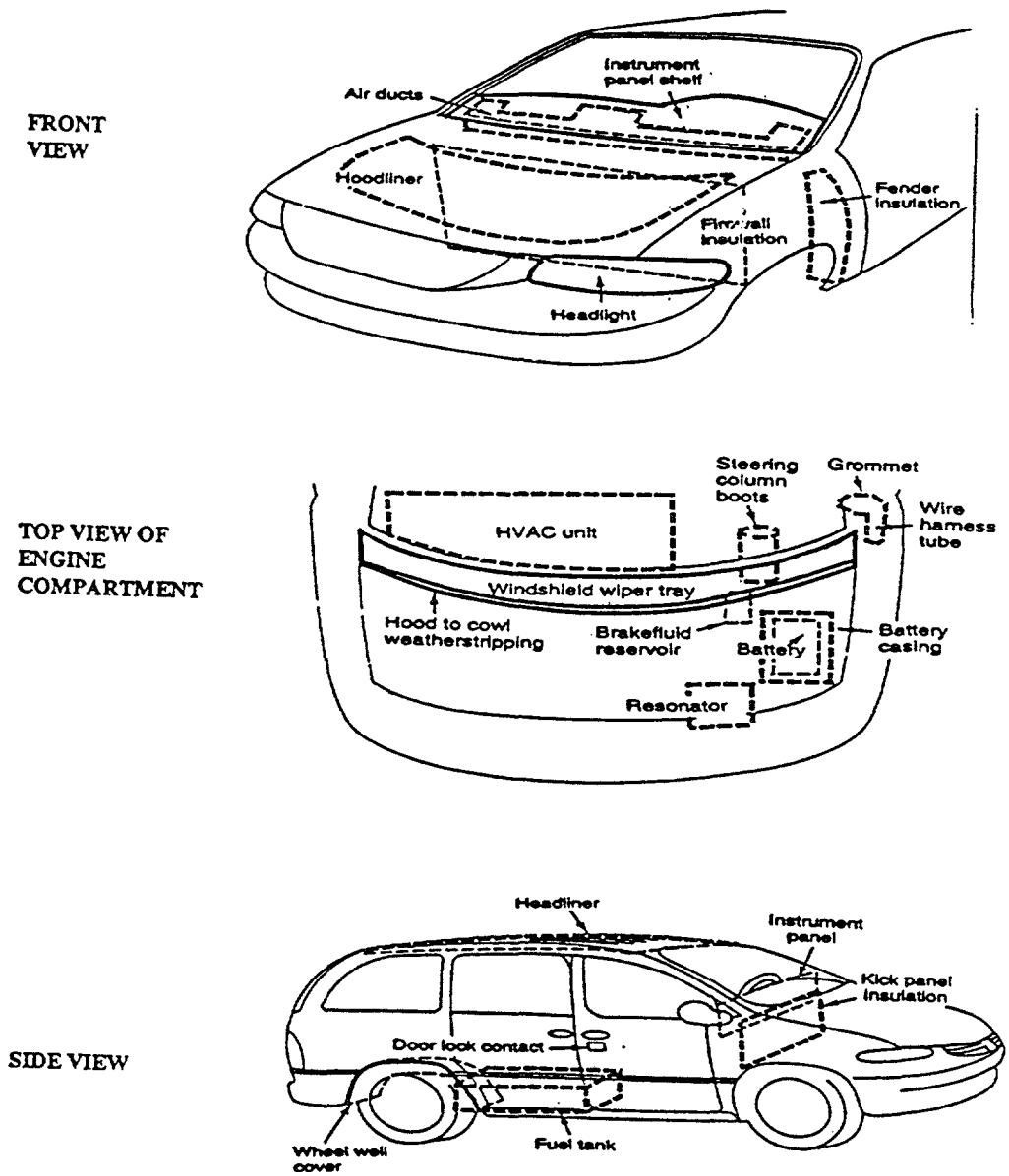


Figure 1. Schematic diagram showing the locations of components and parts of a 1996 passenger van.

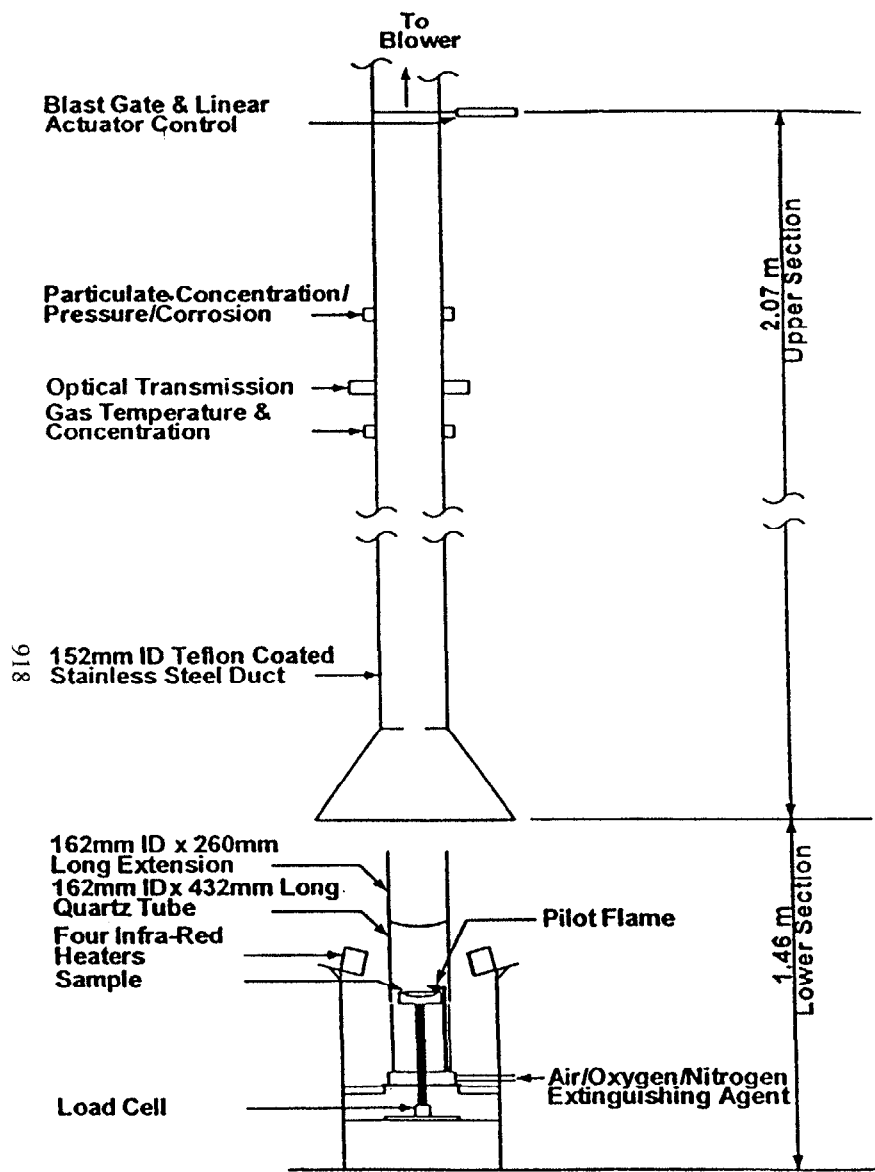


Figure 2. Flammability apparatus.

TGA

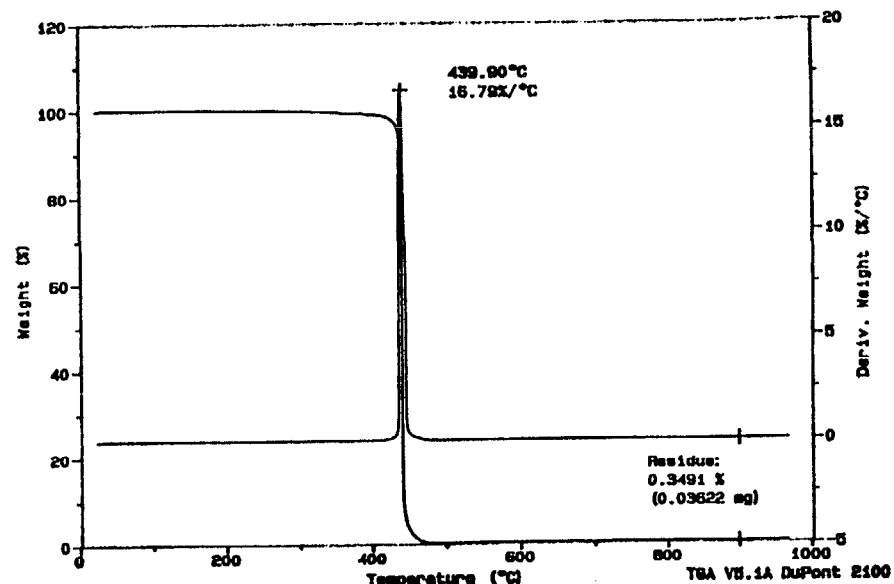


Figure 3. High resolution thermal gravimetric analysis of high density polyethylene conducted in nitrogen.

TGA

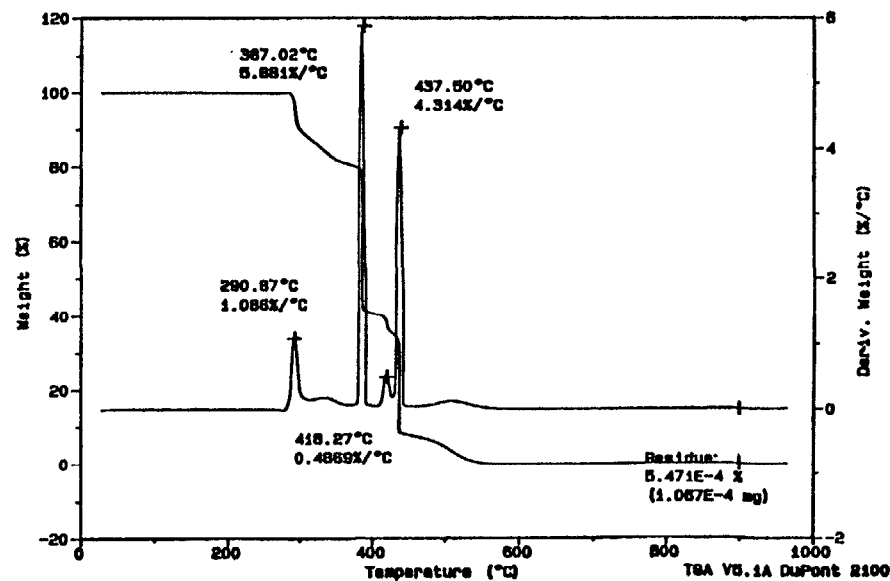


Figure 4. High resolution thermal gravimetric analysis of high density polyethylene conducted in air.

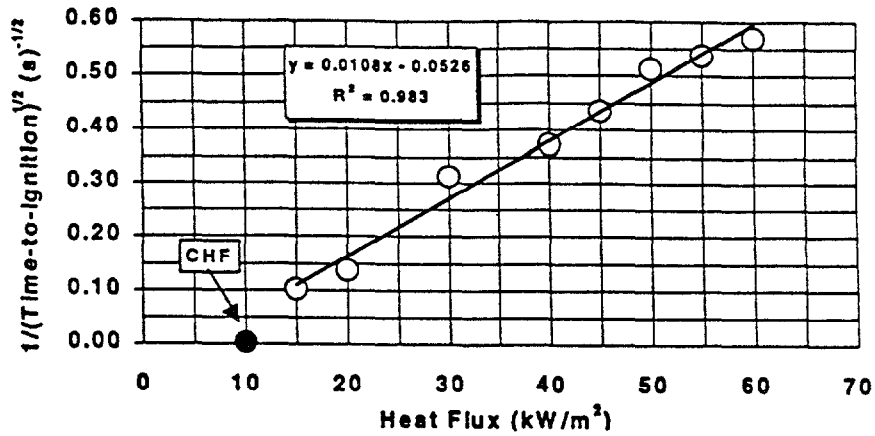


Figure 5. Inverse of the square root of time to ignition versus external heat flux for 25-mm thick sample of VAC #870 (part #4716832B, polyethylene terephthalate hood liner face). Measured CHF value (dark symbol) = 10 kW/m²; TRP (inverse of the slope) = 93 kW-s^{1/2}/m².

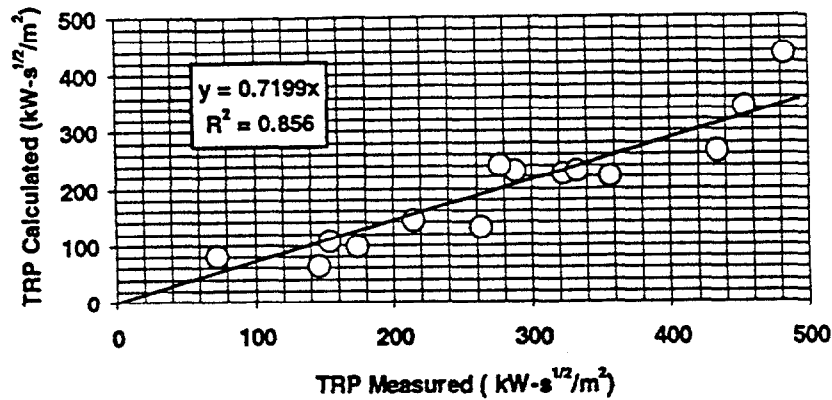


Figure 6. Correlation between the measured and calculated Thermal Response Parameter Values for the plastic parts examined in this study. Ignition data were measured in the Flammability Apparatus.

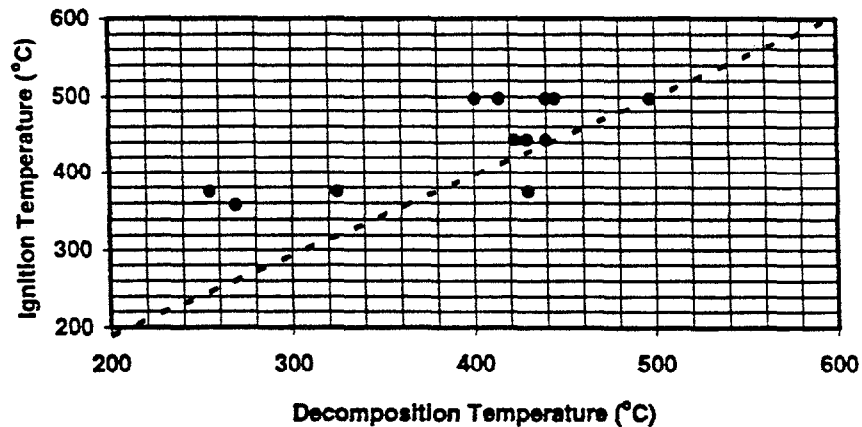


Figure 7. Decomposition temperature versus the ignition temperature for plastic parts.