DE84-010668

CHARACTERIZATION OF POLYETHERETHERKETONE AND OTHER ENGINEERING THERMOPLASTICS

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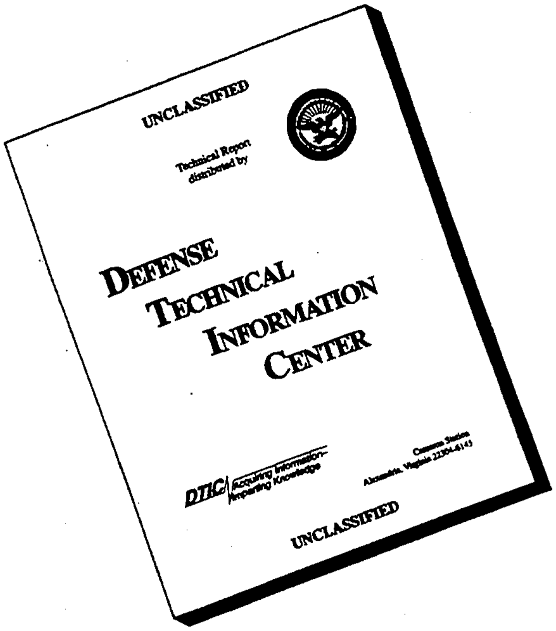
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Characterization of Polyetheretherketone and Other Engineering Thermoplastics

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Issued: April 13, 1984

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CONTENTS

Page

ABSTRACT 3
INTRODUCTION 3
EXPERIMENTAL METHODS 4
RESULTS AND DISCUSSION 9
SUMMARY AND CONCLUSIONS 24
ACKNOWLEDGEMENTS 26
REFERENCES 26
DISTRIBUTION 27

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Abstract

Three engineering thermoplastic materials were characterized by thermal/spectroscopic means to assess their suitability in fiberglass-filled molding resins for Mound applications. The three resins examined were: polyetheretherketone (PEEK) from ICI, Ltd., polyetherimide (PEI) from General Electric, and polyethersulfone (PES) from ICI.

Thermogravimetric analysis of the three thermoplastics in N_2 showed that all had a decomposition onset temperature $\geq 525°C$ with PEEK > PEI > PES. Melt thermal stability analyses of glass-filled PEEK and of PEI showed <1% weight loss after 2 hr (N_2). Thermomechanical analysis (TMA) of glass-filled PEEK revealed a low temperature ($\sim$60-70°C) transition below T_g ($\sim$150°C). This transition disappeared on subsequent TMA runs and did not reappear on aging at room temperature, which suggests it was the result of molding stresses. "Extra" transitions below T_g were also noted for PES and PEI.

Direct probe/mass spectroscopy reconstructed ion chromatograms showed water and phenyl sulfone ions to be present in both PES and PEEK (and volatilized below 200°C in vacuum). Water only was observed in PEI. The presence of phenyl sulfone in PEEK was confirmed by FT-IR, and sulfur was found in amounts up to 0.23% by weight in 30% glass-filled molding compounds. A polymerization solvent, such as diphenyl sulfone, is a probable source. Fluoride (from a monomer used in the PEEK polymerization) was also detected in amounts up to 0.17% by weight in the 30% fiberglass molding compounds.

Introduction

In recent years, several new, thermally stable engineering thermoplastic resins have been introduced by various manufacturers. Some of these may well be suited for applications in Mound components manufactured for DOE. Of particular interest is a crystalline thermoplastic resin produced by Imperial Chemical Industries, Ltd. (ICI), namely polyetheretherketone (PEEK). Also of some potential interest are two amorphous thermoplastics, polyetherimide (PEI), introduced by General Electric Co. (GE) and polyethersulfone (PES), also produced by ICI. In most applications at Mound, these resins would probably be fiberglass filled (20-30% by weight).

While considerable information is available from the manufacturers on mechanical, electrical, and some thermal properties of these thermoplastic resins, little or none is available on their chemical constituents, particularly in terms of trace amounts of ions, elements, or of volatile products produced on heating below decomposition temperatures. These can be, however, of considerable importance in potential Mound applications, especially where compatibility with explosive or pyrotechnic materials is required. Therefore, a more complete chemical characterization of these materials, and their readily volatilized by-products, was undertaken.

In addition, thermal analyses were performed to confirm and supplement the manufacturer's data on glass transition temperatures (Tg), expansion coefficients, melt thermal stability, and decomposition temperatures. This report will detail the findings of this initial study on these three engineering thermoplastic resins. Both neat and glass-filled PEEK and PES were studied; only unfilled PEI was included, however.

Experimental Methods

The description of the experimental methods used in this study is divided as follows: Information on resin samples (including manufacturer's data); thermal analytical methods; direct probe mass spectroscopy (DIP/MS); Fourier transform infrared spectroscopy (FT-IR); and other analytical methods used.

Resin Samples and Manufacturer's Information:

The types of samples studied for each resin,their sources, and the types of analyses conducted are listed in Table 1. Not every type of analysis was performed on every sample; this was a factor both of required sample form for the analyses and relative importance of obtaining multiple analyses. In general, PEEK, because of its recognized potential for application, was the most extensively characterized engineering thermoplastic. Table 2 lists relevant manufacturer's property data for each of the three thermoplastic resins (filled and unfilled). Their data should be valid in general for these three resins. There may, however, be differences in the results obtained here (wherever any duplication of the manufacturer's tests were performed) as a result of either sample-to-sample or testing variations. Other information obtained from the literature on these resins will be included where pertinent.

Thermal Analytical Test Methods:

Two types of thermal analyses were performed on the thermoplastic resins examined in this study: thermogravimetric (TG) and thermomechanical (TMA) analyses. A general description of methods for each will be given with variations of parameters specified in the Results and Discussion section.

TG: A DuPont 951 TGA was employed, interfaced with the DuPont 1090 Thermal Analyzer. All of the TG analyses in this study were performed in N_2 ($\simeq$70-75 mL/min) atmospheres. The scanning rate was 20°C/min for dynamic runs, over the range: $\sim$50°C to $\sim$1000°C. Sample sizes were $\sim$25-45 mg.

TABLE 1 - RESIN SAMPLE INFORMATION AND ANALYSES PERFORMED

RESIN SAMPLES					ANALYSES PERFORMED					
					THERMAL		SPECTROSCOPIC ANALYSES			
RESIN TYPE	SOURCE OF SAMPLE	DESIGNATION	WEIGHT % FIBERGLASS	SAMPLE FORM	TG	TMA	MS	FTIR	EMISS.	GRAVIMETRIC CHROMATOGRAPHIC
PEEK	ICI	PEEK-1	20	1/8 in. molded disc	X	X	X	X	--	--
PEEK	ICI	PEEK-2, 3	None	1/8 in. molded discs	X	X	X	X	--	--
PEEK	LNP Corp.	PDX-79737 Lot 120010	30	Pellets	X	--	--	--	X	X
PEEK	Fiberfill Corp.	P061616 Lot 46-35176	30	Pellets	X	--	--	--	X	X
PEEK	Collier Corp.	Coated Wire	None	PEEK-Insulated (1) Tin-coated Cu wire (2) Ag-Coated Cu Wire	(1) X (2)	-- --	-- --	-- --	X X	-- X
PEI	GE Corp.	Ultem 1000	None	1/8 in. molded test bars	X	X	X	X	--	--
PEI	GE Corp.	Ultem 1000	None	Pellets	--	--	--	--	X	X
PES	ICI	Grade 300-P	None	1/8 in. molded test bars	X	X	X	X	--	--
PES	ICI	Grade 420-P	20	1/8 in. molded test bars	X	X	--	--	--	--

TABLE 2 - MANUFACTURER'S PROPERTY DATA

RESIN/ MFRS. DESIGNATION	WEIGHT % FIBERGLASS	Tm °C	Tg °C	MAX. % CRYSTALLINITY	SPEC. GRAVITY	MELT THERMAL STABILITY	THERMAL EXPANSION COEFFICIENT m/m/°C	H_2O ABSORPTION (% BY WEIGHT)	SOLUBILITY
PEEK (ICI)	None	334	143	35	Amorphous 1.265 cryst. 1.320	1 hr/ 400°C	46 x 10^{-6}	0.15 (24 hr @40% RH)	concentrated H_2SO_4
PEEK PDX-79737 (LNP Corp)	30%		280°C (HDT) (264 psi)	--	1.49	--	--	--	--
PEI Ultem1000 (GE)	None	--	200°C (HDT) (264 psi)	Amorphous	1.27	--	62X 10^{-6}	0.25 (24 hr/ 73°F) 1.0 (equilibrium)	Partially halogenated hydrocarbons
PEI Ultem2300 (GE)	30%	--	210°C (HDT) (264 psi)	--	1.51	--	20X 10^{-6}	0.18 (24 hr/ 73°F) 0.90 (equilibrium)	--
PES 300 P (ICI)	None	--	203°C (HDT) (264 psi)	Amorphous	1.37	--	55X 10^{-6}	0.15 (equilibrium 50% RH/20°C) 0.3 (saturation, 100°C)	N-Me pyrollidone, di-Me formamide, partially halogenated hydrocarbons, polar aromatics
PES 420 P (ICI)	20%		210°C (HDT) (264 psi)	--	1.51	--	26X 10^{-6}		

(Continued next page)

TABLE 2 (CONTINUED)

RESIN/ MFRS. DESIGNATION	WEIGHT % FIBERGLASS	SOLVENT RESISTANCE: STRESS-CRACKING	DIELECTRIC STRENGTH	Tg ANALYSIS IN AIR	LIMITING O_2 INDEX	SELF-IGNITION TEMP °C	MAJOR COMBUSTION PRODUCTS	LONG-TERM SERVICE TEMP °C
PEEK (ICI)	None	Acetone (1 hr @ 3% strain)	480kV/in. (0.002 in. film)	1) 5% wt. loss @ 520°C 2) 50% @610°C	--	595	CO, CO_2	--
PEEK PDX-79737 (LNP Corp)	30%	--	500 V/mil	--	--	--	--	205-235
PEI Ultem1000 (GE)	None	$CHCl_3$ (<1 hr @ 600 psi) CH_2Cl_2 (<24 hr @ 600 psi) 1, 1, 2-Trichloroethene (<1 hr @ 600 psi)	620 V/mil (in oil) 830 v/mil (in air)	--	47	--	CO,CO_2,H_2O	170
PEI Ultem2300 (GE)	30%	--	769 V/mil (in air)	--	50 (20% FG)	--	--	170
PES 300 P (ICI)	None	$CHCl_3$, CH_2Cl_2, 1,1,1, tri-Chloroethane; di-ester & phosphate ester based oils (& others)	400 kV/in	--	34 (0.020 in.) 38 (0.063 in.)	--	CO,SO_2 (minor products)	180
PES 420 P (ICI)	20%		162 kV/in (30% glass)	--	40 (0.063 in.)	-- --	-- --	180

TMA: A DuPont 943 TMA interfaced with the DuPont 1090 Thermal Analyzer was employed. All analyses were in N_2, as above, using the expansion probe and a 2 g load. Scanning rates were 10°C/min and sample thicknesses ≈3.0 mm. Samples were cut from flat, molded test specimens of the various resins. Free cooling (no quenching) was used between TMA runs, whenever multiple runs were made. A 396 µm aluminum shim was employed for the static calibration and a 7.80 mm aluminum slug was used for the dynamic calibration of the TMA.

Mass Spectrometric Methods:
Instrumental Parameters:

- Instrument: MS-25 double focusing magnetic sector mass spectrometer
- Sample introduction mode: direct insertion probe
- Ionization: electron impact at 70 eV
- Accelerating voltage: 2 kV at 600 amu
- Scan Speed: 10 seconds per decade
- Source Temperature: 220°C
- Source Pressure: 10^{-7} to 10^{-6} torr
- Probe Temperature: temperature programmed from 30°C to 280°C @ 10°C/min
- Data acquisition: repetitive scanning (under computer control)

Procedure: A small specimen of each plastic was placed into the reservoir of the direct insertion probe, which was then inserted into the ion source of the mass spectrometer. The probe, initially at 30°C, was programmed to reach 280°C at a rate of 10°C/min while the mass spectrometer scanned repetitively over a range of 17 to 600 amu. Any outgassing that may occur within this temperature range results in an increase in intensity of the total ion current within the mass spectrometer. The resulting mass spectrum allows one to identify the components being given off during the heating step. Next, by observing the current of a single ion, e.g. M/Z 18 (H_2O), and its relation to the total ion current versus temperature, the temperature of the onset and decay of these outgassed species can be determined. Since the ion source of the mass spectrometer operates in the 10^{-6} to 10^{-7} torr region, the temperatures in the probe may be related to atmospheric conditions by adding approximately 80°C. By comparing relative differences in outgassing characteristics of these plastic materials, information pertaining to relative thermal stability can be obtained.

Fourier Transform Infrared Spectroscopy:

All infrared spectra were recorded by attenuated total reflectance infrared spectroscopy (ATR/FT-IR). The spectra were recorded from 4000 to 550 cm^{-1} with an IBM IR95 spectrometer, equipped with a broad-band, liquid N_2 cooled, mercury cadmium telluride detector (Infrared Assoc., $D^*=6.5\times10^9$ cm $Hz^{1/2}/W$), a Ge/KBr beamsplitter, and a globar source. The instrument was purged with dry nitrogen to remove atmospheric H_2O and CO_2. The interferograms were transformed using the Happ-Ganzel apodization function and a zero filling factor of 4.

The procedure used was to press the flat surface of a 1 cm^2 piece of the thermoplastic (from a molded test specimen) against the ATR plate. The result is a spectrum of the plastic to a depth of several microns. The spectra of PES and PEI were very strong, but the initial spectrum of PEEK was relatively weak.

Sanding the PEEK surface flattened it and improved the physical contact with the ATR plate, resulting in a substantial increase in band intensities in later PEEK spectra.

Other Analytical Methods:

Emission Spectroscopy was used to determine the trace amounts of metallic elements present. Ion chromatography was used to determine F^- and Cl^-, following Parr Bomb combustion (in the original specimens, these halogens were not necessarily present in ionic form). Sulfur was detemined gravimetrically, following Parr Bomb combustion (or, as noted, by ion chromatography, as $SO_4^=$).

Results and Discussion

The results and discussion are divided into two sections: thermal analyses and chemical analyses. The latter will include the mass spectrometric, FT-IR and other chemical analytical results.

Thermal Analyses:

Results of TG analyses are described for the engineering TP's first, then the results of the TMA analyses.

Thermogravimetric (TG) Analyses: TG Analytical results for the three engineering thermoplastic resins (glass-filled and neat) are summarized in Table 3 (scanning analyses from ∿50 to ∿950°C). Typical thermograms of each thermoplastic resin are shown in Figures 1-3 (including the derivative scans). Also included in Table 3, for comparison, are TG data for a molded o-diallylphthalate-fiberglass (DAP-FG) thermoset resin, which is commonly used in Mound components. That this component was 100% cured (by a "postcure" after molding) was verified by differential scanning calorimetry (DSC), as described previously [1]. The DAP-FG TG thermogram is shown in Figure 4 compared with thermograms of glass-filled PEEK and PES, and unfilled PEI resins.

The results given in Table 3 show that all three engineering thermoplastic resins have very high decomposition onset temperatures, ≥525°C, even unfilled. PEEK is the highest at ≥560°C. PEEK is also the lowest in volatile components, up to as high as 400°C. The unfilled PEI and the molded DAP component are next lowest in volatiles (DAP was measured only up to 280°C, since its decomposition onset is ≤350°C). In terms of volatiles before decomposition, the PES samples appear to be the least stable of the four resins tested here. The DAP-FG decomposes completely to leave only the fiberglass, but the three engineering thermoplastics all have a black, charred residue remaining at 950°C (in addition to any fiberglass present) in a N_2 atmosphere.

The thermograms of the PEI and PES (Figures 2 and 3) both show a small, but distinct, change in the derivative scans at ∿240°C. This probably corresponds to observations made in the TMA analyses of these resins of a large expansion with internal bubble formation above 200°C, as will be described.

Isothermal TG scans of PEEK and PEI were run both in the melt and at 200°C, in N_2, and the results are given in Table 4. In all cases, weight losses were ≤1%, and both resins were unchanged in appearance at 200°C. In the melt, the PEEK compound changed from grey to brownish black, while the PEI became a darker, but still

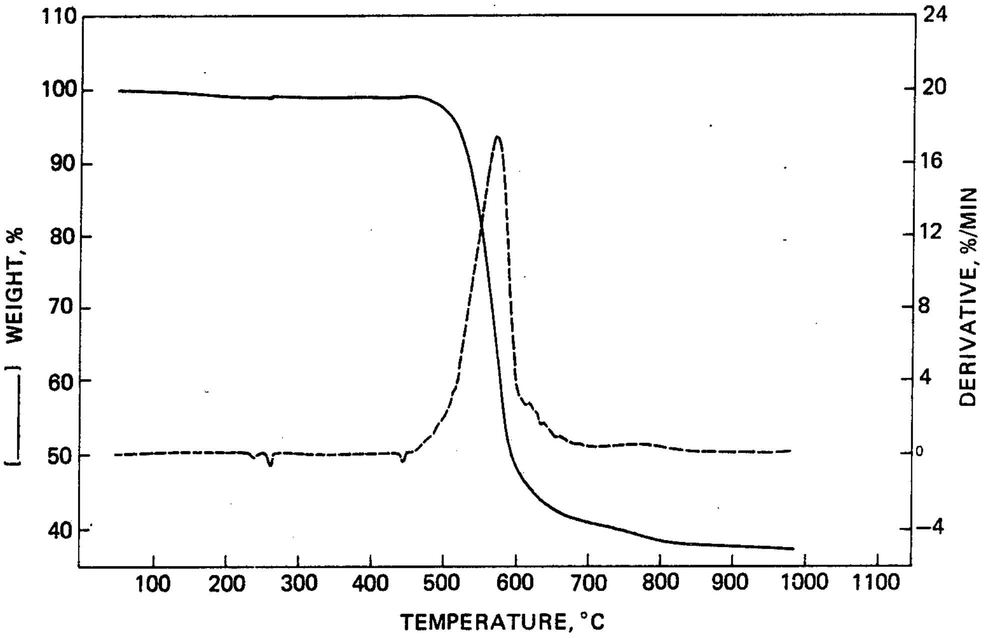

Figure 1 - TG analysis of molded PES 300P resin(in N_2).

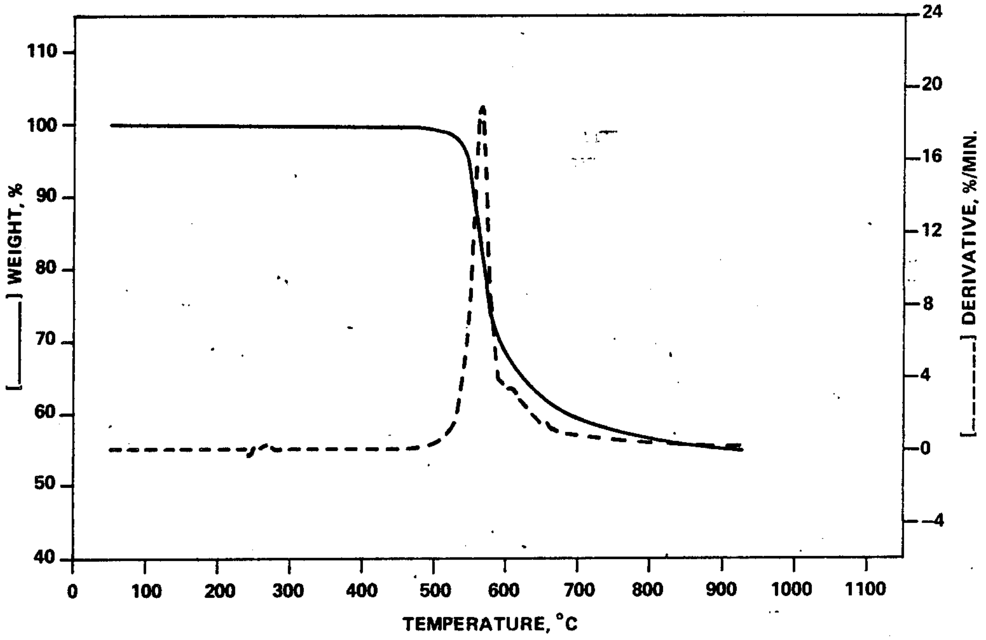

Figure 2 - TG analysis of neat molded PEI (in N_2).

TABLE 3 - THERMOGRAVIMETRIC ANALYSES OF ENGINEERING THERMOPLASTICS IN N_2

RESIN	WEIGHT % FIBERGLASS	WEIGHT % VOLATILES/ TO TEMP, °C	POLYMER DECOMPOSITION ONSET, °C	INFLECTION, °C	COMPLETION °C	% WEIGHT LOSS (POLYMER)	WEIGHT % RESIDUE ≥ 930°C
PES 300P	None	0.87/to 300	525	566	609	61.3	37.3
PES 420P	20	1.54/to 350	547	584	620	48.8	48.6
PEI Ultem 1000	None	0.29/to 400	538	564	602	43.9	54.0
PEEK-3 ICI (Molded disc)	None	0.25/to 400	578	607	643	49.8	49.8
PEEK-1 ICI (Molded disc)	20	≤ 0.1/to 400	578	602	631	34.6	64.8
PEEK Coating on copper wire Collier Corp.	None	≤ 0.1*/to 350	567	591	627	17.3 (to 850°C)	82.0
PEEK Molding Resin Fiberfill (Lot 46-35176)	30	≤ 0.03*/to 400	558	591	626	37.8	61.8
PEEK Molding Resin LNP (PDX79739 Lot 120010)	30	≤ 0.2*/to 400	585	610	640	35.2	64.5
DAP^x-FG Molded Component	60	≤0.3*/to 280	365	410	459	36.9	62.8

^{x}DAP = O-Diallyl Phthalate Resin

* = Weight levels at or below instrument's quantitative measurement limits.

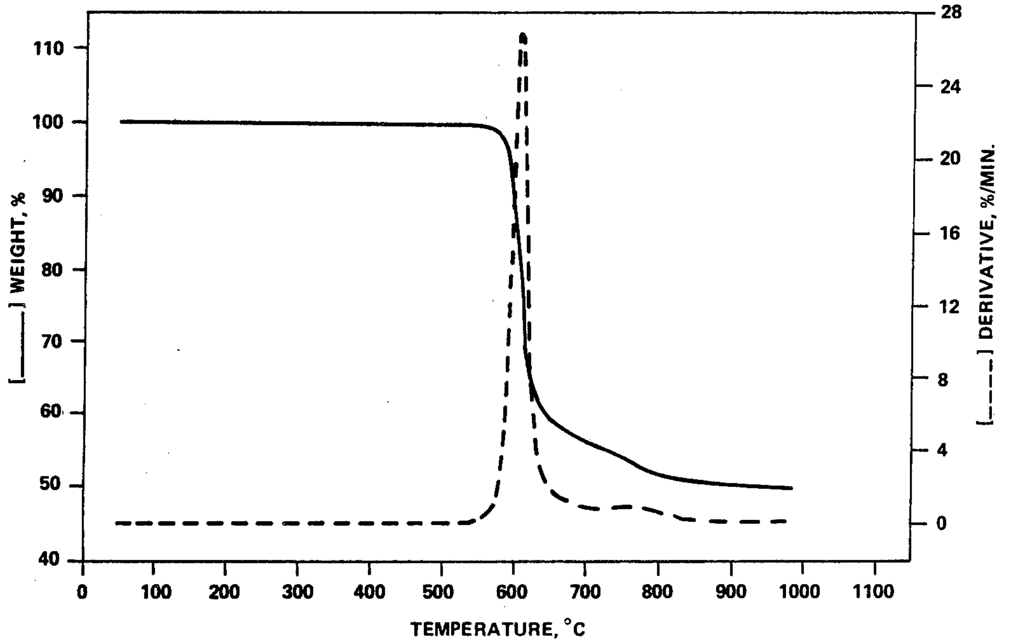

Figure 3 - TG analysis of neat molded PEEK (in N_2).

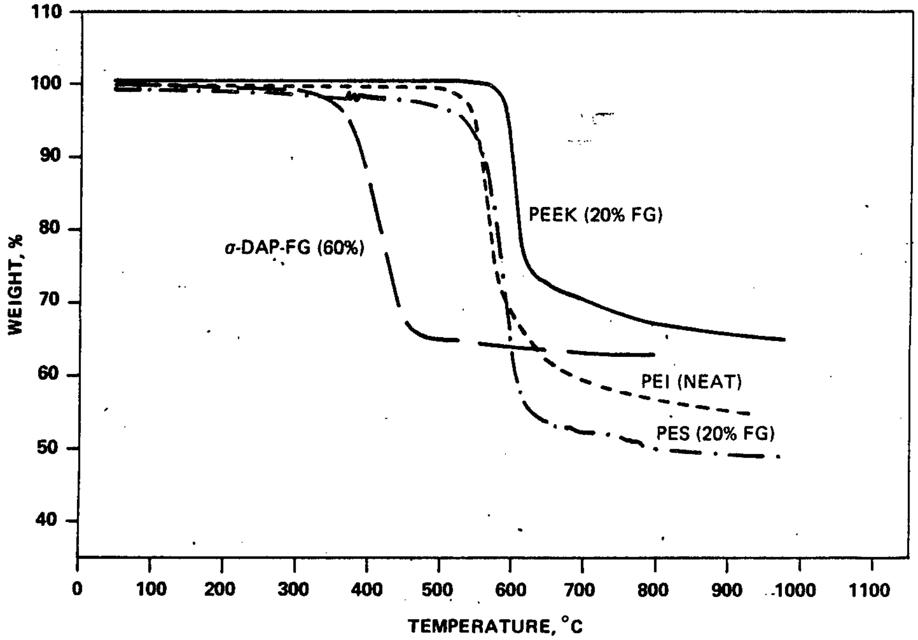

Figure 4 - TG analyses of molded fiberglass-containing resins: PEEK, PES, and *o*-DAP, and of PEI (neat) in N_2.

TABLE 4 - ISOTHERMAL TG ANALYSES OF ENGINEERING THERMOPLASTICS IN N_2

TP RESIN SAMPLE	WEIGHT % FIBERGLASS	TEMP °C	TIME, HOURS	WEIGHT LOSS, %	CHANGE IN APPEARANCE
PEEK LNP-79739	30	200	4	None	None
PEEK LNP-79739	30	400 (melt)	2-3/4	0.3	Grey → Brown-Black
PEI Ultem 1000	None	200	4	0.5	None
PEI Ultem 1000	None	360 (melt)	2-1/2	0.6	light → dark amber

clear, amber color. Thus the melt thermal stability of both PEEK and PEI, for times far exceeding the normal processing times required for molding, appears to be good. No analyses of possible chemical or molecular weight changes were included here, however.

Thus, overall relative thermal stabilities, based on the dynamic TG analyses appear to be: PEEK PEI > PES >o-DAP; however, in terms of volatiles up to ∿300°C DAP appears to be superior to PES.

Thermomechanical Analyses:

Results of the TMA analyses of PEI and PES resins are described first, and then those for PEEK and DAP-FG. Transitions observed, and thermal expansion coefficients (α) calculated, are summarized in Table 5 for PEI and PES. The temperature regions for which the calculated α values apply are also given, and do not include the immediate regions about any transition temperature where the changes in α are large.

One phenomenon observed in both PEI and PES above 200°C was a large expansion, accompanied by internal bubble formation. These temperatures correspond approximately to the manufacturer's reported heat distortion temperature (HDT) values. This phenomenon was investigated to some extent by TG analyses and mass spectroscopic (MS) analyses. No significant outgassing by either thermoplastic was observed by MS, and for PEI, no significant weight loss by TG. Thus, any gaseous product produced at these temperatures is for the most part, trapped internally, resulting in the large (up to ∿20% in volume) expansions observed by TMA.

The Tg values for both PES and PEI are generally in the 180-200°C range. In some cases, the exact position of Tg (especially on the first TMA run) is difficult to determine. Also, "extra" low-temperature transitions may be observed, particularly for the glass-filled PES. The Tg is more clearly defined and the extra transitions (probably resulting from residual molding stresses) disappear on subsequent TMA runs.

Values for α obtained for PEI and PES are not in all cases identical to the manufacturer's reported values. Differences in samples, test instruments, and testing

TABLE 5 - THERMOMECHANICAL ANALYSES OF MOLDED PEI AND PES RESINS

Resin Sample #	Sample Thickness, mm	TMA Run No.	Transitions, °C	Expansion Coefficient, (By Linear Fit to Region)		Observations
				α, μm/m/°C	Region, °C	
PEI/ Ultem 1000 -#1	3.21	1	202 (T_g)	13	30-180	Internal bubble formation and large expansion >200°C
PEI/ Ultem 1000 -#2	3.21	1	180 (T_g)	34	40-174	No bubble formation up to 200°C
PEI/ Ultem 1000 -#3	3.10	1	66			No bubble formation up to 200°C
			155			
		2	179 (T_g)	38	40-180	
PES/300P	2.96	1	201 (T_g)	80	50-180	Internal bubble formation >200°C and large sample expansion
PES/420P -#1	3.00	1	84	23	40-80	Same phenomenon observed
			183 (T_g)	58	90-180	
				122	185-195	
PES/420P -#2	2.98	1	88	58	25-85	No bubble formation up to 200°C
			188 (T_g)	78	90-180	
				112	185-195	
		2		56	-5-100	No well-defined T_g
				77	105-195	
		3	176 (T_g)	69	40-170	Large expansion of sample at 215°C

procedures (i.e., ranges of temperature used, etc) may all be responsible for these differences. The values obtained here are reasonably repetitive for each given resin from sample to sample (over identical temperature ranges), and thus are useful for comparison purposes.

Table 6 summarizes the TMA results for PEEK - both unfilled and glass-filled - and typical TMA thermograms of PEEK are shown in Figure 5. The glass-filled PEEK resins, in particular, exhibit a very distinct low temperature (generally, ≃ 60-70°C) transition on the first TMA run, in addition to the expected Tg at ≃150-65°C. This transition disappears on the second TMA run (Figure 5), as does the "negative" dip in the expansion curve observed near the Tg. This suggests that these effects were due to residual molding stresses, or possibly to physical aging effects. This was resolved by rerunning one of the glass-filled PEEK samples again after six months aging at room temperature (see Figure 5). No additional transitions, other than Tg, were observed. Thus, these effects are most probably due to residual molding stresses. Similar effects were also observed in the molded glass-filled PES and, in one instance, in an unfilled PEI resin (Table 5).

Some sample-to-sample variation in Tg values for PEEK may be related to factors such as: fiberglass filling (which would raise Tg); residual solvent acting as a plasticizer (which would lower Tg); and any incorporation of PES (which would increase Tg) into the PEEK backbone structure.

The α values determined here for unfilled PEEK above room temperature and below Tg (avg. = 55 μm/m/°C) were in fairly close agreement with the manufacturer's reported value of 46 μm/m/°C over a wider temperature range, -20°C to +150°C. There is reasonably good agreement, at least below Tg (with α generally ∿50 to 70 μm/m/°C), between unfilled and glass-filled PEEK. It is somewhat surprising that there is not a larger difference between the two, as fiberglass filling generally is expected to lower α values. The maximum fiberglass content tested here is only 20%, however, and may have been less if samples were not uniform. Above Tg there was a substantial increase in α, as would be expected. Again little, if any, differences were observed between glass-filled and unfilled samples. All runs were terminated well below the reported melting point of PEEK, and all samples were essentially unchanged in appearance or in thickness on recooling to room temperature.

Also listed in Table 6 are Tg and α values for the same molded DAP-FG component tested by TG. As may be seen, the values obtained below and above the TG (≃170°C) for the DAP-FG are somewhat lower than those of the filled PEEK resin, and closer to the unfilled PEEK.

Chemical/Spectroscopic Analyses:

The results of the various chemical and spectroscopic analyses performed on these resins are discussed in the following order: (a) emission spectroscopic/chromatographic analyses; (b) direct probe/mass spectroscopic analyses; and (c) Fourier transform infrared spectroscopic analyses.

TABLE 6 - THERMOMECHANICAL ANALYSES OF MOLDED PEEK and o-DAP-FG RESINS

MOLDED RESIN SAMPLE	SAMPLE THICKNESS, MM.	TMA RUN NO.	TRANSITIONS, °C	EXPANSION COEFFICIENT, α (BY LINEAR FIT TO REGION, °C) α, µm/m°/C	REGION °C
PEEK/20% GLASS -#1	3.205	1	73	68	25-140
			153(Tg)	209	155-245
		2	155	59	25-150
				155	160-240
PEEK/20% GLASS -#2	3.190	1	64	71	60-140
			161(Tg)	213	160-240
		2	162	62	20-140
				204	165-250
After 6 mo. aging/RT		3	165	64	40-140
				165	180-280
PEEK-#2 (unfilled)	3.353	1	166(Tg)	61	40-130
				172	190-275
		2	166	51*	40-140
				149	180-275
PEEK-#2 (unfilled)	3.416	1	162(Tg)	47	40-140
				152	165-280
		2	163	54	40-140
				145	180-280
PEEK-#3 (unfilled)	3.327	1	90	76	40-80
			149(Tg)	4.3	80-120
				156	160-260
		2	155(Tg)	59	40-140
				147	165-280
PEEK-#3 (unfilled)	3.350	1	78	44	40-140
			160(Tg)	146	170-265
		2	156(Tg)	55	40-140
				143	165-265
DAP-FG(60%) (Molded Component)	0.800	1	171(Tg)	41	50-150
				159	175-210

*Average of four α values for unfilled PEEK (2nd TMA runs) = 55 µm/m°C (below Tg).

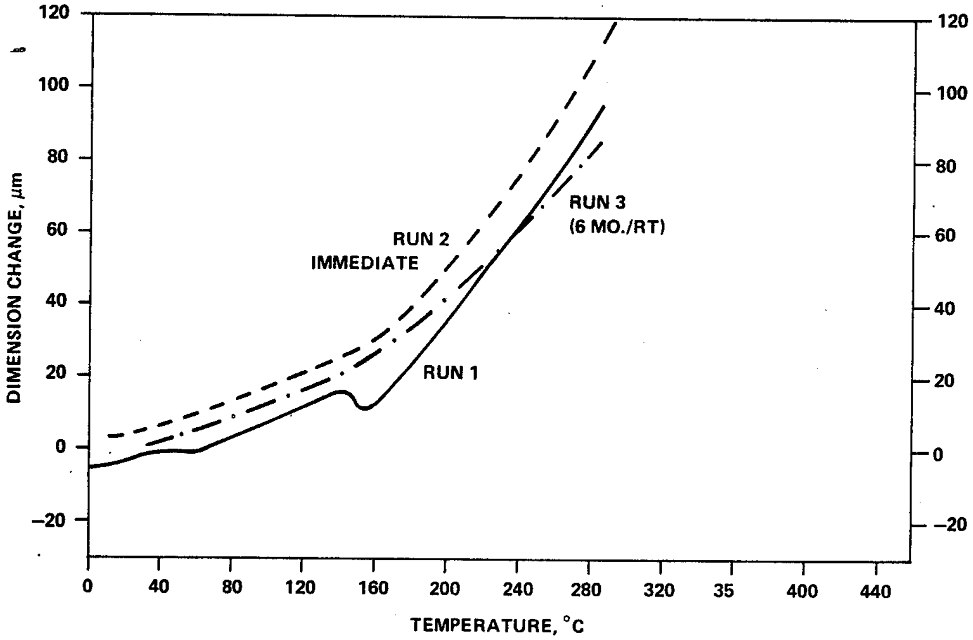

Figure 5 - TMA of molded PEEK (20% FG).

Emission Spectroscopic and Other Chemical Analyses:

The emission spectroscopic and other gravimetric/ chromatographic chemical analyses performed on two of the three engineering TP resins are summarized in Table 7. The ions and elements listed first in Table 7 are those of primary concern, in terms of potential problems involving compatibility, corrosion, etc., in any actual component usage. In particular, these are S, Fe, Cl^- and, to a lesser extent, F^-. The halogen ions were not necessarily present in ionic form in the molding compounds, but were transformed and analyzed as such in the analytical procedure (ion chromatography). The fluoride is probably from a KF by-product of the polymerization of PEEK (or from residual monomer - see Figure 6) and as such may always be expected to be present in small amounts [2].

The sulfur (total and ionic) concentration is of concern, particularly in relation to potential sulfide formation. Its presence may be the result of polymerization solvent used (Figure 6). The LNP Corporation PEEK-FG molding compound, which has a lower sulfur content than does the Fiberfill PEEK, was chosen for further PEEK-component molding and compatability testing. The percent Fe in the LNP PEEK-FG is also slightly lower than in the Fiberfill PEEK-FG. Results given for the PEEK-coated wires tested are based on total sample weight, including the wire.

The PEI resin showed no elements or ions of concern present in excessive amounts. The suggested polymerization route for PEI is given in Figure 7 [3]. Based on these analytical results, either no potentially harmful constituents are used in the PEI polymerization, or they are completely removed following it.

TABLE 7 - EMISSION SPECTROSCOPIC/CHEMICAL ANALYSES OF TP MOLDING COMPOUNDS (AND PEEK COATED WIRE)

ELEMENT (OR ION)		PEEK COATED Cu WIRE (Wt. %)	FIBERFIL PEEK (P061616) (LOT 4635176) (30% GLASS-FILLED) (Wt. %)	LNP PEEK PDX 79737 (LOT 120010) (30% GLASS-FILLED) (Wt. %)	POLYETHERIMIDE (PEI) ULTEM 1000 (UNFILLED) Wt. %
F^-		0.032$^+$	0.13$^+$	0.17$^+$	<0.001$^+$
Cl^-	Wire	0.003+	0.01$^+$	0.02$^+$	0.008$^+$
S (total)	Sample	0.022^{+x}	0.23	0.04	<0.005^{+x}
S (ionic)	#2	none detected	<0.01	<0.01	None detected
Fe		0.01	0.05	0.04	<0.001
Ba		--	0.02	0.01	<0.001
Sb	Wire	--	<0.01	<0.01	--
B	Sample	--	0.4	0.4	≤0.001
Si, Al, Ca	#1	Ea <0.01	Ea >0.6	Ea >0.6	Ea <0.002
Mg		<0.01	0.08	0.08	0.001
Na		--	0.2	0.2	<0.002
Ti		--	0.08	0.08	<0.001
Sr		--	0.07	0.05	--
Mn,Cr,Ga,V,Cu,Zr		--	Ea <0.01	Ea <0.01	Ea ≤0.001
Ag		<0.01	--	--	--
Cu, Sn		≥0.6	--	--	--
Cd, Co		--	--		Ea <0.001
Ni		--	--		<0.002
Zn		--	--		<0.001

$^+$Analyzed in ionic form by ion chromatography

^{x}As $SO_4^=$

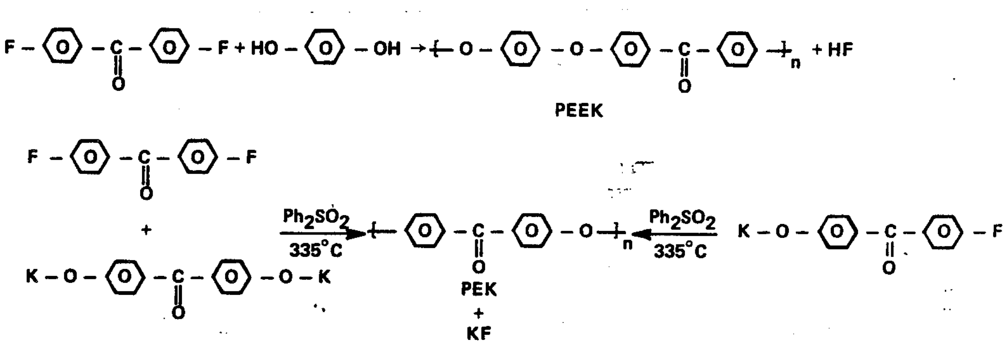

Figure 6 - Routes for PEEK and PEK synthesis (Attwood et al, Polymer, 1981, 22, 1096).

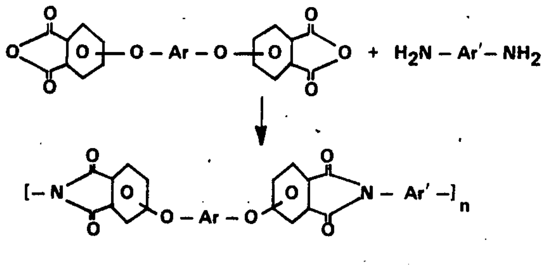

Figure 7 - PEI synthesis route (Takekoshi et al, Polymer Preprints, 1979, 20, 179).

No similarly detailed chemical analyses were performed on the PES resin since it is of less interest than either PEEK or PEI in terms of potential component usage. Some of the reasons for this include: sulfur content (in the polymer backbone), and the TG evidence of substantially higher volatiles.

Direct Probe/Mass Spectrometry:

Direct probe/mass spectrometry was used to identify volatilizable constituents of the three engineering thermoplastic resins (and of a molded DAP-FG component for comparison), and also to examine relative polymer backbone thermal stabilities. Results will be correlated with those of the TG and the FTIR analyses.

The total ion current profile for PES (neat) is given in Figure 8. A large initial value of total ions is observed between 30° and 100°C (add ∿80°C for a comparable atmospheric analysis) and a minor increase in the number of total ions beginning at approximately 188°C. These have been attributed respectively to water (M/Z 18) and to phenylsulfone, (M/Z 125). This indicates degradation of the polyethersulfone polymer at elevated temperature or, alternately, some other mechanism of phenyl sulfone release. Figure 8 shows, along with the total ion current, the individual ion currents of M/Z 18 $(H_2O)^+$ and M/Z 125 $(C_6H_5SO)^+$. Water is being liberated by the polymer (in the high vacuum of the ion source) from 30°C to approximately 100°C. Observation of the phenyl sulfone fragment at M/Z 125 begins at approximately 188°C and remains reasonably intense to 280°C. Since the PES degradation observed by TG does not commence until ≥450°C, the phenyl sulfone fragments observed here by MS may be the result, in part, of trapped

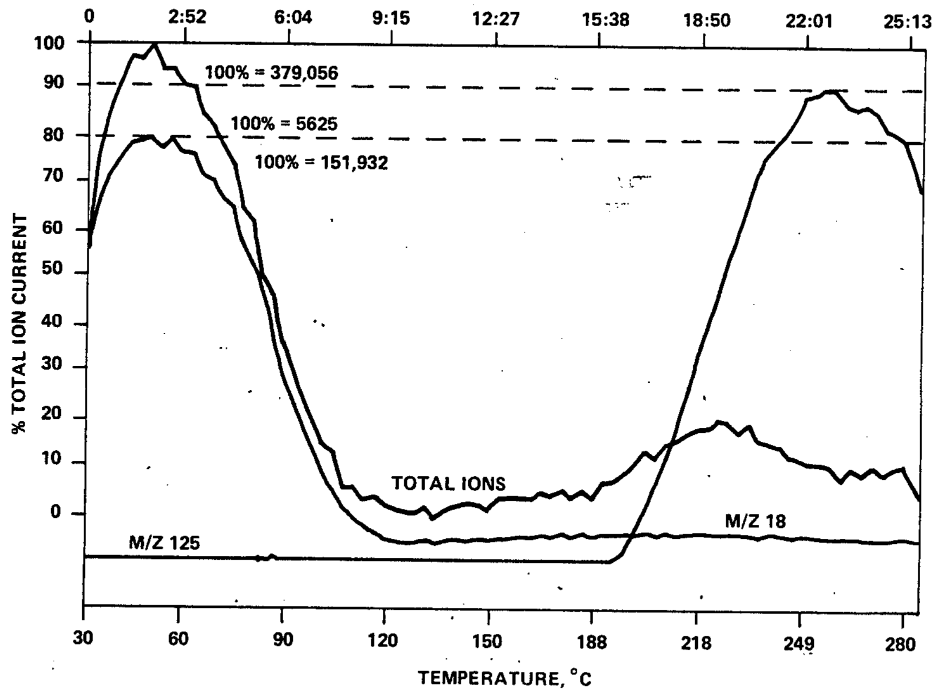

Figure 8 - DIP/MS of polyether sulfone (neat).

solvent or monomer. Actual polymer degradation under the high vacuum conditions, cannot be ruled out, however.

Figure 9 shows the total ion profile for PEI (polyetherimide). Water again is observed as a large ion signal at the start of the experiment and returns to baseline at approximately 100°C. Only a slight increase in ion current is observed throughout the remainder of the experiment. Examination of the mass spectra indicates a very slight degradation of the polymer beginning to occur at approximately 220°C, under the high vacuum conditions. In Figure 9, the total ion current profile is shown along with the M/Z 18 ion current and the M/Z 505 ion (the PEI degradation fragment, which is shown in Figure 7). Thus, as shown by the total ion current, degradation of PEI is virtually negligible below ≥360°C (ambient atmosphere). Also, the only trapped solvent removed from PEI is H_2O.

The total ion current profile for the analysis of PEEK (identical for neat or glass-filled) is shown in Figure 10. As with the other thermoplastics, water is present to about 100°C. A second increase in ion current is noted beginning at approximately 120°C, reaching a maxima at about 190°C and slowly returning to baseline. The total ion current along with the M/Z 18 ion and the phenyl sulfone ion at M/Z 125 are given in Figure 10. The earlier release of the phenyl sulfone in PEEK, as compared to PES, indicates it is the result of a trapped solvent, such as diphenyl sulfone, rather than any polymer degradation. This is compatible with the polymerization route shown in Figure 6, also.

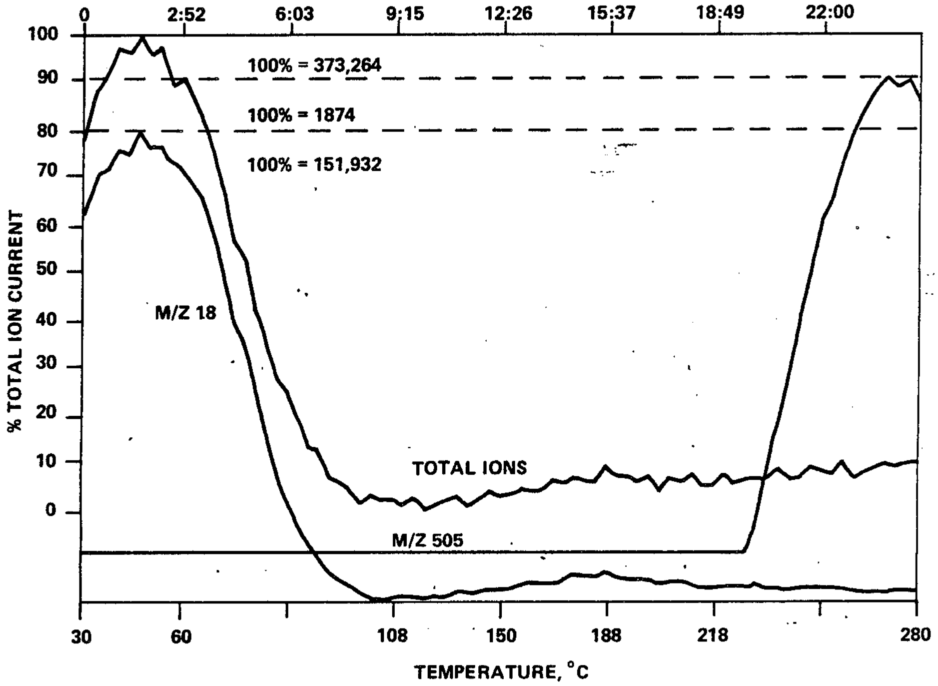

Figure 9 - DIP/MS of polyetherimide (neat).

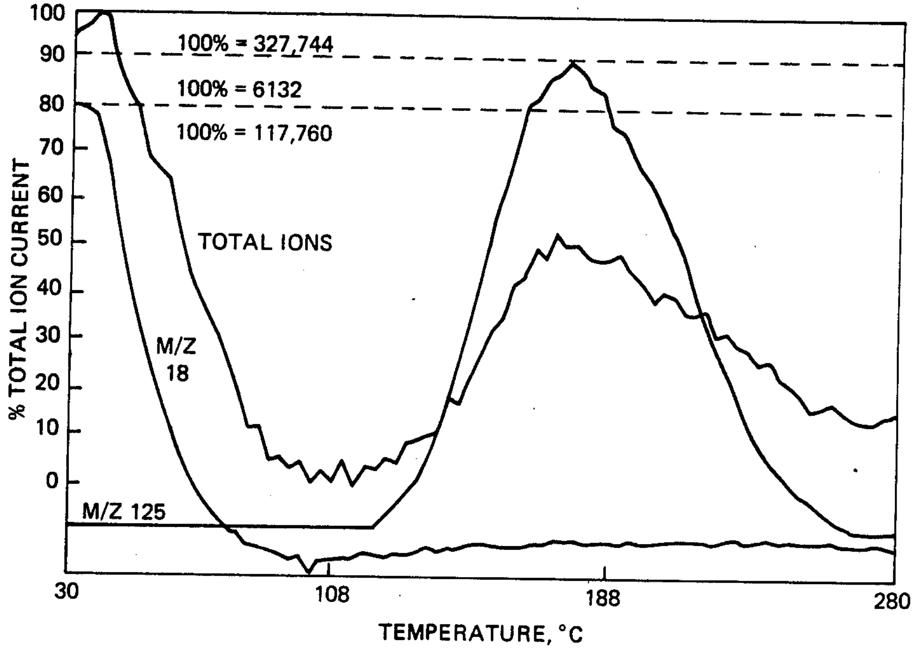

Figure 10 - DIP/MS of fiberglass-filled PEEK.

For comparison, a DIP/MS experiment was performed on the same DAP-FG component as tested previously by TG and TMA. The total ion profile is shown in Figure 11, which also shows a release of H_2O from 30°C to approximately 180°C. The polymeric degradation fragment of DAP at M/Z 104 (phthalic anhydride) is observed at temperatures as low as approximately 70°C under high vacuum. At approximately 210°C (in vacuum) a sharp increase in ion current occurs, indicating decomposition of the polymer. Since the N_2 atmospheric decomposition of this DAP-FG begins at ≥320°C by TG analysis, this vacuum decomposition value is not unexpected.

Also, this is an o-DAP-based component, which is known to be less thermally stable than a comparable m-DAP-based material.

In summary, in terms of extractables that can be volatilized under the high vacuum conditions of the DIP/MS experiments performed here, the relative stabilities of the three engineering thermoplastics and DAP appear to be: PEI > PES > PEEK > o-DAP. This is strictly in terms of initial observation of outgassing of the plastic (other than H_2O) in the MS vacuum envelope. The phenyl sulfone fragments from the PES may be, however, a result of polymer decomposition, whereas in PEEK they are probably due to trapped solvent (eg., diphenylsulfone). Thus, in terms of relative polymer backbone thermal stability the results appear to be: PEEK > PEI > PES > o-DAP. These latter results are in qualitative agreement with those obtained by the TG analyses.

Direct probe mass spectrometry has thus proven to be useful in determining both the relative thermal stabilities and the compositions of volatilized constituents of the three engineering thermoplastics resins (and also o-DAP). The presence or absence of the glass filler does not appear to affect the results of the analyses.

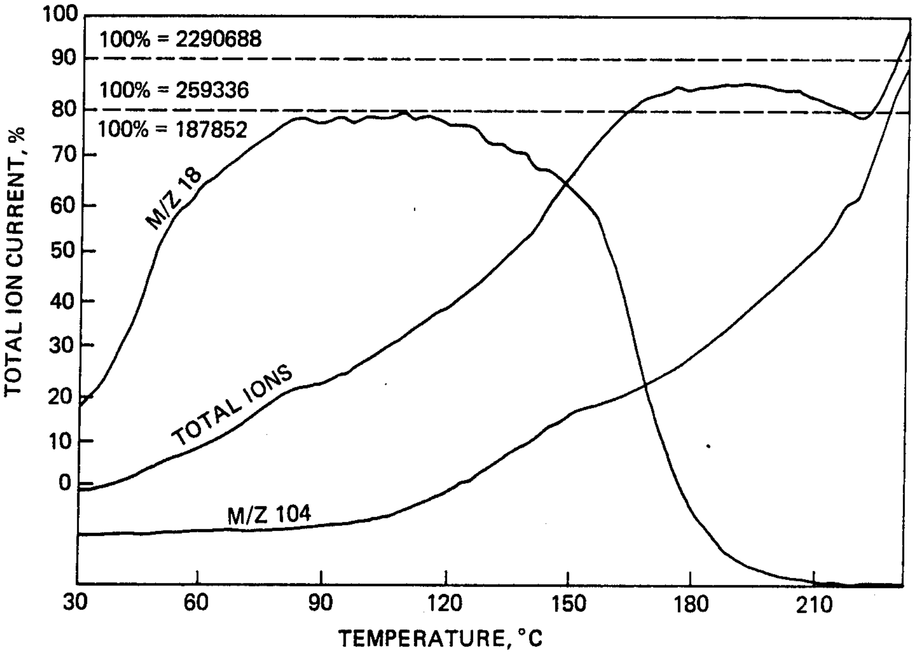

Figure 11 - DIP/MS of DAP-FG molded component.

Fourier Transform-Infrared Spectroscopy:

Expanded portions of the infrared spectra of the three engineering thermoplastic resins, as obtained by ATR/FT-IR, are shown in Figures 12-14. These portions of the spectra contain the 2000 to 600 cm^{-1} region used in the chemical characterizations given here. All three spectra are quite complex, but some useful information about chemical moieties can be deduced. First, the spectrum of Victrex 300P PES shown in Figure 12, matches the Sadtler library spectrum of this plastic (D6400K). A notable difference between Figure 12 and Sadtler Spectrum D6400K is the extra band at 1067 cm^{-1} in Figure 12 - this band is the result of an unidentified additive. This band should be a good measure of the amount of that particular additive. Also noteworthy are three bands at 1320, 1295, and 1008 cm^{-1}. These bands are certainly the result of the sulfone moiety ($-SO_2-$). The 1228 and 1096 cm^{-1} bands are assigned to the ether linkage. The remaining bands are the result of the aryl groups and need not be assigned individually. These bands, however, form an excellent fingerprint for these compounds.

The expanded spectrum of the second plastic, Ultem 1000 PEI is shown in Figure 13. This spectrum has a number of bands that support the polyetherimide structure, shown in Figure 7. The strong band at 1714 cm^{-1} is perfect for the imide group. Likewise the bands at 1346 cm^{-1} and 1230 and 1081 cm^{-1} are assigned to the N-Ar and Ar-O-Ar groups, respectively. Notably absent is a peak between 1500 and 1530 cm^{-1} which is always present for aromatic nitro groups. This excludes the presence of an aromatic nitro group in the plastic.

Finally, Figure 14 shows the expanded spectrum of PEEK. The sharp bands at 1650, 1484, and 923 cm^{-1} are characteristic of a diphenyl ketone. However, the characteristic band at 1240 cm^{-1} for an arylether is missing; the other character-

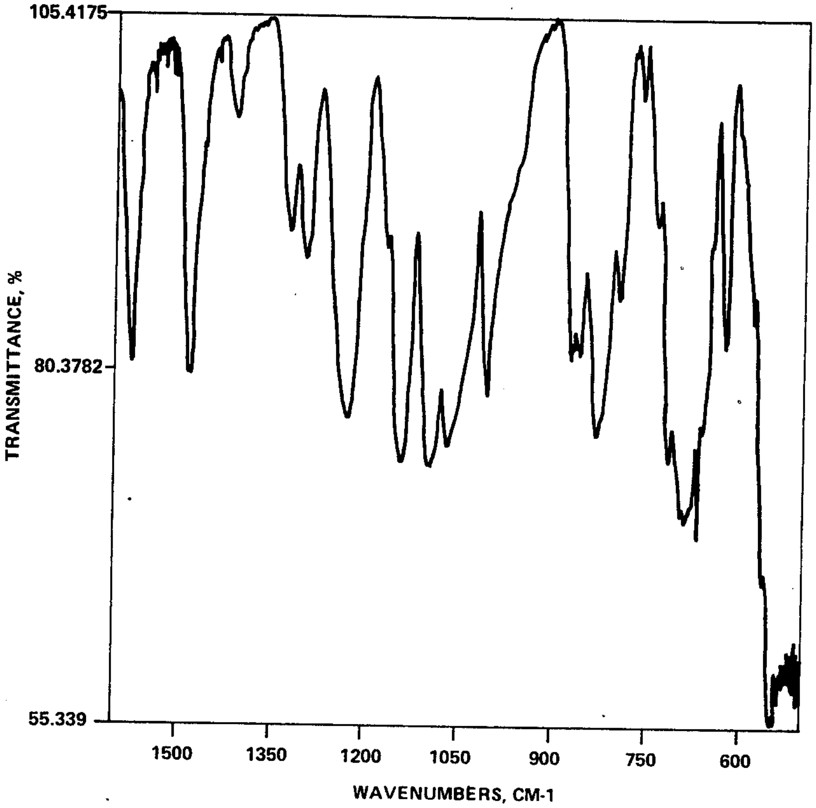

Figure 12 - ATR/FT-IR spectrum of molded PES (neat).

istic arylether band is present at 1041 cm^{-1}. It is interesting to note that there are bands observed at 1230 and 1050 cm^{-1} in the spectra of the amorphous PEI and PES resins. Also of interest are the three bands at 1008, 1275, and 1305 cm^{-1}. As mentioned above, these are characteristic bands of the sulfonyl group. These bands alone are not conclusive proof that a sulfonyl solvent is retained by the plastic, but are strongly indicative of its presence. The presence of halogens in PEEK is difficult to determine with certainty. First, arylfluorine compounds result in bands between 1100-1270 cm^{-1}. While there are three bands in this region, these bands by themselves are not proof that fluorine compounds are present. Chloro- and bromo-aryl compounds result in bands between 1100 and 1030 cm^{-1}. Since there are no unassigned bands in this region, the presence of these haloaryl compounds is unlikely.

The results of the FT-IR analyses of PEEK (two different molded PEEK samples gave identical results) support the DIP/MS observation that a phenylsulfone is present. While neither analysis is quantitative in nature, an estimate of the actual amounts of diphenyl sulfone present can be obtained from the sulfur analyses of the 30% fiberglass PEEK molding compounds (assuming that no sulfur is present in the fiberglass itself). These estimates range from 0.31% by weight diphenylsulfone in the LNP Corporation PEEK-FG to 1.77% by weight in the Fiberfill PEEK-FG (or up to 2.5% in PEEK itself). Knowledge of the

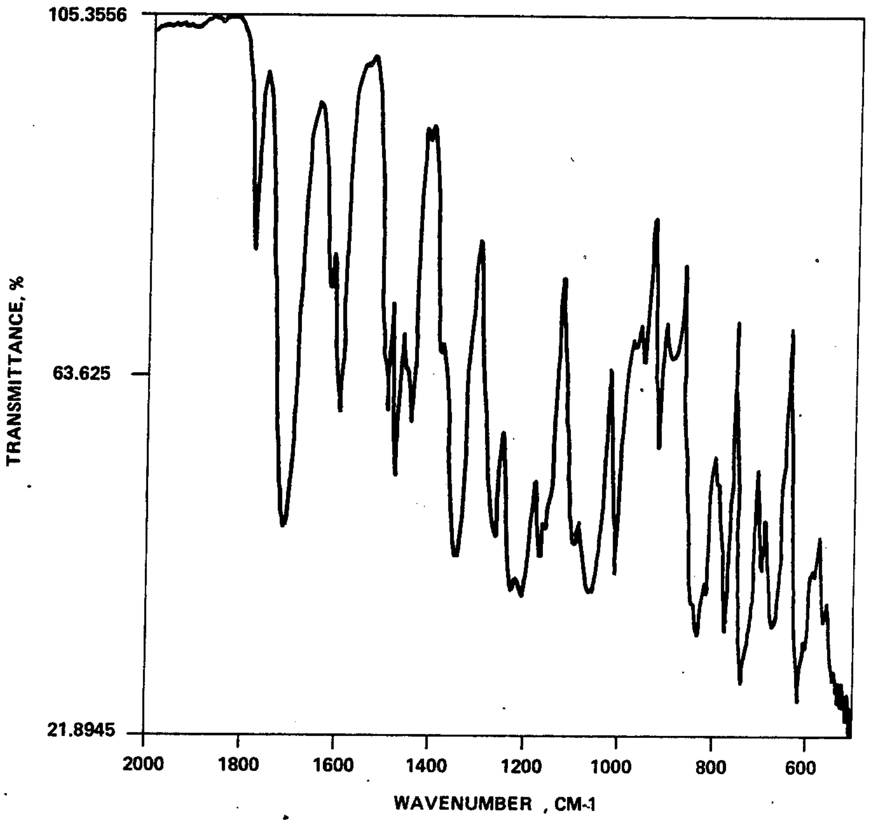

Figure 13 - ATR/FT-IR spectrum of molded PEI (neat).

potential amounts of an extractable (or volatilizable) diphenyl sulfone constituent present in the PEEK resin is of importance as far as compatibility and processing are concerned.

The FT-IR data do not indicate whether the F^- present in PEEK-FG is a part of the KF byproduct of the polymerization or part of any residual aryl-fluorine monomers. Further, the other analytical data do not establish with certainty whether the fluoride present in PEEK is initially in ionic or in covalent form.

Summary and Conclusions

As a result of the characterization work reported here on the three engineering thermoplastics, the following conclusions may be drawn in regard to their potential applicability in Mound components (assuming satisfactory mechanical properties and moldability).

PES Resins: Although its thermal stability, in terms of decompositon onset temperature, is good, PES has more serious drawbacks than any of the three resins tested: (1) the volatilization of a phenyl sulfone (whether from the polymer itself or from a trapped solvent) could present potential problems in terms of compatability and corrosion; (2) the "bubble" formation and expansion exhibited above 200°C in TMA experiments could present a problem if any brief temperature excursions occurred above this temperature in processing or testing; and (3) chemical/solvent resistance (although not specifically tested here)

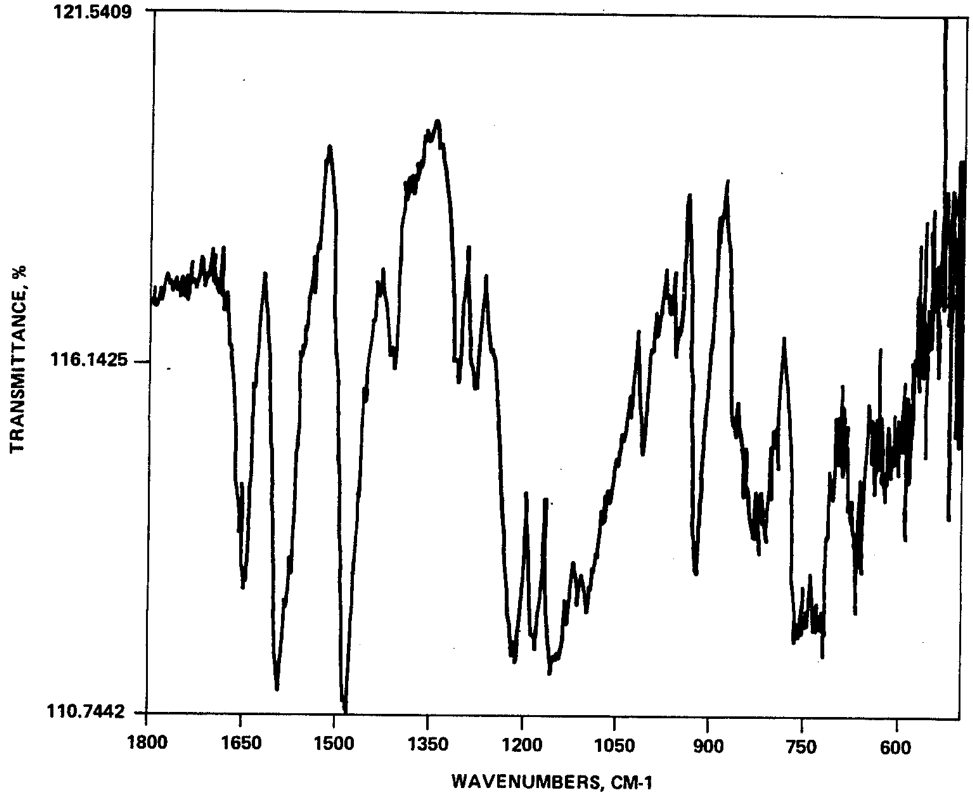

Figure 14 - ATR/FT-IR spectrum of molded PEEK (neat).

is the poorest of the three thermoplastic resins, according to the manufacturer's information.

PEI Resins: PEI was only tested in an unfilled resin, but its thermal stability was very good and should be even better in glass-filled grades. It did not appear to have any "trapped" solvents (except H_2O) or potentially harmful minor constituents. Its thermal expansion coefficient (below Tg) was close to that of a O-DAP-FG. It does have two potential drawbacks, however; (1) its water absorption is the highest of any of the three thermoplastics tested (which could require special drying precautions); and (2) the same bubble formation above 200°C exhibited by PES was observed here also; thus this resin requires precautions to avoid exceeding this temperature even briefly in processing or testing operations.

PEEK Reins: The PEEK resins were the most outstanding in terms of thermal stability (highest degradation onset temperature). According to the manufacturer's information, it is also the best of the three thermoplastics in chemical resistance (as is expected, since PEEK is a semi-crystalline polymer). Expansion coefficients below Tg are close to that of DAP-FG (for the unfilled resin). The potential problem areas are: (1) a phenyl sulfone (probably from a polymerization solvent) can be volatilized under high temperature/ high vacuum conditions; (2) fluoride (ion?) is always present in small amounts, as it is a byproduct of the polymerization reaction (as well as being part of a starting monomer); and (3) the very pronounced "extra" transitions observed below Tg in the TMA experiments suggest that annealing, both to remove residual molding stresses and enhance crystallinity, may be desirable and should be investigated.

Future Work: Since the PEEK thermoplastic resins are of primary interest in terms of immediate applicability in Mound component manufacture, PEEK is the focus of continuing studies on engineering thermoplastics. These include: (1) compatability studies with the appropriate explosives, pyrotechnics, and other materials of construction; (2) adhesive bonding studies; (3) studies on crystallinity and the effects of molding, annealing, and aging on crystallinity; and (4) a more definite determination of the chemical structure of the PEEK polymer.

Acknowledgements

The authors would like to acknowledge the contributions of: W. M. Preston, E. B. Nunn, Y. G. Ishida, and L. T. Brehm for the gravimetric/chromatographic and emission spectroscopic analyses. They would also like to thank W. R. Bergenn of ICI Americas Inc. and R. O. Johnson of the General Electric Company for providing the PEEK, PES, and PEI molded samples tested here.

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