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COMPOSITIONAL ANALYSIS OF POLYPHENYLENE SULFIDE CONTAINING PTFE AND CARBON FIBERS

N.A. PAMPHILIS

AC Spark Plug, Division of General Motors Corporation, Flint, MI 48556 (U.S.A.)

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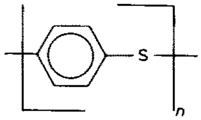
ABSTRACT

Carbon fibers (ca. 30%) were determined in samples containing polyphenylene sulfide, inorganic filler and polytetrafluoroethylene (PTFE) by means of thermal analysis using both thermogravimetry (TG) and differential scanning calorimetry (DSC).

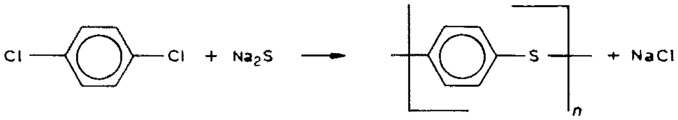
Two different, but related, methods were used to determine quantitatively the contents of the sample. The first, which was nominally called the "Indirect Approach", utilizes DSC for the determination of the polymeric components and TG for determination of the residue, i.e. glass, fillers, etc. The amount of carbon is then determined by difference. The second method, which was nominally called the "Direct Approach", utilizes DSC for the determination of PTFE and TG for the determination of all other components. The agreement between the two methods is good.

INTRODUCTION

Poly(*p*-phenylene sulfide), frequently referred to as polyphenylene sulfide or PPS, is composed of a series of alternating aromatic rings and sulfur atoms



Although it was prepared in the laboratory some time ago, PPS did not attain commercial importance until a new and improved process for making PPS was reported in 1967 [1]. It involved the reaction of *p*-dichlorobenzene with sodium sulfide in a polar organic solvent to produce PPS as follows



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PPS was first produced commercially in 1973 under the trade name of Ryton. PPS possesses a unique set of characteristics including good thermal stability, unusual insolubility, resistance to chemical environments and inherent flame resistance [2,3]. Cross-linked and substituted polyphenylene sulfides were prepared and were compared with PPS [4] by thermogravimetry in air. It was found that PPS has the best thermal stability. PPS is superior to most injection moldable polymer systems. The resin flows easily into intricate mold cavities and its low shrinkage allows molding to close tolerances [5]. In general PPS injection moldings, particularly glass-filled specimens, are classified as being hard, tough and rigid with high flexural modulus. Thus, glass is added to PPS for good mechanical stability. Teflon and carbon are added to PPS to enhance lubricity. PPS also possesses good overall electrical, i.e. insulative, properties (a low dielectric constant) [6].

Materials that contain PPS are presently being used in automobile components exposed to severe chemical and temperature environments. Such materials are ideal in-fuel-tank components where the combination of gasoline and temperatures fluctuating from −40 ° C to 77 ° C would be tough on most plastics. A method was needed which could determine quantitatively the amount of composites in the sample so that the claim by the vendor of 30% carbon, 15% PTFE and 55% PPS could be substantiated.

The ideal solution to this problem would be to determine the composition of the sample using one thermal analysis method, either TG or DSC. If TG were taken as the method of choice, all sample components (PTFE, PPS and carbon fibers) could conceivably decompose leaving only a residue, e.g. glass, filler, etc. PTFE decomposes cleanly in a narrow temperature range (450–600 ° C) in a nitrogen atmosphere [7]. Carbon fibers, on the other hand, degrade at much higher temperatures (above 600 ° C) with no substantial decomposition commencing unless the TG nitrogen atmosphere is switched to air or oxygen [8]. Ryton-4 (PPS with glass) in a nitrogen atmosphere begins to decompose at 450 ° C, but a considerable amount of the polymer remains at 1000 ° C as shown in Fig. 1 [2]. However, in the aforementioned figure, the same polymer displays a two-stage weight loss in an air atmosphere. The first decomposition curve commences at about 450 ° C, while the second starts at about 600 ° C. It would be expected, then, that a TG thermal curve of a sample containing PPS, PTFE and carbon in an atmosphere of air would consist of a two-stage weight loss curve. The first weight loss curve would stem from PTFE and a fraction of PPS, whilst the second weight loss curve would stem from carbon and the remaining fraction of PPS. It is apparent, then, that a sample containing PPS, PTFE and carbon cannot be determined by TG alone. If the quantity of one of the components (i.e. PTFE) were to be determined by DSC then the amount of PPS, carbon and inorganic fillers could be determined by TG and the compositional analysis of the sample would be complete. This method, which was nominally called the "Direct Approach", utilizes DSC for the

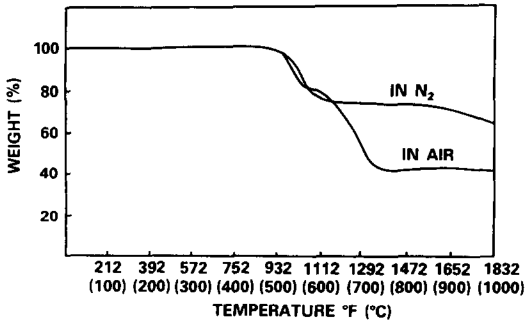

Fig. 1. TG thermal curves for Ryton R-4.

determination of PTFE whilst all other components were determined by TG [9].

For small concentrations of carbon fibers in a sample containing PPS it is assumed that PTFE and carbon decompose cleanly. That is, the decomposition of PTFE occurs only during the first stage of the weight loss whilst the decomposition of carbon occurs only during the second stages of the weight loss. PTFE and carbon thus would not interfere with the quantitation of PPS, the decomposition of which occurs during both the first and second stages of the weight loss curve. In reality, a small amount of carbon (ca. 2%) "bleeds" or decomposes during the first weight loss. For samples containing small amounts of carbon, this "bleeding" does not have a significant impact on the quantitation of PPS, whilst for samples containing PPS and large amounts of carbon, this "bleeding" of carbon during the first TG weight loss can have a significant impact on the quantification of PPS. Thus for more accurate calculations, especially in samples containing large amounts of carbon, the contribution of carbon to the first TG weight loss must be taken into account.

Both PTFE and PPS are thermoplastic materials, display crystallinity and, as such, possess an endothermic melting point profile in DSC. PPS has a melting point of 285 °C and PTFE has a melting point of 327 °C [10]. The area under the DSC melting point curve is the enthalpy of fusion (ΔH_f). This is the enthalpy change on transition from the crystalline state of the polymer to its liquid state and is directly related to the amount of crystallinity in the sample. If, for example, the ΔH_f for pure PTFE that is 90% crystalline were calculated to be 40 J g^{-1}, a sample containing 10% of PTFE (90% crystalline) would have a ΔH_f of 4 J g^{-1}. The same analogy can be drawn for a sample containing PPS. The correlation between crystallinity and the amount of a polymer in a sample depends on the assumption that the polymer in the sample is of a similar crystallinity and was processed in a manner similar to the reference polymer. The thermal properties of the reference polymer and the same component in a polymer mixture thus would be treated as being the same. Thus, the amount of a polymer as measured by DSC from the ΔH_f is directly related to its purity until a maximum ΔH_f value is obtained for a sample in its purest form for a given crystallinity and molecular weight. Even though the amount of PTFE and PPS in the vendor sample can be determined by DSC, the amount of residue (i.e. glass, filler, etc) has to be determined by another method (i.e. TG). By determining the amount of PTFE and PPS by DSC and the amount of residue by TG, the amount of carbon in the sample can be obtained from the material balance of the blend. The method described above was nominally called the "Indirect Approach". The amount of carbon found by this method is expressed by the following material balance equation

$$\begin{aligned}\%\ \text{carbon} = 100\% - \%\ \text{PPS (by DSC)} - \%\ \text{PTFE (by DSC)} \\ - \%\ \text{residue (by TG)}\end{aligned} \qquad (1)$$

EXPERIMENTAL

Differential scanning calorimetry

PTFE, PPS and the vendor sample obtained from RTP Co. were studied by DSC using the Perkin–Elmer 7 series thermal analysis system. The heating run conditions were as follows

Temp. 1	50 °C
Rate	10 °C min^{-1}
Temp. 2	340 °C
Sample weight	5–15 mg
Gas	Nitrogen (25 ml min^{-1})

where Temp. 1 is the initial or starting temperature for the DSC analysis, Rate is the rate of temperature rise from Temp. 1 to the final temperature (Temp. 2) and Temp. 2 is the final temperature.

Each sample was evaluated a minimum of three times. Each test consisted of a slow heating run (10 °C min^{-1}) followed by a fast cooling run (100 °C min^{-1}) and finally by a second slow heating run (10 °C min^{-1}). The values for the melting point (T_m) and enthalpy of fusion (ΔH_f) of the particular sample under investigation were obtained from the second heating run. The instrument was calibrated for temperature and energy using indium as the standard. The transition temperature for indium (onset) was set at 156.3 °C whilst the transition energy (ΔH_f) for indium was calculated to be 28.73 J g^{-1}. The theoretical transition temperature and transition energy for indium are 156.6 °C and 28.45 J g^{-1} respectively.

Thermogravimetric analysis

PTFE and the vendor sample from RTP Co., PPS with glass from Phillips Corp. and carbon fibers from LNP Corp. were analyzed by TG using the Perkin–Elmer 7 series thermal analysis system. The conditions in all cases were as follows

Temp. 1	30 ° C
Time 1	0 min
Rate	20 ° C min^{-1}
Temp. 2	900 ° C
Time 2	0 min
Sample weight	10–20 mg

where Temp. 1 is the initial or starting temperature for the TG analysis, Time 1 is the time of residence of the sample specimen at Temp. 1, Rate is the rate of temperature rise from Temp. 1 to the final temperature (Temp. 2), Temp. 2 is the final temperature and Time 2 is the time of isothermal hold at 900 ° C (Temp. 2).

The balance head gas was nitrogen at a flow rate of 50 ml min^{-1}. The purge gas was switched from nitrogen to oxygen 35 min into the heating program (i.e. at 730 ° C). The TG furnace chamber was purged with oxygen for the remainder of the TG run. The purge gas flow rate was 25 ml min^{-1}. A Curie point calibration was performed on the TG furnaces using nickel and Perkaloy as magnetic standards with magnetic transitions at 354 ° C and 596 ° C respectively.

RESULTS AND DISCUSSION

Differential scanning calorimetry (Indirect Approach)

Typical DSC thermal curves from the second heating of the vendor sample and PPS and PTFE from RTP (reference samples) are illustrated in Figs. 2–4.

Although in most cases a great deal of information (thermal history) is obtained from the DSC thermal curve of a sample from the first heating, the thermal curves of the second heating, having similar thermal histories, give better resolved and more reproducible T_m and ΔH_f values. It was for the latter two reasons that the ΔH_f values were calculated from the DSC thermal curve of a sample from the second heating. The DSC thermal curve of the vendor sample in Fig. 2 (second heating) possesses a peak at 279 ° C from PPS and a peak at 326 ° C from PTFE. The thermal curve of the reference sample (second heating) shown in Fig. 3 contains a T_m peak at

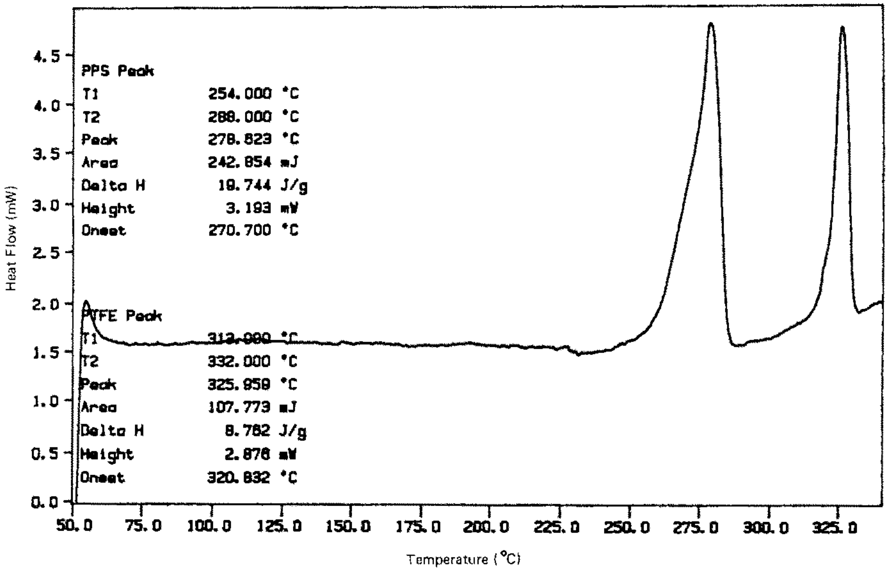

Fig. 2. The DSC thermal curves of vendor sample—second heating. (Sample weight 12.300 mg).

272 ° C from PPS. The thermal curve of PTFE from RTP is shown in Fig. 4. The results from the DSC thermal curves are summarized in Table 1. The ΔH_f of PTFE from RTP was calculated as 52.437 J g^{-1} (Table 1). In polymer

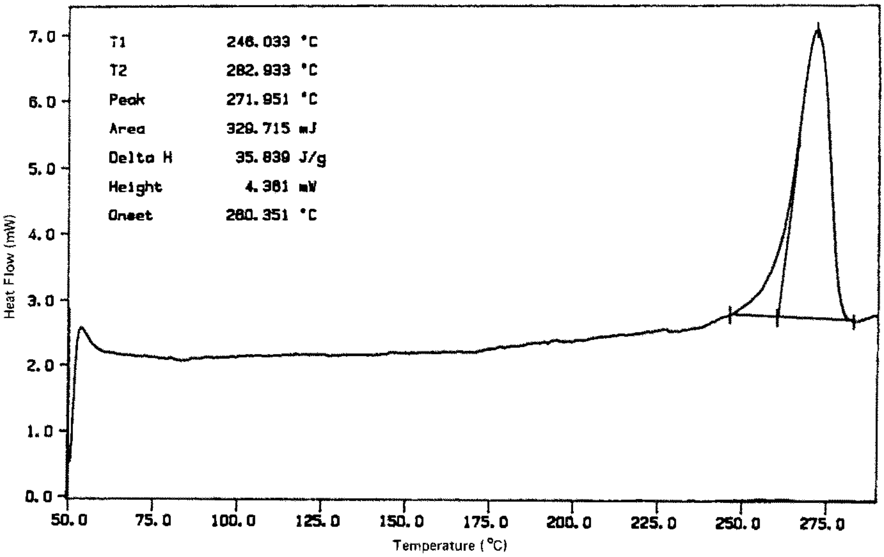

Fig. 3. The DSC thermal curve of PPS from RTP—second heating. (Sample weight 9.200 mg).

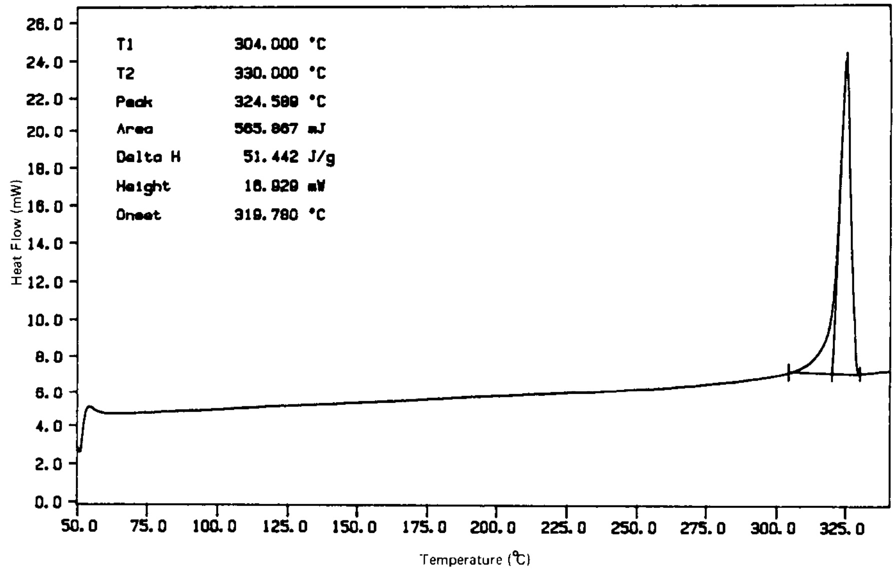

Fig. 4. The DSC thermal curve of PTFE from RTP—second heating. (Sample weight 11.000 mg).

blends the ΔH_f of PTFE should be directly related to the amount of PTFE present provided that this component and the reference polymer are structurally similar and possess the same degree of crystallinity. For example, the ΔH_f of a PTFE sample from DuPont and LNP were calculated as 19.87 J g^{-1} and 44.13 J g^{-1} respectively, as opposed to 52.44 J g^{-1} for the RTP sample. The PTFE from RTP was used as a reference sample because it was ascertained from the vendor that this type of PTFE was present in the sample under investigation. The amount of PTFE in the vendor sample was obtained using eqn. (2) and was calculated as 15.21%.

$$\%\ \text{PTFE} = \frac{\Delta H_f\ \text{PTFE (vendor sample)}}{\Delta H_f\ \text{PTFE (reference)}} \times 100 \tag{2}$$

TABLE 1

The enthalpies of fusion (ΔH_f) of PTFE and PPS

	$-\Delta H_f$ (J g^{-1})			
	Run A	Run B	Run C	Average
Reference sample				
PPS	35.839	35.854	35.317	35.670
PTFE	51.442	52.941	52.929	52.437
Turbine impeller				
PPS	19.744	19.686	18.819	19.426
PTFE	8.762	7.721	7.448	7.977

TABLE 2

The TG weight losses of the vendor sample

Run	Weight loss (%)	
1	41.15	58.02
2	40.76	58.65
3	41.49	58.02
4	41.39	57.94
5	41.11	58.89
Average	41.18	58.30

A sample of PPS was obtained from RTP. Again the assumption was made that PPS in the reference sample and in the sample to be analyzed are structurally similar and possess the same degree of crystallinity. The ΔH_f of PPS was calculated as 35.67 J g^{-1}. Using 35.67 J g^{-1} as the ΔH_f of PPS, the amount of PPS in the turbine impellers was obtained according to eqn. (3) and was calculated as 54.46%.

$$\% \text{ PPS} = \frac{\Delta H_f \text{ PPS (vendor sample)}}{\Delta H_f \text{ PPS (reference)}} \times 100 \qquad (3)$$

The percentage of carbon can then be determined according to eqn. (1).

% carbon = 100% − 54.46% PPS − 15.21% PTFE − 0.52% residue = 29.81%

The amount of residue in the vendor sample was obtained by TG from Table 2 (100% − 41.18% − 58.30% = 0.52% residue).

Thermogravimetry (Direct Approach)

Typical TG thermal curves of PTFE from RTP, carbon fibers from LNP, PPS with glass from Phillips (reference sample) and the vendor sample are illustrated in Figs. 5–8 respectively. The TG results of the vendor samples, reference samples and carbon fibers are summarized in Tables 2–4 respectively.

In order to choose the temperature limits for calculating the first and second weight loss of PPS, it was important to examine the thermal curves of PTFE and carbon fibers. Hopefully, temperature limits could thus be chosen whereby PTFE decomposed completely during the first set of temperature limits whereas the carbon fibers would not begin to degrade until the commencement of the second set of limits. The TG thermal curve of PTFE in Fig. 5 shows a 100% weight loss at 640 °C. Carbon fibers, on the other hand (Fig. 6), do not show appreciable degradation until the purge gas switches to oxygen at 730 °C and then decompose completely at 830 °C. Thus, the temperature limits for calculating the first weight loss of PPS were set between 30 and 650 °C, since all of the PTFE decomposes within these

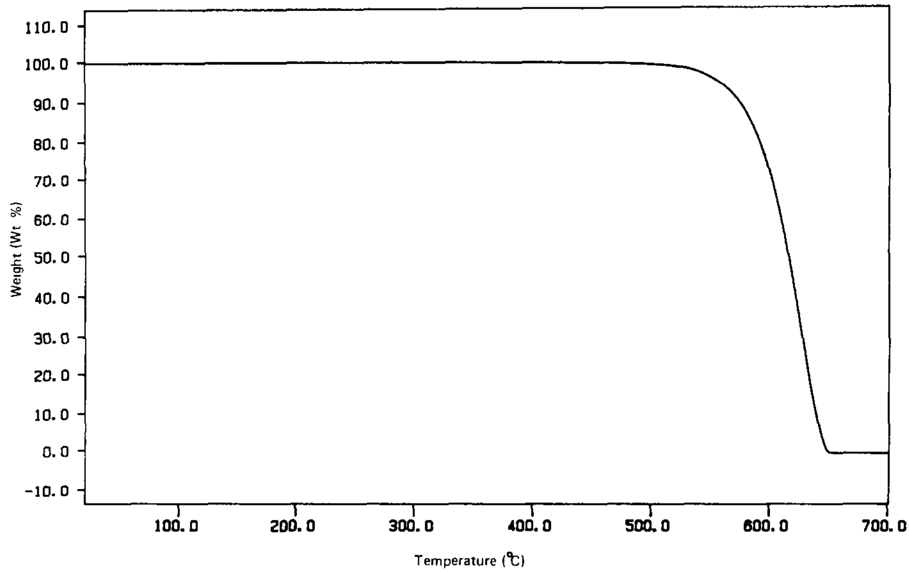

Fig. 5. The TG thermal curve of PTFE from RTP. (Sample weight 11.811 mg).

limits. In addition, the temperature limits for calculating the second weight loss of PPS were set between 650 and 900 ° C, since practically all the carbon fibers decompose within these limits. The TG thermal curves of the reference and vendor samples are shown in Figs. 7 and 8 respectively. In both curves, no appreciable decomposition occurs under a nitrogen atmosphere

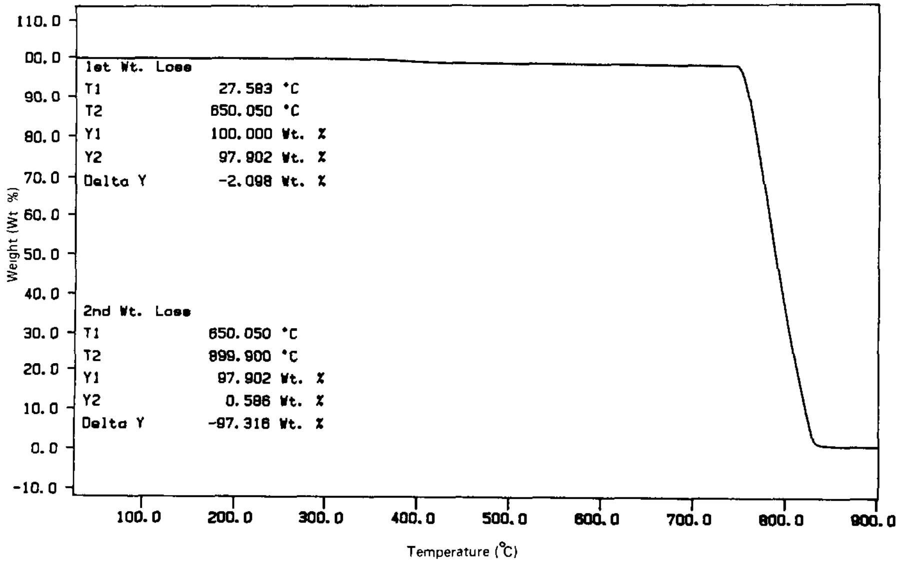

Fig. 6. The TG thermal curve of carbon fibers. (Sample weight 8.295 mg).

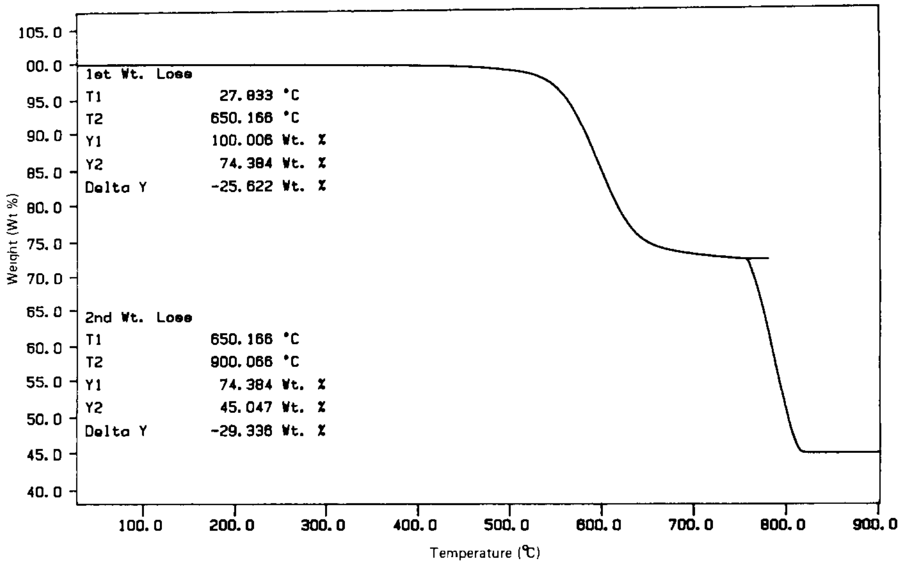

Fig. 7. The TG thermal curve of PPS with glass. (Sample weight 15.260 mg).

until the temperature approaches 500 °C. The first weight loss curves level off at about 630 °C and, finally, vigorous decomposition begins again at 730 °C which is the temperature at which the purge gas is switched to oxygen.

A closer look at the TG thermal curve of carbon fibers (Fig. 9), where the abscissa was expanded by a factor of 20, reveals that about 2% of the carbon

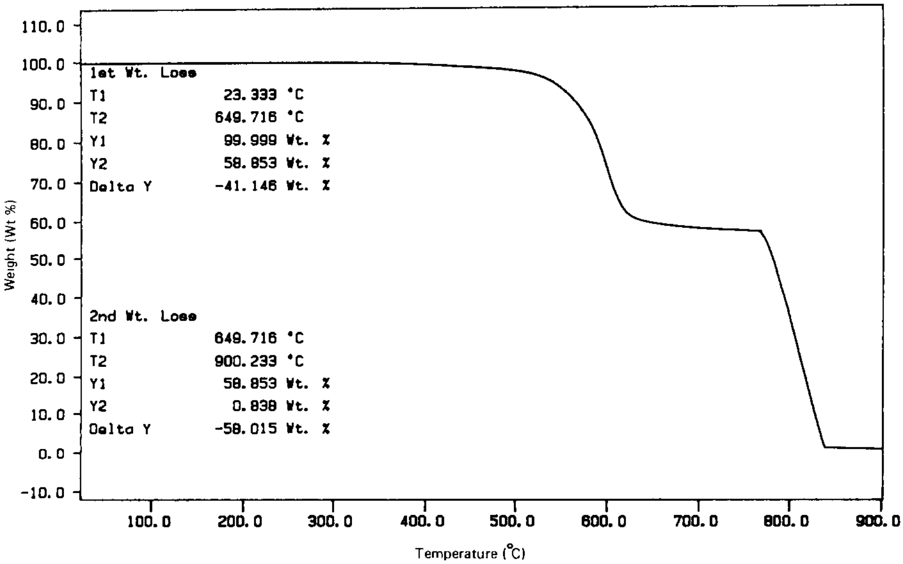

Fig. 8. The TG thermal curve of the vendor sample. (Sample weight 12.218 mg).

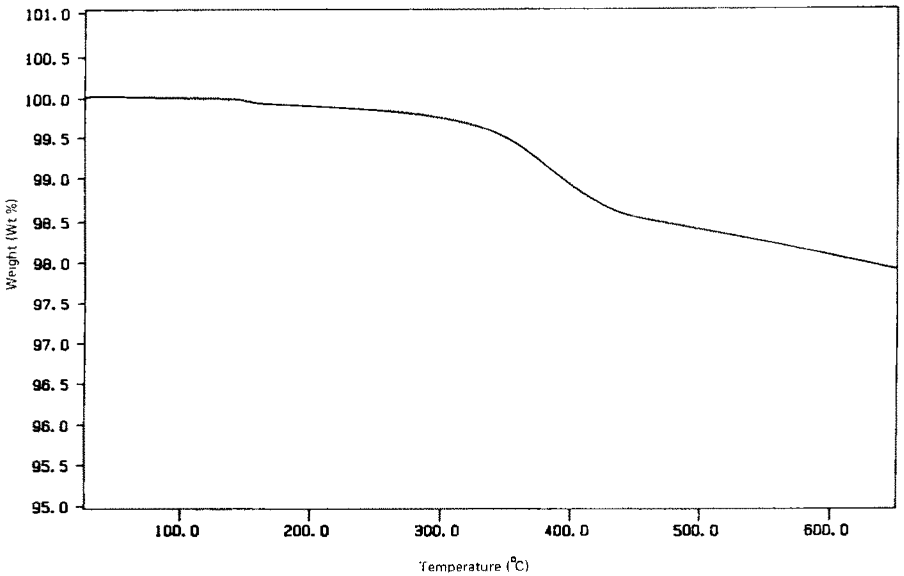

Fig. 9. The TG thermal curve of carbon fibers—expanded scale. (Sample weight 8.295 mg).

fibers decompose or "bleed" within the temperature limit of 30–650 °C set in order to calculate the first weight loss.

It was important, then, to determine the total amount of PPS present in the two-stage weight loss of the vendor sample. It was also important to determine the amount of carbon fibers present not only in the second stage of the weight loss curve of the sample but also in the first stage of the weight loss curve, which can be considerable when the amount of carbon fibers in the sample is large. The task of determining the amount of PPS and carbon fibers in the vendor sample was resolved by the use of the following simultaneous equations

$$\Delta Y1 - X = \text{PPS fraction } 1 \times A + \text{carbon fibers fraction } 1 \times B \tag{4}$$

$$\Delta Y2 = \text{PPS fraction } 2 \times A + \text{carbon fibers fraction } 2 \times B \tag{5}$$

where $\Delta Y1$ is the % weight loss in the 1st weight loss curve, $\Delta Y2$ is the % weight loss in the 2nd weight loss curve, PPS fraction 1 is the fraction of PPS in the 1st weight loss curve, PPS fraction 2 is the fraction of PPS in the 2nd weight loss curve, carbon fibers fraction 1 is the fraction of carbon fibers in the 1st weight loss curve, carbon fibers fraction 2 is the fraction of carbon fibers in the 2nd weight loss curve, A is the % PPS in the two-stage weight loss of the vendor sample, B is the % carbon in the two-stage weight loss of the vendor sample and X is the % PTFE in the 1st weight loss step (value determined by DSC as 15.21).

Substituting a set of values for all components in eqns. (4) and (5), except for A and B, the following two simultaneous equations are obtained with

TABLE 3

The TG weight losses of PPS with glass

Run	Weight loss (%)	
	1st	2nd
1	26.72	28.60
2	25.59	29.58
3	26.73	28.80
4	26.09	30.35
5	25.62	29.34
6	24.43	30.38
7	24.85	30.30
8	26.44	28.98
Average	25.81	29.54
Percentage of PPS in weight loss curves	46.63	53.37

two unknowns

$41.15 - 15.21 = 0.4663A + 0.0186B$

$58.02 = 0.5337A + 0.9814B$

The values of 41.15 and 58.02 were obtained from Run 1 in Table 2. The values of 0.4663 and 0.5337, the PPS fractions, were obtained from Table 3. Finally, the carbon fiber fractions of 0.0186 and 0.9814 were obtained from Table 4. After solving for A and B, the amount of PPS and carbon fibers in the vendor sample was found to be 54.45% and 29.51% respectively. Using simultaneous equations (4) and (5), the amount of PPS and carbon fibers for all 5 runs (Table 2) was determined. The material balance for all 5 runs is summarized in Table 5. The residue in each run was determined by subtracting from 100% the % PTFE, % C and % PPS in the sample.

TABLE 4

The TG weight losses of carbon fibers

Run	Weight loss (%)	
	1st	2nd
1	2.10	97.32
2	1.67	97.62
3	1.60	98.41
4	1.84	98.07
5	2.05	97.91
Average	1.85	97.87
Percentage of carbon fibers in weight loss curves	1.86	98.14

TABLE 5

Material balance of the vendor sample

Run	PTFE (%)	Carbon (%)	PPS (%)	Residue (%)
1	15.21	29.51	54.45	0.83
2	15.21	30.63	53.57	0.57
3	15.21	29.10	55.20	0.49
4	15.21	29.14	54.98	0.67
5	15.21	30.47	54.32	0.00
Average	15.21	29.77	54.50	0.52

EDX (energy dispersive X-ray fluorescence) of the vendor sample TG residue showed that it is composed mostly of sulfur (Fig. 10). X-ray diffraction spectra indicate that the residue is crystalline and that, although the structure could not be determined, it could possibly be that of a high-molecular-weight polysulfide which is formed during the TG run from the decomposition of PPS.

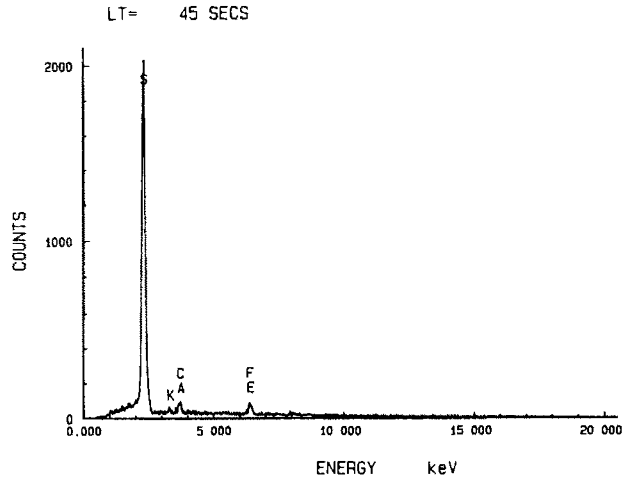

Fig. 10. The EDX spectrum of a TG residue from the vendor sample.

TABLE 6

Comparison of material balance results between the two methods

	Indirect Approach	Direct Approach
PTFE	15.21%	15.21%
PPS	54.46%	54.50%
Residue	0.52%	0.52%
Carbon	29.81%	29.77%

CONCLUSIONS

The agreement between the two methods of compositional analysis, the one where the results are obtained mostly by DSC and the other where the results are obtained mostly by TG, is good. The data obtained from the two methods are summarized in Table 6.

The fact that the two alternative approaches give similar results depends on several factors, the most important of which are (a) the reference PTFE must have been similar to that used in the actual blend (same ΔH_f), (b) the reference PPS must have been similar to that used in the actual blend (same ΔH_f), (c) the ΔH_f of PTFE was not biased by any partial solvation of PTFE by molten PPS and (d) the PTFE decomposed completely during the first weight loss curve.

ACKNOWLEDGEMENT

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