Chemical modification of poly(ether ether ketone) for size exclusion chromatography at room temperature: 2. On the reliability of the derivatization procedure for PEEK molecular-mass determination—application to PEEK–carbon fibre composite

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Some poly(ether ether ketone) (PEEK) samples were analysed by light scattering (l.s.) before and after complete sulfonation. Afterwards, the average molecular masses and molecular-mass distribution of the same PEEK samples are determined by high-temperature size (steric) exclusion chromatography (s.e.c.) for unmodified PEEK and by room-temperature s.e.c. (r.t.s.e.c.) for totally sulfonated PEEK. From this work, it appears that l.s. and s.e.c. measurements using sulfonated or unsulfonated PEEK sample give identical results within the limit of the s.e.c. and l.s. accuracy. This verification assesses the reliability of the derivatization method used to perform r.t.s.e.c. It is also shown that number-average molecular masses ($\bar{M}_n$) of fully fluoroarylketone-terminated PEEK determined by ^{19}F nuclear magnetic resonance experiments agree very well with $\bar{M}_n$ values from s.e.c. These results support the validity of both s.e.c. methods used in this work. Finally, a PEEK–carbon fibre composite is characterized. The fibre content is evaluated. The derivatization process is applied to the matrix and the molecular parameters are obtained by r.t.s.e.c.

(Keywords: molecular-mass determination; size exclusion chromatography; PEEK–carbon fibre composite)

INTRODUCTION

Poly(oxy-1,4-phenylene oxy-1,4-phenylene carbonyl-1,4-phenylene) (poly(ether ether ketone) or PEEK) is a fully aromatic crystallizable high-performance thermoplastic that is mostly used as a matrix for glass- and carbon-fibre-reinforced composites[1]. These composites are subject to intense research activities. Crystallization, mechanical properties, effects of physical and thermal ageing, moisture, solvents and radiation are among other topics of recent works and publications[2].

All these studies were hindered by the lack of easy analytical methods suitable for the separation of the matrix from the fibre and the determination of its molecular masses and molecular-mass distribution, which are fundamental parameters in the field of physical properties and rheological behaviour. Indeed, until recently, only one complete high-temperature size (steric) exclusion chromatography (h.t.s.e.c.) study by Devaux *et al.*[3] has been reported for the characterization of neat PEEK. The solvent mixture used appears not to be systematically very efficient for the separation of polymer and fibre.

This is not the case for concentrated sulfuric acid, which is an excellent PEEK solvent but also a sulfonating agent. Indeed, this acid allows a complete and easy extraction of the matrix at room temperature. This interesting characteristic and the improvement of solubility of the sulfonated PEEK are the main positive factors that have led to the development of a room-temperature (r.t.) s.e.c. suitable not only for neat PEEK but also and especially for PEEK as a matrix of composites.

A detailed description of the derivatization procedure based on sulfonation by concentrated sulfuric acid at room temperature and of the s.e.c. of neat sulfonated PEEK (H-SPEEK) was reported in the previous paper[4].

The present paper is more particularly devoted to the assessment of the validity of this chemical derivatization applied to PEEK from the perspective of its molecular-mass characterization by s.e.c. In other words, it will be shown by three ways that the average molecular masses and the molecular-mass distribution of the original polymer are calculable from the analytical results

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describing the derivative polymer. Taking into account the necessary correction of molar mass due to complete sulfonation ($M_{\text{H-SPEEK}} = 1.278\ M_{\text{PEEK}}$)[4]:

(i) Light scattering experiments of sulfonated PEEK or unsulfonated PEEK must give similar results.

(ii) Room-temperature s.e.c. of sulfonated PEEK must provide identical average molecular masses and distribution curves as high-temperature s.e.c. of PEEK.

(iii) Number-average molecular masses ($\bar{M}_n$) of unsulfonated fluorine-terminated PEEK obtained by ^{19}F n.m.r., which is an absolute method for $\bar{M}_n$ determination[5], must confirm the $\bar{M}_n$ values from sulfonated PEEK s.e.c.

The last part of this paper is devoted to an application of the derivatization procedure for the characterization of PEEK composites. In this field, the fibre content and the molecular-mass parameters of a PEEK–carbon fibre composite are determined.

EXPERIMENTAL

Products

PEEK powder samples. Eleven experimental PEEK samples supplied by ICI were used throughout this study.

PEEK composite. An APC-2 prototype PEEK–carbon fibre composite, where the matrix is Victrex™ PEEK, was supplied by ICI.

Solvents

Methanesulfonic acid (MSA) (Fluka, ref. 64280) was selected for l.s., viscometry and ^{19}F n.m.r. analyses. It was used as received.

For light scattering and for APC-2 characterization, sulfuric acid (UCB, 99–100%, ref. 1102) was used without further purification.

Hydrochloric acid (min. 37%) was a Merck product (ref. 1027).

N-Methyl-2-pyrrolidone (NMP) from GAF Corporation was used for an l.s. experiment and for s.e.c. analyses at room temperature. It was purified by distillation under reduced pressure at 100°C over calcium hydride.

Phenol (Janssen, ref. 1493493) and 1,2,4-trichlorobenzene (Janssen, ref. 1579076) were used for high-temperature s.e.c.

Dissolution procedures

In concentrated sulfuric acid and in methanesulfonic acid (MSA). Acid solutions of PEEK or totally sulfonated PEEK (H-SPEEK) were prepared at room temperature with vigorous shaking for a period of about 24 h.

In NMP + LiCl (0.1 M). For light scattering measurements, H-SPEEK was dissolved in NMP + LiCl (0.1 M) at room temperature for 15 h with mechanical shaking.

In NMP + LiBr (0.1 M). H-SPEEK or Li-SPEEK sample was dissolved at room temperature during 12 h with strong mechanical shaking. The solution was heated for 1 h at 80°C before room-temperature s.e.c. characterization.

In phenol/1,2,4-trichlorobenzene (50/50 by weight). PEEK dissolution was made at the boiling point (~183°C) of the mixture. The solution was then hot filtered on Millipore FHLP 01300 (0.5 μm) filter.

Light scattering (l.s.)

The l.s. experiments of PEEK and H-SPEEK were performed on a FICA 42000 Photo Gonio Diffusiometer fitted with a He–Ne laser source at 632.8 nm, vertically polarized. The variations of refractive index with concentration were determined at the same wavelength with a Brice-Phoenix refractometer.

The light scattering analyses were performed as follows: in MSA for unsulfonated PEEK; in H_2SO_4 for totally sulfonated PEEK; in MSA and NMP + LiCl (0.1 M) for totally sulfonated PEEK recovered from H_2SO_4 solutions.

The procedures for fully sulfonated PEEK preparation and for the determination of the absolute mass concentrations of H-SPEEK are described in full detail in the first paper of this series[4].

Viscometry

The viscometry measurements were carried out with an Ubbelohde viscometer modified by Desreux. Four solutions of PEEK in MSA were prepared (initial concentration ~1 g dl^{-1}). The intrinsic viscosity was taken as the arithmetic mean of the reduced and inherent viscosities extrapolated to zero concentration. No polyelectrolyte behaviour of PEEK in MSA was observed during the viscometric analyses.

^{19}F nuclear magnetic resonance

Spectra were obtained with a Bruker WM250 spectrometer working at 235.34 MHz for ^{19}F. The experimental conditions were the same as the ones described in ref. 4. The $\bar{M}_n$ values (exclusively for totally fluoroarylketone-terminated PEEK) were determined following a procedure reported in a previous paper[5] using the relationship:

$$\frac{S_{IS}}{S_P} = \frac{[F]_{IS}}{[F]_P}$$

where S_{IS} is the peak area of the internal standard, S_P is the area of the polymer peak and $[F]_{IS}$ and $[F]_P$ are the fluorine contents of the internal standard and of the polymer respectively; and the relationship:

$$\bar{M}_n = \frac{38 \times 10^6}{[F]_P}$$

where $[F]_P$ is expressed in ppm.

Size (steric) exclusion chromatography

For H-SPEEK. The s.e.c. apparatus consists of a mobile phase stabilization accessory for degassing by He, a set of two mixed-bed Shodex columns from Showa Denko (ref. AD-80 M/S), a column heater module, a LC-55 u.v. detector from Perkin–Elmer, a 410 Millipore-Waters differential refractometer (d.r.i.) and a Digital MicroVAX 2000 computer. The operating conditions were: mobile phase, *N*-methyl-2-pyrrolidone + LiBr (0.1 M); stationary phase, styrene–divinylbenzene copolymer gel; flow rate, 0.5 ml min^{-1}; oven temperature, 25°C; wavelength, 270 nm; sample size, 50 μl; Li-SPEEK concentration for u.v. detection, 0.5 g l^{-1}, and for d.r.i. detection, 1 g l^{-1}.

For PEEK. The s.e.c. chromatograph (Millipore-Waters 150 C) was connected with a Digital MicroVAX 2000 computer for data handling. Two Shodex (mixed-

Table 1 Comparative l.s. characteristics of unsulfonated PEEK and sulfonated PEEK samples in solution in 99.5% H_2SO_4, CH_3SO_3H and NMP

	Samples	Solvent	dn/dc (ml g^{-1})	$\bar{M}_w$[a]	R_G (Å)	10^3A_2 (mol ml g^{-2})
PEEK-2	Unsulfonated	CH_3SO_3H	0.360	37 800	250	4.1
	Sulfonated and recovered	CH_3SO_3H	0.295	49 000	230	3.2
	Sulfonated	H_2SO_4	0.327	47 500	220	1.9
PEEK-9	Unsulfonated	CH_3SO_3H	0.360	20 300	–	2.5
	Sulfonated and recovered	CH_3SO_3H	0.295	25 800	–	1.9
	Sulfonated and recovered	NMP + LiCl (0.1 M)	0.150	24 800	–	1.0

[a]Depolarization factor was taken into account ($0.04 < \rho_V < 0.10$)

bed) columns (ref. AT-80M/S) from Showa Denko were used in series. The working temperature was 115°C. Sample concentrations and flow rate were approximately 2 g l^{-1} and 0.5 ml min^{-1} (for more details see ref. 3).

RESULTS AND DISCUSSION

Demonstration of the reliability of the derivatization method

As mentioned in the 'Introduction' of this work, three independent ways were used in order to prove the reliability of the method.

Comparative light scattering measurements on unsulfonated and sulfonated PEEK. As the reliability of any s.e.c. method depends first on the quality of the standards used for the calibration, it was essential to verify the following:

(i) H_2SO_4 does not degrade PEEK during the dissolution and sulfonation process. In other words, it was necessary to check that reliable weight-average molecular masses of unsulfonated PEEK were obtained from light scattering characterization of totally sulfonated PEEK in 99.5% H_2SO_4.

(ii) The sulfonated sample is not modified during the recovery procedure from the H_2SO_4 solution.

For this purpose, the correspondence between $\bar{M}_w$ results obtained from H-SPEEK in H_2SO_4, from PEEK in CH_3SO_3H, which is known to be a non-sulfonating solvent of PEEK, and from H-SPEEK in NMP was examined. The results are given in *Table 1*. *Figure 1* illustrates the Zimm plot for unsulfonated PEEK-2 sample in CH_3SO_3H.

These results confirm that: there is no polymer degradation in H_2SO_4, the recovery procedure is free of degradation, and the factor of mass increase upon sulfonation is 1.278 (viz. one $-SO_3H$ per repeat unit).

On the other hand, the viscometric law of unmodified PEEK in methanesulfonic acid was determined and compared with the viscometric law of Roovers *et al.*[6], who have analysed narrow PEEK samples by light scattering and viscometry in methanesulfonic acid. *Table 2* summarizes the values of the intrinsic viscosities $[\eta]$ and of the $(\bar{M}_w)_u$ of PEEK standards used in the course of this work. This table also includes the $[\eta]$ and $(\bar{M}_w)_u$ data of Roovers *et al.*

The values given in *Table 2* have allowed the determination of the Mark–Houwink–Sakurada parameters, which are shown in *Table 3*.

The straight line of *Figure 2* illustrates the double-logarithmic plot of the intrinsic viscosities against weight-average molecular masses for values of this work.

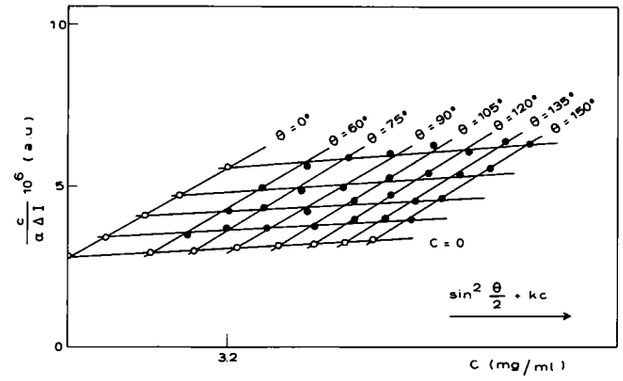

Figure 1 Illustration of the Zimm plot of PEEK-2 in methanesulfonic acid

Table 2 Weight-average molecular masses $(\bar{M}_w)_u$ and intrinsic viscosities $[\eta]$ of various PEEK samples in methanesulfonic acid

Samples			$[\eta]$ (dl g^{-1})	
This work	Roovers[6]	$(\bar{M}_w)_u$	25°C	30°C
	PREK 004D/1	79 500[a]		2.09
PEEK-1		56 500[b]	1.64	
	PREK 001A22/1	54 100[a]		1.87_5
	PREK 004E/1	39 200[a]		1.29_5
PEEK-2		37 200[b]	1.32	
	PREK 001B/1	31 100[a]		
PEEK-3		22 600[b]	0.82	
	PREK 002C/1	18 000[a]		0.65
PEEK-4		14 300[b]	0.53	
	PREK 001C/1	14 100[a]		0.54_8
	PREK 002D/1	8 300[a]		0.36
	PREK 002E/1	4 600[a]		0.18_1

[a]From light scattering analyses in CH_3SO_3H
[b]From light scattering analyses in H_2SO_4: $(\bar{M}_w)_u = (\bar{M}_w)_s/1.278$

Table 3 Viscosity laws of PEEK in methanesulfonic acid[a]

Temperature (°C)	a	10^5K	$\bar{M}_w$ range	Ref.
25	0.842	17.31	14 300–56 500	This work
30	0.818	22.60	4 600–79 500	Roovers[6]

[a]$[\eta]$ is expressed in dl g^{-1}

The experimental data of Roovers *et al.* are also plotted on this figure. It can be seen that they agree remarkably well with the values given in the present paper. The similarity of both viscosity laws in the same solvent and at almost the same temperature shows in another way that reliable and accurate weight-average molecular masses of unsulfonated PEEK can be obtained from light

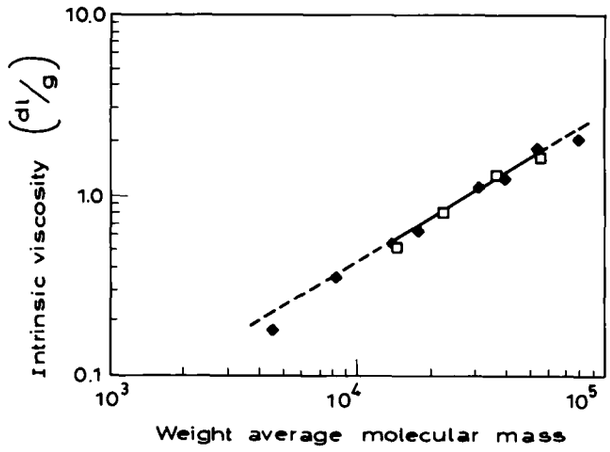

Figure 2 Logarithmic plot of the intrinsic viscosity against the weight-average molecular mass in methanesulfonic acid: (□) PEEK standards PEEK-1, PEEK-2, PEEK-3 and PEEK-4 at 25°C; (◆) fractions of PEEK at 30°C[6]

Table 4 Molecular masses obtained from high-temperature s.e.c. and room-temperature s.e.c.

	H.t.s.e.c.[a]			R.t.s.e.c.[a]		
Sample	$\bar{M}_w$	$\bar{M}_n$	H	$\bar{M}_w$[b]	$\bar{M}_n$[b]	H
PEEK-5	41 400	17 300	2.5	37 600	15 600	2.4
PEEK-11	34 500	15 700	2.3	31 900	15 500	2.0
PEEK-6	29 000	15 000	1.9	27 100	13 600	2.0
PEEK-7	25 100	12 300	2.2	24 100	11 600	2.0
PEEK-8	19 500	10 000	2.0	18 500	9 800	1.9
PEEK-9	19 000	9 300	2.0	18 400	9 900	1.9
PEEK-10	6 700	4 000	1.7	6 500	3 400	1.9

[a] From the specific calibration
[b] $\bar{M} = \bar{M}_{\text{sulfonated}}/1.299$

Table 5 Average molecular masses of PEEK-9 sample analysed by high-temperature s.e.c. and room-temperature s.e.c.

Method	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$	H
H.t.s.e.c.	18 900	9 400	30 400	2.01
R.t.s.e.c.	19 000	9 600	30 100	1.97

scattering experiments performed with PEEK/99.5% H_2SO_4 solutions.

Comparison between molecular characteristics of PEEK samples from h.t.s.e.c. and r.t.s.e.c. Besides their characterization by room-temperature s.e.c., different PEEK samples were analysed by high-temperature s.e.c. according to the method reported by Devaux *et al.*[3]. The similarity of the molecular characteristics given by both analytical methods in the limit of experimental accuracy will obviously be the criterion that will be discussed.

(a) Molecular mass. The average molecular masses of seven PEEK samples provided by h.t.s.e.c. and r.t.s.e.c. are quoted in *Table 4*. The agreement between r.t.s.e.c. and h.t.s.e.c. absolute molecular masses can be regarded as very satisfactory. Indeed, the difference between both number-average and weight-average molecular masses remains within the limit of the experimental accuracy (between 5 and 10%).

(b) Molecular-mass distribution. For a comparison of weight molecular-mass distributions, PEEK-9 was selected as reference sample. This sample was analysed by h.t.s.e.c. and after complete sulfonation by r.t.s.e.c. The average molecular masses and weight distributions were calculated with the help of specific calibrations. The molecular-mass results are given in *Table 5*. *Figure 3* demonstrates the similarity of both weight molecular-mass distributions.

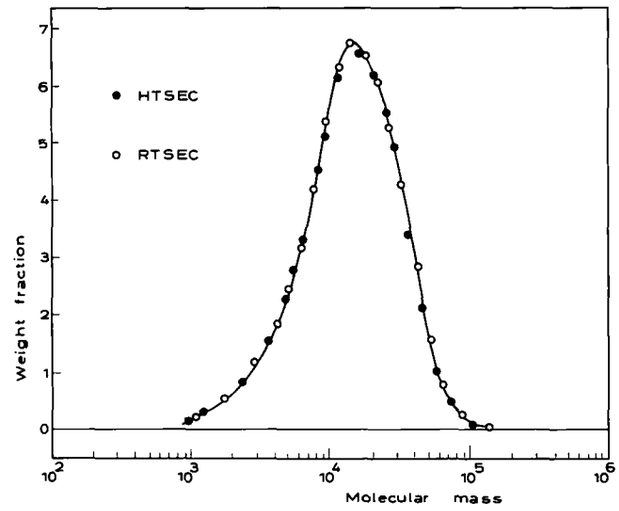

Figure 3 Weight differential molecular-mass distributions of PEEK-9 characterized by high- and room-temperature size exclusion chromatography

Table 6 Number-average molecular masses ($\bar{M}_n$) from ^{19}F n.m.r. and s.e.c. experiments

Samples	^{19}F n.m.r.	S.e.c.[a]
PEEK-11	13 100	15 500
PEEK-9	10 000	9 900
PEEK-8	8 400	9 800
PEEK-4[b]	6 400	7 500
PEEK-10	3 000	3 400

[a] From r.t.s.e.c. of sulfonated PEEK
[b] See previous paper[4]

This overall agreement confirms the validity of the assumption that functionalization of PEEK upon dissolution in 99.5% concentrated sulfuric acid is an appropriate way to obtain soluble samples useful for r.t.s.e.c. Furthermore, it is proved that the molecular-mass parameters of the original polymer can be found from the analytical results given by the r.t.s.e.c. analysis of the derivative polymer.

Determination of $\bar{M}_n$ of totally fluorine-terminated PEEK samples by ^{19}F n.m.r. and comparison with the $\bar{M}_n$ from s.e.c. experiments. From a quantitative point of view, ^{19}F n.m.r. is a very reliable method for the determination of the F end-group concentration in PEEK samples. When all the PEEK chain ends are aromatic fluorine, their quantitative analysis provides a way to determine the number of molecules and thereby the number-average molecular mass ($\bar{M}_n$)[1,5]. This procedure was followed for the molecular characterization of five fully fluoraryl-ketone-terminated PEEK samples. The solvent used was methanesulfonic acid. The results are given in *Table 6* together with the $\bar{M}_n$ values determined by s.e.c.

It can be seen that the experimental values agree very well, keeping in mind the accuracy of both techniques in the field of the number-average molecular-mass deter-

mination. This observation supports the validity of the s.e.c. methods developed for the molecular-mass characterization of PEEK.

PEEK-carbon fibre composite characterization

This second part is devoted to an application of the PEEK derivatization procedure in the field of the characterization of PEEK aromatic polymer composites.

Aromatic polymer composites (APC) are a new class of advanced structural materials based on continuous carbon fibres embedded in a PEEK matrix. The present analysis deals with a prototype of the particular commercial grade APC-2, where the matrix is Victrex™ PEEK. Two samples were characterized: an APC-2 sample 'as received' and an APC-2 sample treated for 1 h at 400°C in air. The molecular-mass parameters and the fibre content were determined following an H_2SO_4 extraction procedure described in *Figure 4*. This method simultaneously allows the physical separation of the polymer from the fibre and the sulfonation of the matrix. The recovery of the sulfonated PEEK from the acid medium is described in full detail in the 'Experimental' part of the previous paper[4]. The r.t.s.e.c. analyses are illustrated by the chromatograms of *Figure 5* and the molecular-mass results are shown in *Table 7*.

To check the validity of the H_2SO_4 extraction method for the fibre content determination, an 'acid digestion' procedure described in *Figure 6* was also used. This procedure separates the fibre by an acid chemical destruction of the polymer. The agreement between the results obtained is quite satisfactory: 66.0 and 65.5 wt% of fibre content respectively for the 'acid extraction' and 'digestion' methods.

CONCLUSION

The same PEEK samples before and after sulfonation were analysed by light scattering. The results confirmed that no polymer degradation takes place during the

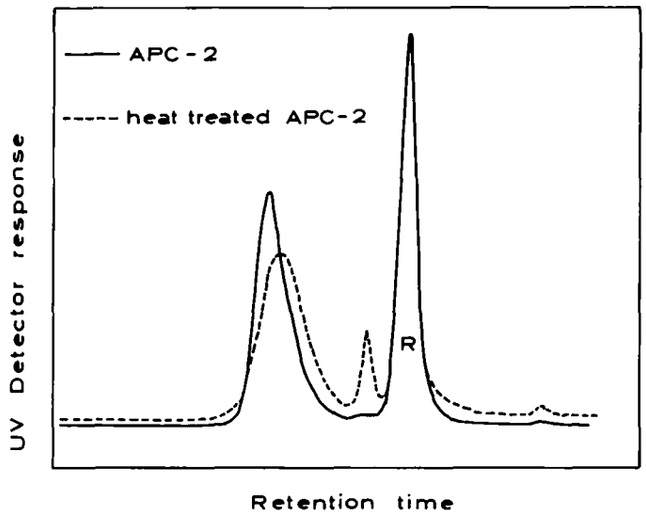

Figure 5 Room-temperature size exclusion chromatography of APC-2 and APC-2 heat treated for 1 h at 400°C in air (R is an internal reference peak)

Table 7 Comparison between molecular masses of APC-2 and heat-treated APC-2

Samples	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$	M_p[a]	H
APC-2	25 500	11 500	40 700	26 600	2.3
Heat-treated APC-2[b]	22 400	7 200	68 700	18 100	3.1

[a]Molecular mass at the top of the peak
[b]1 h at 400°C in air

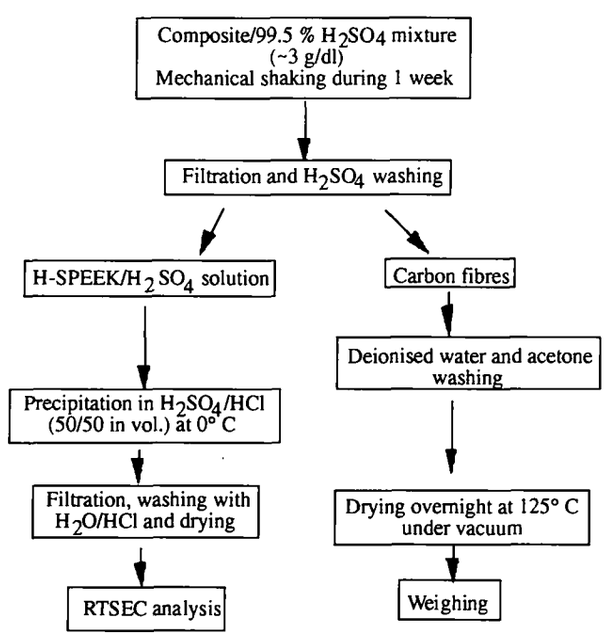

Figure 4 PEEK–carbon fibre composite characterization procedure: acid extraction method and PEEK sulfonation

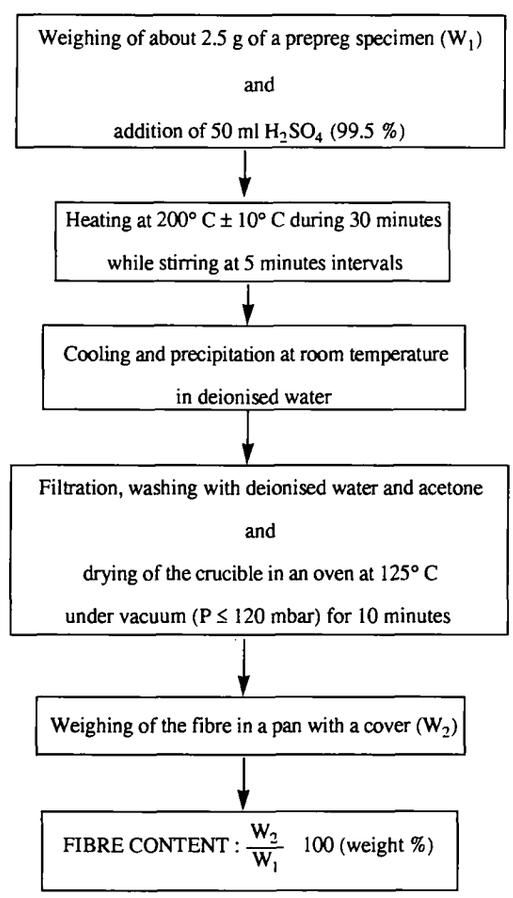

Figure 6 PEEK–carbon fibre content determination by an 'acid digestion' method

sulfonation process and the recovery procedure of the sulfonated sample from the H_2SO_4 solution.

Furthermore, PEEK average molecular masses and molecular-mass distributions were obtained from high-temperature s.e.c. and from room-temperature s.e.c. The comparison between the results given by both techniques showed a satisfactory agreement. This fact undoubtedly proves the validity of the derivatization procedure.

It is also of interest to emphasize the fact that two viscosity laws of PEEK in MSA determined in different laboratories were compared. They are based on weight-average molecular masses provided from light scattering experiments performed, on the one hand, in MSA (Roovers *et al.*[6]) and, on the other hand, in 99.5% H_2SO_4 (this work). Their similarity reinforces the reliability of the analytical methods proposed, which are, of course, mainly dependent on the quality of the characterization of the PEEK samples selected as standards.

In other respects, number-average molecular masses ($\bar{M}_n$) of fully fluoroarylketone-terminated PEEK determined by ^{19}F n.m.r. experiments also support the validity of light scattering and s.e.c. measurements.

Finally, the derivatization procedure was extended to PEEK–carbon fibre composite characterization and allowed the determination of the fibre content and of the molecular-mass parameters.

At the end of this work, it appears that the presently available PEEK characterization methods are effective, accurate and reliable analytical tools for any fundamental or applied research concerning the neat material or the matrix of composites.

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REFERENCES

1 Kausch, H. H. 'Advanced Thermoplastics and Their Composites. Characterization and Processing' (Ed. H. H. Kausch), Carl Hanser Verlag, Munich, 1992
2 Nguyen, H. X. and Ishida, H. *Polym. Compos.* 1987, **8**(2), 57
3 Devaux, J., Delimoy, D., Daoust, D., Legras, R., Mercier, J. P., Strazielle, C. and Nield, E. *Polymer* 1985, **26**, 1994
4 Daoust, D., Godard, P., Devaux, J., Legras, R. and Strazielle, C. *Polymer* 1994, **35**, 5491
5 Devaux, J., Daoust, D., Legras, R., Dereppe, J. M. and Nield, E. *Polymer* 1989, **30**, 161
6 Roovers, J., Cooney, J. D. and Toporowski, P. M. *Macromolecules* 1990, **23**, 1611