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Sulphonated poly(ether ether ketone): Synthesis and characterisation

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The sulphonation of commercially available PEEK in powder form (Gatone^{TM}, Gharda Chemicals Limited, India) was carried out using conc. H_2SO_4 under different reaction conditions. The duration of reaction was varied from 3–5 h, polymer concentration 4–10% (w/v) and temperature 35–50°C. Structural characterisation of sulphonated polymers was done by elemental analysis, FT-IR and ^{1}H-NMR spectroscopy. The degree of sulphonation as calculated from ^{1}H-NMR and elemental analysis (S-content) was found to be in the range of ~50–80%. Multistep mass loss was observed in thermogravimetric traces (recorded in N_2 atmosphere). The first step (50–225 ± 25°C) was due to loss of moisture (1–10%) and second step (250–425 ± 25°C) has been attributed to volatilization of SO_3 from the sulphonic group. The backbone degradation takes place above 450°C. The mechanical properties and proton conductivities of various sulphonated samples was also evaluated.

1. Introduction

The unique combination of properties such as excellent thermal stability, high electrical and mechanical performance (even at elevated temperatures), high chemical resistance and very easy chemical modification have established poly(aryl ketone)s such as poly(ether ether ketone) (PEEK) as general purpose molding and extrusion materials in both virgin and reinforced forms. However, these polymers are hydrophobic in nature. Hydrophilicity of PEEK can be increased by sulphonation. The possibility of using these ionic materials as proton exchange membranes or direct methanol fuel cell membranes has increased the technical interest in the sulphonation of such polymers. Membranes based on sulphonated PEEK are also very promising materials for fuel cell applications [1–3].

The sulphonation of PEEK using 96–98% sulphuric acid [4–7], mixture of sulphuric acid and methane sulphonic acid [8], mixture of sulphuric acid and oleum [9], sulphur trioxide-triethyl phosphate complex [10] and chlorosulphonic acid [11] has been reported in the literature. The kinetics of PEEK sulphonation in conc. H_2SO_4 was investigated by Shibuya and Porter [5, 6] in the temperature range of 25–75°C. Activation energy of sulphonation was around 82.8 kJ/mol. Commercially available PEEK (Victrex) was generally used in these studies.

It was observed that 100% sulphuric acid yields a crosslinked structure as a result of sulphone formation [11], which is negligible in aqueous sulphuric acid i.e. 97.4% because water decomposes the postulated aryl pyrosulphonate intermediate which is required for sulphone formation. Chlorosulphonated polymers may be formed on treating with chlorosulphonic acid. Degradation of polymers occurs, if a high degree of chlorosulphonation is desired. Jin and coworkers [4] reported that sulphonation takes place only on the phenyl flanked by two ether groups of the PEEK repeat unit. This phenyl ring has four equivalent ortho positions for sulphonation, with only one of the four positions on the ring being substituted in concentrated sulphuric acid. The other two phenyl rings, connecting an ether group and a carbonyl group, are deactivated for the electrophilic sulphonation by the electron withdrawing effect of the carbonyl group. Further sulphonation (i.e. DS > 1) on the same phenyl ring does not take place, because of the electron withdrawing effect of the $-SO_3H$ group.

The extent of sulphonation is controlled by the reaction time, acid concentration, and temperature, which can provide a sulphonation range of 30–100% per repeat unit [4].

The kinetics of PEEK sulphonation in H_2SO_4 at room temperature [12] indicated that sulphonation was first order with respect to the unsulphonated repeat unit of PEEK. These kinetic studies ruled out the possibilities of the sulphonation-desulphonation competing reaction suggested earlier by Shibuya and Porter [5, 6]. Two types of substitution have been reported by Huang and coworkers [13]. The degree of sulphonation is

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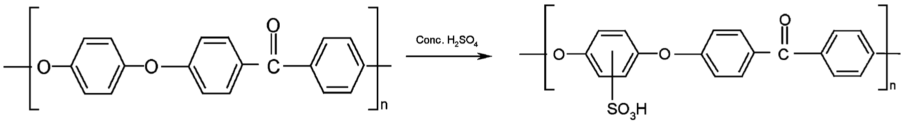


PEEK SPEEK

Scheme 1 Sulphonation of Gatone^{TM} 5300P

controlled by reaction time and temperature. The latter is found to have a more remarkable effect on the degree of sulphonation [13].

The thermal degradation mechanism of sulphonated PEEK with various degrees of sulphonation has been studied by pyrolysis gas chromatography/mass spectrometry and thermogravimetry [14]. Sulphonation of poly(ether ether ketone) based on phenolphthalein [15] or containing phthalazinone units in the backbone [16, 17] has been investigated for proton conducting materials [16, 17] or for permeation behaviour of gases. Kobayashi and coworkers have reported the sulphonated proton conducting polymers derived from poly(ether ether ketone) and poly(4-phenoxybenzoyl-1, 4-phenylene). Sulphonated poly(4-phenoxybezoyl-1, 4-phenylene) showed much higher and more stable proton conductivity than sulphonated PEEK [18].

The commercially available PEEK (Victrex) has been extensively used for sulphonation [1–14] and very few studies are reported on sulphonation of Gatone PEEK (Gharda Chemicals Limited, India). Recently, Xing and coworkers [19] have carried out comparative studies of sulphonation of Victrex and Gatone for proton exchange membranes. The sulphonation was carried out at 22°C for 140–240 h and at 55°C for 10 h. Degree of sulphonation ranging from 0.59–0.97 was obtained. However, no systematic studies have been reported on the effect of temperature and duration of reaction on degree of sulphonation of Gatone, and properties of sulphonated polymers. The present paper reports such studies.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) was procured from Gharda Chemicals Limited, India under the trade name of Gatone^{TM} 5300P. The properties as given in manufacturer's data sheet are given in Table I. 98% concentrated sulphuric acid, N,N-dimethyl formamide and NaCl were purchased from Merck chemicals.

2.2. Synthesis of sulphonated PEEK

The sulphonation of PEEK in powder form was carried out in a round bottom flask in air atmosphere at a constant temperature. The desired amount of PEEK and conc. H_2SO_4 were added to the flask and the solution was stirred mechanically for a period of 3 h. In order to study the effect of polymer concentration, and temperature on the extent of sulphonation, the reactions were done using 4–10 w/v% of polymer concentration at 35–50°C (Scheme 1). The sulphonated PEEK (SPEEK) was then precipitated by dropwise addition of solution to 500×10^{-6} m^3 of ice cooled distilled water. The samples were washed till the excess acid was removed and dried in an oven at 70°C for 12 h. These dried samples were kept in a dessicator.

The films were obtained by casting a 3.3% SPEEK solution in dimethyl formamide on a glass plate. The conditions for sulphonation and sample designations are given in Table II.

2.3. Structural characterisation

Structural characterisation of sulphonated polymers was done by elemental analysis, FT-IR and ^{1}H-NMR spectroscopy. A Carlo ERBA, EA 1108 elemental analyzer (CHNSO) was used to find out the % of carbon, hydrogen and sulphur. FT-IR spectra of polymer samples either in film form or as powder (using KBr pellet) were recorded on NICOLET FT-IR spectrometer. A BRUKER AC300 spectrometer was used to record ^{1}H-NMR using tetramethyl silane as an internal standard and DMSO-d_6 as a solvent.

TABLE I Properties of Gatone^{TM} (as given in Manufacturers Data sheet)

S. No.	Property	Test method	Gatone^{TM}5300P
1.	Density	ISO1183	1320 kg/m^3
	Mechanical properties		
2.	Tensile Strength	ISO527	95 MPa
3.	Tensile Modulus	ISO527	3800 MPa
4.	Elongation at Break	ISO527	>50%
5.	Flexural Strength	ISO178	160 MPa
6.	Flexural Modulus	ISO178	3800 MPa
7.	Izod Impact	ISO179	6.0 kJ/m^2
		ISO180/1A	–
	Thermal properties		
8.	HDT at 1.82 MPa	ISO75	150°C
9.	Glass Transition	DSC	148°C
10	Melting Point	DSC	338°C
11.	Continuous use temperature	UL-746B	260°C

TABLE II Sample designations of SPEEK samples

S. No.	Reaction time (h)	Reaction temp (°C)	Conc. of PEEK (w/v%)	Sample designation
1	3	35	6.25	EK-1
2	3	35	7.81	EK-2
3	3	35	10.41	EK-3
4	3	40	5.00	EK-4
5	3	40	6.25	EK-5
6	3	40	8.33	EK-6
7	3	45	5.00	EK-7
8	3	45	6.25	EK-8
9	3	45	7.14	EK-9
10	3	50	4.16	EK-10

2.4. Thermal behaviour

Thermal characterisation was done using a TA instrument 2100 thermal analyzer having a 951 TG module and a 910 DSC module. Thermogravimetric analysis was carried out in the temperature range of 50–850°C in N_2 atmosphere (flow rate $= 60 \times 10^{-6}$ m^3/min) at heating rate of 20°C/min. A sample mass of 10 ± 2 mg was used.

DSC studies were done using PERKIN-ELMER DSC7 instrument in the temperature range of 50–380°C in static air using heating rate of 5°C/min. A sample mass of 5 ± 2 mg was used.

2.5. Water uptake

SPEEK film samples were first dried at 120°C for 20 h. The dried polymer films were kept immersed in water at ambient temperature. Water uptake was then determined by taking out the samples at definite intervals of time and removing surface water by using a filter paper. Water uptake was then calculated as follows

$$\text{Water uptake} = \frac{W_1 - W_2}{W_2}$$

Where, W_1 and W_2 are mass of the sample after keeping in water and initial dried sample respectively.

2.6. Proton conductivity measurements

Proton conductivity of all the samples were tested by the method of impedance spectroscopy using an EGandG PARC potentiostat/galvanostat (model 273) and a Schlumberger 1255HF frequency response analyser unit.

2.7. Mechanical properties

Tensile testing of SPEEK film samples was done according to ASTM D 658 using a Zwick tensile testing machine at the strain rate of 50 mm/min. The test specimens were cut from the films as strips using a sharp knife. PMMA sheet was used for strengthening the grip and epoxy resin as adhesive. 4–5 strips of each sample were used for measuring the tensile properties and an average of these values are reported.

3. Results and discussion

Sulphonation of PEEK was carried out as per the procedure reported earlier [4–7]. The reaction was carried out at 35, 40, 45 and 50°C and the duration of the reaction was 3 h. A few sulphonation reactions were also carried out for 5 h. However, the samples obtained after 5 h of reaction were either completely soluble in water (when the reaction temperature was 45°C) or were highly swollen (at a reaction temperature of 35°C). Isolation of such samples in dry form was difficult therefore, the results of sulphonated samples obtained after 3 h of reaction are given in Table II. Sulphonated samples were flaky in nature and pinkish in color. The films obtained were transparent with yellowish tinge.

3.1. Characterisation of polymers

TABLE III Results of elemental analysis of sulphonated PEEK samples

S. No.	Sample designation	Carbon (%)	Hydrogen (%)	Sulphur (%)	Empirical formulae
1	EK-1	62.96	3.98	4.94	$C_{34}H_{26}O_{11}S_1$
2	EK-2	63.05	4.24	5.79	$C_{29}H_{23}O_9S_1$
3	EK-3	64.21	4.38	4.98	$C_{103}H_{84}O_{32}S_3$
4	EK-4	63.34	4.72	5.11	$C_{33}H_{30}O_{10}S_1$
5	EK-5	63.37	4.44	5.83	$C_{29}H_{24}O_9S_1$
6	EK-6	65.15	5.23	4.95	$C_{35}H_{34}O_{10}S_1$
7	EK-7	59.68	4.79	6.54	$C_{49}H_{47}O_{18}S_2$
8	EK-8	62.94	4.62	6.11	$C_{55}H_{48}O_{17}S_2$
9	EK-9	63.73	4.16	6.28	$C_{27}H_{21}O_8S_1$
10	EK-10	60.40	5.24	6.36	$C_{76}H_{79}O_{26}S_3$

TABLE IV Degree of sulphonation calculated from elemental analysis and ^{1}H NMR

S. No.	Sample designation	DS (%) Elemental analysis	DS (%) ^{1}H-NMR
1	EK-1	57.32	52.75
2	EK-2	67.27	61.82
3	EK-3	57.26	47.51
4	EK-4	59.54	63.15
5	EK-5	67.15	57.25
6	EK-6	56.96	55.07
7	EK-7	74.57	79.82
8	EK-8	70.49	64.62
9	EK-9	72.87	59.6
10	EK-10	73.45	81.37

The results of elemental analysis and empirical formula of sulphonated samples are given in Table III. From the sulphur content, the degree of sulphonation (DS) was calculated according to the following equation,

$$\mathrm{DS} = \frac{S_E \times 100}{S_T}$$

where, S_E and S_T represent experimental and theoretical (assuming one $-SO_3H$ per repeat unit of PEEK) sulphur content of SPEEK.

The degree of sulphonation was found in the range of 56–75% (Table IV). Higher sulphur content as well as degree of sulphonation was found for samples prepared at 45 or 50°C (EK-7 to EK-10). Concentration of PEEK in sulphuric acid did not affect the extent of sulphonation, but increase in temperature increased the DS values.

In sulphonated samples, additional absorption bands associated with sulphonic acid groups were observed at 3440, 1252, 1080, 1024 and 709 cm^{-1}. The broad band at $\sim$3440 cm^{-1} is assigned to the O—H vibration of $\sim SO_3H$ as well as to the absorbed moisture. The other bands are due to sulphur-oxygen vibrations; asymmetric O=S=O stretch (1252 cm^{-1}), symmetric O=S=O (1080 cm^{-1}), S=O stretch (1024 cm^{-1}), and S—O stretch (709 cm^{-1}) (Fig. 1).

The aromatic C—C absorption band of PEEK at $\sim$1492 cm^{-1} was split upon sulphonation. The absorption band at $\sim$1414 cm^{-1}also split upon sulphonation and a new band appeared at 1402 cm^{-1}. The intensity of the new absorption peak $\sim$1472 cm^{-1} increased while that at 1492 cm^{-1} decreased with increase in

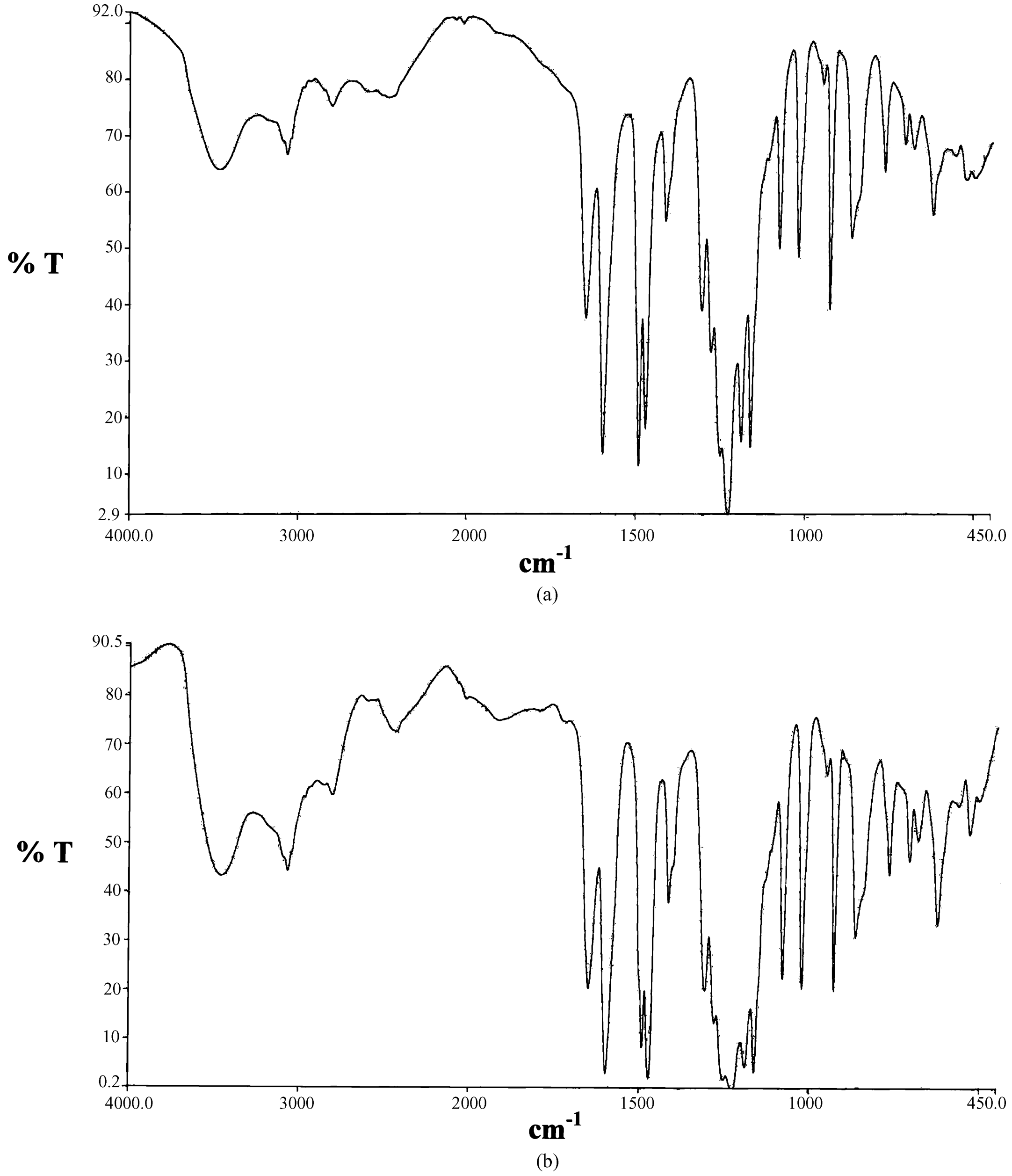


Figure 1 IR Spectra of SPEEK (a) EK-7 and (b) EK-3.

temperature of the sulphonation (i.e. increase in degree of sulphonation).

Both PEEK and sulphonated PEEK samples had an absorption peak at ~840 cm^{-1} which is characteristic of the out-of-plane bending of two hydrogens of 1,4-disubstituted benzene ring. In addition, the sulphonated samples had a new band at ~867 cm^{-1} which is characteristic of the out-of-plane C—H bending of an isolated hydrogen in a 1,2,4-trisubstituted phenyl ring. So, the changes observed in the IR spectra indicate the presence of $-SO_3H$ groups and the relative extent of sulphonation.

An attempt was made to correlate the extent of sulphonation by taking the ratio of 1492:1472 absorption peaks. The intensity of the 1492 cm^{-1} peak of PEEK reduced on sulphonation. Thus an increase or decrease in the ratio of 1492:1472 absorption peaks may be used to get some idea about sulphonation. These ratios were determined by drawing a base line between 1450–1500 cm^{-1} and measuring the heights of these peaks. A plot of DS vs. ratio of 1472/1492 IR absorption bands was linear with the slope of 0.0074 and an intercept of 0.4973 (Fig. 2) thereby indicating that FT-IR technique can be used for determination of extent of sulphonation.

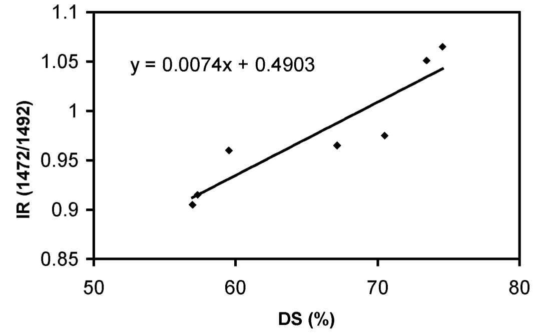


Figure 2 Plot of % DS (calculated from elemental analysis) vs. ratio of 1472/1492 cm^{-1} IR absorption bands.

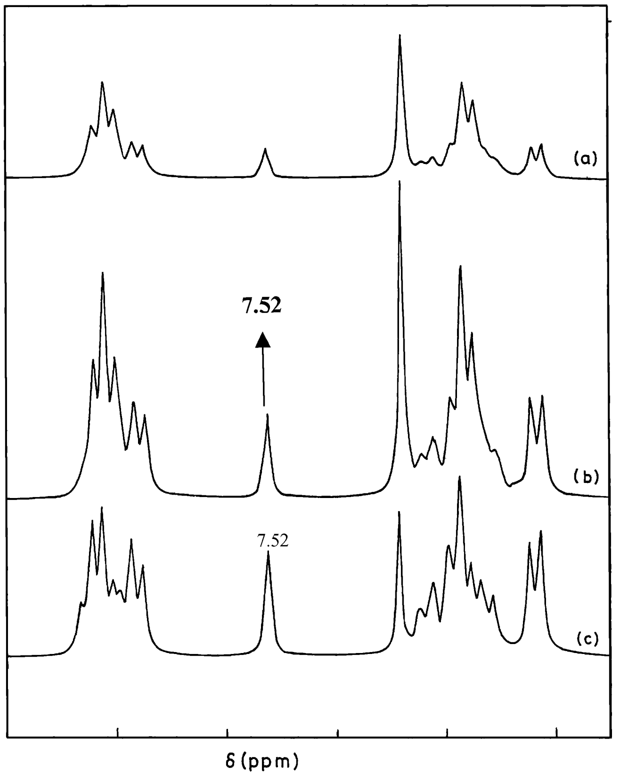
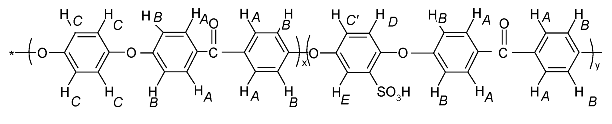


Figure 3 ^{1}H-NMR of SPEEK (a) EK-2 (b) EK-8 and (c) EK-7.

The ^{1}H-NMR spectra of SPEEK samples are shown in Fig. 3. Since non-sulphonated PEEK was insoluble in most organic solvents therefore its ^{1}H-NMR spectrum could not be recorded. The ^{1}H-NMR signal for the SO_3H proton was difficult to record, because of its labile nature.



In the ^{1}H-NMR spectra, the aromatic proton resonance signals were observed in the range of 7–7.75 ppm. In sulphonated samples, H_B appears as a doublet at 7.00 ppm. H_c and H_D appear as a doublet at 7.12 ppm and triplet at 7.27 ppm respectively. The multiplet at $\delta = 7.87$–7.92 ppm corresponds to H_A protons. Presence of the sulphonic acid group in the hydroquinone ring of SPEEK will lead to a downfield shift of H_E protons compared to H_C, or H_D protons. Therefore the observed signal at 7.50 ppm should correspond to H_E protons.

The area of the H_E signal therefore may yield an estimate of the H_E (AH_E) content which is equivalent to the SO_3H content. The ratio between the peak areas of the signals corresponding to all other aromatic protons may be expressed as,

$$\frac{H}{(12 - 2n)} = \frac{AH_E}{\Sigma AH_{A,A',B,B',C,D}}$$

Where 'n' is the number of H_E per repeat unit. An estimate of degree of sulphonation (DS) may be expressed as [20]

$$DS = n \times 100(\%)$$

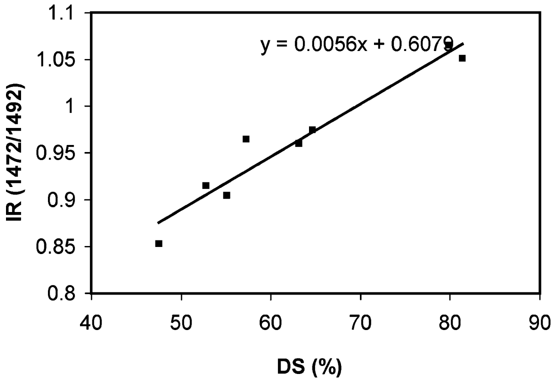


Figure 4 Plot of DS (%) (Calculated from NMR) vs. ratio of 1472/1492 cm^{-1} IR absorption bands.

The calculated DS values are given in Table IV. Depending on the temperature and duration of sulphonation reaction DS values ranged from 47–81%. The degree of sulphonation calculated by elemental analysis and ^{1}H-NMR are marginally different from each other but the trend is similar.

Fig. 4 shows the plot of % DS (calculated from NMR) vs. ratio of 1472/1492 cm^{-1} IR absorption bands. The plot shows a very good correlation between NMR and FT-IR analysis.

3.2. Thermal behaviour

In PEEK samples, melting was indicated by an endothermic transition in the temperature range of 330.4°C and in the cooling cycle, the exothermic crystallization peak was observed at 262.3°C. In SPEEK samples, two endothermic transitions at ~297 and ~375°C were observed. However, no crystallization peak was observed in the cooling cycle (Fig. 5).

The TG traces showed multistep mass loss in sulphonated samples while single step decomposition was observed in PEEK above 400°C (Fig. 6). Three-step degradation was observed in SPEEK samples i.e. from 50–250°C, 250–450°C and 450–800°C. The mass loss from 50–250°C in SPEEK is due to loss of physically and chemically bound water. The observed mass loss between 250–450°C (6.6–20.8) in SPEEK samples may be attributed to decomposition of the sulphonic acid group, which on cleavage will eliminate SO_3. The mass loss in the range of 250–450°C may therefore be correlated with DS on the basis of the assumption that it represents the decomposition of the $-SO_3H$ group only. A linear relationship was observed showing thereby that increase in extent of sulphonation leads to an increase in mass loss in the temperature range of 250–450°C. Theoretically, in a sample having 100% DS (i.e. one sulphonic acid group per repeat unit of PEEK), the mass loss due to SO_3 volatilization would be around 21.7%. However, if one calculates the theoretical mass loss on the basis of DS, the observed mass loss is on higher side. Random chain scission catalysed by acid

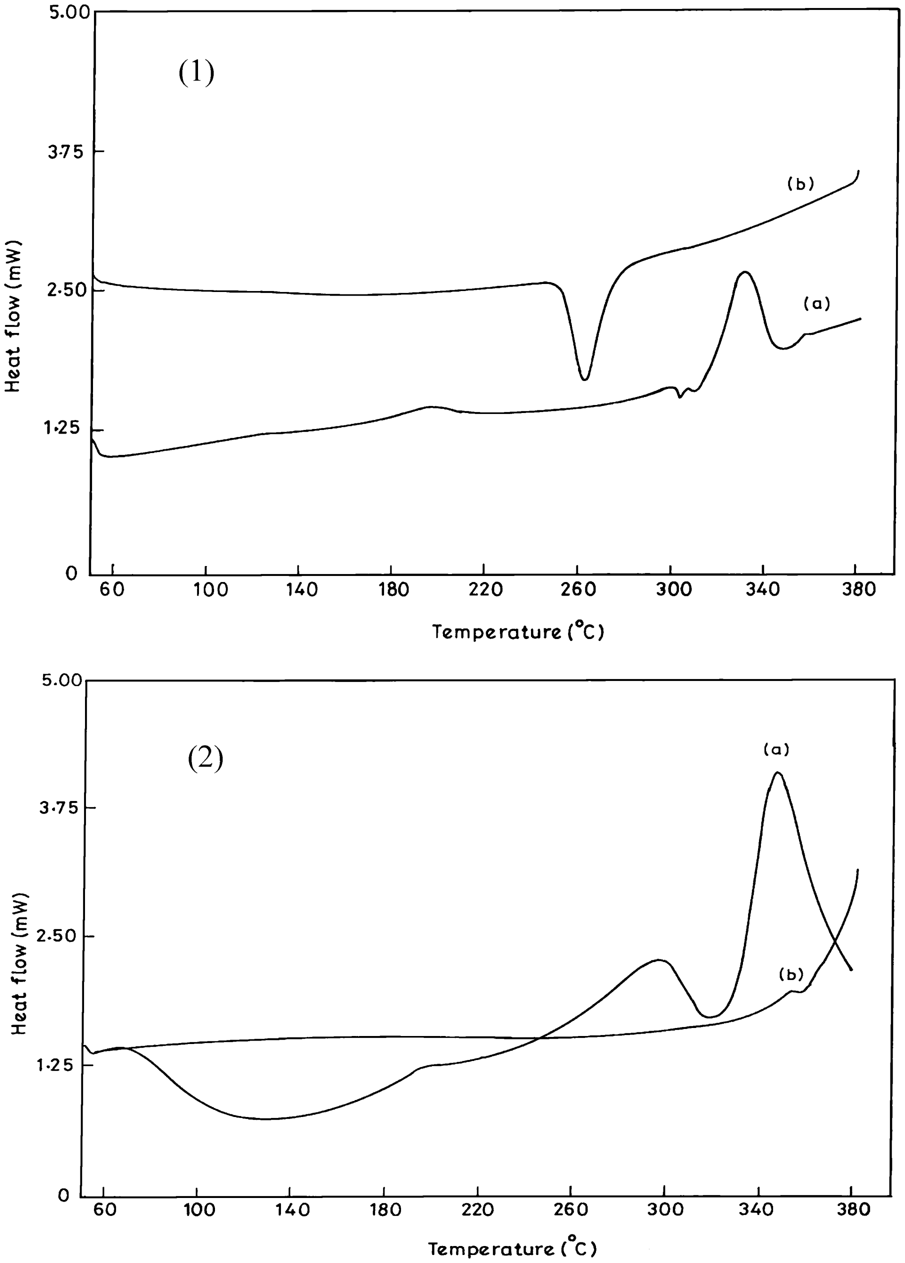


Figure 5 DSC scans of (1) PEEK and (2) SPEEK (EK-10) (a) in heating cycle and (b) in cooling cycle.

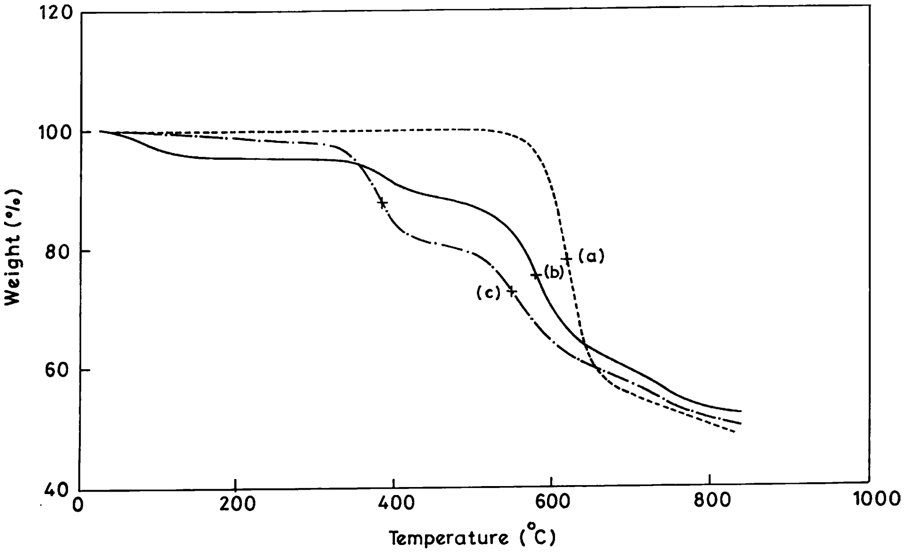


Figure 6 TG traces of (a) PEEK and SPEEK (b) EK-2 and (c) EK-7.

TABLE V Results of TG analysis of PEEK and SPEEK samples

		Mass loss (%)			
S. No.	Sample designation	50–200°C (%)	200–450°C (%)	Above 450°C (%)	Char residue (%)
PEEK	PEEK	–	–	49.8	50.2
1	EK-1	7.6	–	39.2	53.2
2	EK-2	6.4	11.8	36.2	45.6
3	EK-3	4.8	6.6	36.1	52.5
4	EK-4	2.0	9.3	38.3	50.4
5	EK-5	5.0	14.8	35.4	55.2
6	EK-6	8.0	13.5	–	–
7	EK-7	1.0	18.0	29.6	51.4
8	EK-8	10	16.0	30.0	44.0
9	EK-9	7.4	18.0	31.7	42.9
10	EK-10	1.4	20.8	50.8	27.0

Char residue indicate the mass remaining at 800°C.

groups may have taken place leading to loss of phenol along with the loss of SO_3 groups in this temperature range. Such a scission has been indicated by Luo and coworkers [14]

Breakdown of the polymer backbone takes place above 450°C (Table V).

3.3. Water uptake

The presence of water facilitates proton transfer and increases the conductivity of solid-state electrolytes. The enhancement of hydrophilicity by sulphonation of PEEK polymer can be followed by water absorption of SPEEK films as a function of degree of sulphonation (determined by ^{1}H-NMR). For this study, the SPEEK samples, which were kept in water, were taken out at definite intervals of time and the water uptake was found to be almost constant except for the samples with high degree of sulphonation which showed the gradual increase in the uptake of water. A plot of water uptake against DS (%) is given in Fig. 8.

3.4. Proton conductivity

The proton conductivity was high in sample EK-10 (0.235×10^{-2} S/cm) and it was lowest in sample EK-2 (0.034×10^{-2} S/cm). The samples EK-7 and EK-8 had approximately same (0.145×10^{-2} S/cm). These results indicate an increase in proton conductivity with increase in extent of sulphonation.

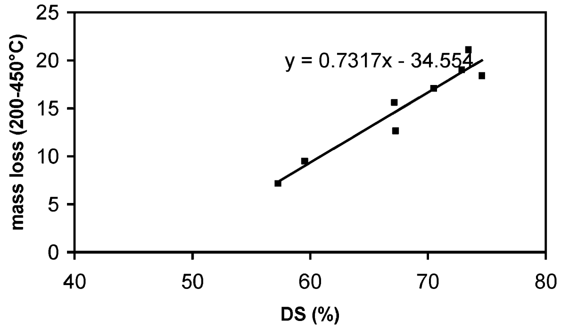


Figure 7 DS (%) (calculated from elemental analysis) vs.% mass loss due to sulphonic acid group.

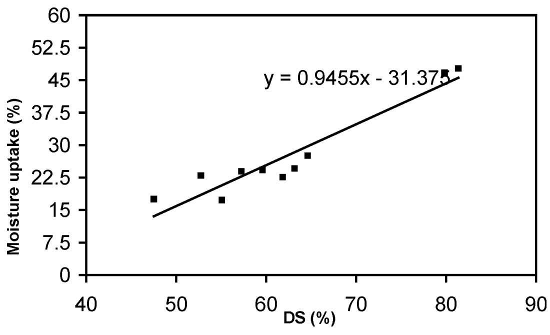


Figure 8 DS (%) (calculated from ^{1}H-NMR) vs. Moisture uptake.

3.5. Mechanical properties

Most of the sulphonated PEEK samples had reasonably good mechanical properties. An increase in degree of sulphonation resulted in a drastic reduction of mechanical properties. Tensile strength, tensile modulus and % elongation of samples having DS less than 70% were 47–66 MPa, 900–1148 MPa and ~34% respectively. In the samples with higher degree of sulphonation (EK-7 and EK-10), the mechanical properties were significantly lower. Therefore PEEK having up to 70% of sulphonation is a potential candidate for proton exchange membranes in fuel cells.

4. Conclusions

A series of sulphonated Gatone PEEK samples were synthesized by varying the reaction time, temperature and the concentration of PEEK in sulphuric acid. The extent of sulphonation (measured by elemental analysis and ^{1}H-NMR) increased by increasing temperature of the reaction and 70–80% sulphonation was attained at 45 and 50°C. In FTIR spectra of SPEEK, additional absorption bands associated with sulphonic acid groups were present at 3440, 1252, 1080, 1024, and 709 cm^{-1}. Splitting of C—C aromatic bands on sulphonation was also observed. An increase in moisture absorption of SPEEK film samples was observed with an increase in degree of sulphonation. Decomposition of sulphonic acid group was indicated by mass loss in the temperature range of 250–450°C in thermogravimetric analysis. In unsulphonated PEEK, no mass loss was observed in this region. The proton conductivities were found to be in the range of $0.04–0.235 \times 10^{-2}$ S/Cm.

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