Research Article

Modification of Poly(ether ether ketone) Polymer for Fuel Cell Application

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Received 10 April 2013; Accepted 1 October 2013

Polyelectrolyte membrane (PEM) is an important part of PEM fuel cell. Nafion is a commercially known membrane which gives the satisfactory result in PEM fuel cell operating at low temperature. Present research paper includes functionalization of Poly(ether ether ketone) (PEEK) polymer with phosphonic acid group. The functionalization was done with the help of nickel-based catalyst. Further, the polymer was characterized by the FTIR, EDAX, DSC, TGA, and 1H NMR, and it was found that PEEK polymer was functionalized with phosphonic acid group with good thermal stability in comparison to virgin PEEK. Finally, the thin films of functionalized polymer were prepared by solution casting method, and proton conductivity of film samples was measured by impedance spectra whose value was found satisfactory with good thermal stability in comparison to commercially available Nafion membrane.

1. Introduction

PEEK is a semicrystalline aromatic polymer having high melting temperature (335°C) and very low or no solubility in ordinary solvents at room temperature. Sulfuric acid is the common solvent which dissolves and also sulfonates PEEK at room temperature. Dilute solutions at high temperatures can also be obtained in hydrofluoric acid, trifluoromethanesulfonic acid, dichlorotetrafluoroacetone monohydrate, phenol 1,2,4-trichlorobenzene, and benzophenone [1]. Therefore, modification of PEEK is typical to some extent but desired for many applications such as polymer electrolyte membrane fuel cell (PEMFC) where acid functionalized polymer is required. In case of PEEK, functionalization in polymer stage is mostly reported on sulfonation and nitration [2]. Phosphonation of polymer is one of the methods to modify their properties such as proton conductivity, mechanical and thermal stability, and in polymer stage it was reported by various groups. Alexandratos et al. [3] reported the phosphonation of polystyrene using PCl3 which gave the cross-linked polymer. However, Jakoby et al. [4] reported that the highly substituted phosphonic acid derivative of polyphenylsulfone (PPS) was achieved via the Pd-dibenzylidenediacetone (dba) complexed catalyst in solvent diphenyl ether. Increase of reaction temperature from 90°C to 120°C also enhanced the substitution level. Bock et al. [5] reported phosphonation of the polysulfones (PSU) using nickel chloride and silylated phosphonates. The route was found less expensive and gave the halogen free product in comparison to palladium-based catalytic route. Lafitte and Jannasch [6] reported a phosphonation of polysulfones via the lithiation of polymer and subsequent conversion of lithiated sites into phosphonate unit. The substitution level in lithiation route was found very low.

The above efforts have been done on polysulfones polymer. However, in present paper we have done phosphonation of PEEK polymer by utilizing the well-known Michaelis-Arbuzov Reaction route [7]. Various characterization techniques such as FTIR, EDAX, and NMR supported the phosphonation PEEK with high thermal stability in comparison to PEEK polymer. The proton conductivity of P-PEEK film was also compared with Nafion at >100°C which showed slightly lower value than Nafion.

2. Experimental

2.1. Materials and Methods. The commercial available Gaton-eTM PEEK polymer was obtained by Gharda Chemical India;
Table 1: Calculated wt% of elements in Br-PEEK.

| Element | PEEK    | Br-PEEK (Br) | 2-PEEK |
|---------|---------|-------------|--------|
| C       | 82.61   | 64.06       | 52.32  |
| O       | 17.39   | 13.48       | 11.01  |
| Br      | 0       | 22.45       | 36.66  |

Table 2: Measured wt% of elements in Br-PEEK.

| Element | PEEK 3h | 6h | 9h | 24h |
|---------|---------|----|----|-----|
| C       | 86.63   | 66.71 | 59.48 | 54.33 | 48.27 |
| O       | 13.37   | 12.86 | 11.73 | 10.80 | 8.31  |
| Br      | —       | 20.43 | 28.79 | 34.87 | 43.42 |

however, reagent grade NiCl₂ and Triethyl phosphate were purchased from Sigma-Aldrich, India. Liquid bromine was obtained from MERK India Ltd, India. Dimethyl acetamide (DMAC) and N-Methyl-2-pyrrolidone (NMP) were purchased from HiMedia Laboratories, India.

2.2. Synthesis of Brominated PEEK (Br-PEEK). All glass wares and PEEK polymer were completely dried at 110°C overnight before use. The reaction assembly was established in fume-hood with help of three necks round bottom flask, mechanical stirrer and gas washing bottle attached with nitrogen supply. 15 g (0.052 mol.) of completely dried PEEK powder were charged in flask containing a mixture of 4 mL (0.156 mol.) liquid bromine and 150 mL of concentrated H₂SO₄. The reaction mixture was stirred at ambient temperature for 24 h. The brominated samples were collected at 3 h, 6 h, 9 h, and 24 h time intervals and attributed as 3 h, 6 h, 9 h, and 24 h respectively. The polymer was precipitated into ice cold distilled water and further washed with several portions of distilled water, methanol, respectively. To ensure bromine free sample, the polymer was extracted with methanol for 8 h. A white modified polymer was obtained which was finally dried in vacuum oven. To obtain the powder sample, the polymer was grinded in Retsch MM 400 Mixture Mill. Modified polymer was readily soluble in a common organic solvent such as Dimethyl sulfoxide (DMSO), DMAC, Chloroform, and Tetrahydrofuran (THF).

2.3. Aryl Phosphonation of Monobrominated PEEK (Br-PEEK)

(a) Tetrakis(triethylphosphite)nickel(0). Tetrakis(triethylphosphite)nickel(0) compound was synthesized by the previously reported method [7]. About 4.0 g of Tetrakis(triethylphosphite)nickel(0) (melting point 106–109°C) was obtained.

(b) Phosphonation of Br-PEEK. Solution of 12 g (0.033 mol) 3 h Br-PEEK in 150 mL DMAC was prepared in a reactor equipped with oil bath, gas inlet and outlet, thermometer, condenser, and dropping funnel. A cold trap was attached to the head of the reflux condenser. The temperature of solution was raised up to 100°C. Subsequently, a solution of freshly prepared tetrakis(triethylphosphite)nickel(0) in DMAC was transferred in to the reaction flask and finally raised the temperature up to 180–200°C. The concentration of catalyst was varied as 5, 10, 15, and 20 mol% and attributed as 5 m, 10 m, 15 m, and 20 m. Application of nitrogen stream provides the inert medium and simultaneously drives off evolved vapors. A homogeneous, brownish solution was obtained. Above the 160°C, 2–4 drops of triethylphosphite were added in the reaction flask. Further, the batch was kept under slow stirring at 180–200°C for 8–10 h. The reaction mixture was turned black as the reaction proceeded. A solid polymer was obtained by precipitation of reaction mixture into methanol. Polymer content was decanted and subsequently suspended in water. For removal of catalyst residue, the water-suspended polymer was sonicated in Ultrasonicator (UTS-120, Unitech Ultrasonics) for 15 min. Polymer was filtered and dried at 100°C. Hydrolysis of phosphonated polymer (P-PEEK) was carried out by refluxing with concentrated HCl for 50 h. After complete washing with distilled water and drying in vacuum oven, the white solid polymer was obtained.

The characterization of polymers were done by the following equipment—elemental analysis by EDAX detector equipped in FEI Quanta 200FC SEM system, IR spectra by Thermo-Nicolet Nexus FT-IR spectrometer, ¹H NMR by Bruker AC500 MHz NMR spectrometer, and thermal analysis by EXSTAR TG/DTA 6300. Proton conductivity of P-PEEK film sample was determined by Impedance Gain Phase Analyzer (SOLARON SLI260) in which Julabo S25 was equipped for temperature variation.

3. Results and Discussion

3.1. Characterization of Brominated PEEK (Br-PEEK)

3.1.1. Elemental Analysis of Br-PEEK by EDAX. The wt% of C, O, and Br in mono- and dibrominated PEEK was calculated theoretically (Table 1) and also measured by EDAX system (Figure 1 and Table 2). EDAX system attached with SEM was unable to measure the hydrogen weight. Therefore, during theoretical calculation we have eliminated the hydrogen weight and calculated the hydrogen weight of the polymer by subtracting the sum of C, O, and Br weight from 100%.
weight and assumed the total weight as 100%. Br level increased with increasing the duration of reaction (Figure 2). The wt.% of Br in sample 3 h was found equal to the calculated wt% of monobrominated PEEK, while in sample 9 h it was found to be close to the calculated wt.% of dibrominated PEEK that is about 37% (Table 2). The wt% was correlated with degree of substitution (DS) by using [12, 13].

\[
DS = \frac{mY}{(100W - W'Y)},
\]

where \(m\) is molar mass of repeat unit, \(W\) is the formula weight of the substituent group, \(W'\) is the net increase in formula weight due to the introduction of substituent group per unit, and \(Y\) is the wt.% of substituent. The value of DS was found to be 0.89 (3 h), 1.60 (6 h), 1.85 (9 h), and 2.65 (24 h).

3.1.2. FTIR Analysis of Br-PEEK. FTIR spectrum of pure PEEK polymer was reported by the Nguyen and Ishida [14], Varsanyi [15], and Bellamy [16]. The typical absorption band reported in PEEK polymer was found almost same as Br-PEEK (Figure 3). In general, the C-Br stretching vibration in organic compound was reported in the range of 700–500 cm\(^{-1}\) while in [17] it was reported that aliphatic hydrocarbon showed the C-Br stretching in the range of 700–500 cm\(^{-1}\) whereas aromatic hydrocarbon showed the C-Br stretching in the region of 1200–1000 cm\(^{-1}\) (strong multiple bands). A new doublet band was observed near 1066–1053 cm\(^{-1}\) in Br-PEEK which may be due to C-Br stretching vibration. Since pure PEEK has many absorption bands in the region of 700–500 cm\(^{-1}\) therefore it is very difficult to assign the specific bands for C-Br stretching in this region.

3.1.3. \(^1\)H NMR Spectra of Br-PEEK. Since pure PEEK is insoluble in organic solvents except in strong acids, therefore its \(^1\)H-NMR spectrum could not be recorded. The \(^1\)H NMR of brominated sample is shown in Figure 4. Br-PEEK (3 h) showed signal between the region 7.78–7.85 (m) ppm, 7.40 (d) ppm, 7.26–7.28 (dd) ppm, 7.17–7.24 (m) ppm, and 7.12–7.14 (dd) ppm. These signals were observed in the aromatic region and associated with Ar-H. The signal 7.40 (d) ppm was found due to substitution of bromine group in the hydroquinone segment.

Further, a distinct signal at 8.00 (d) ppm and 7.62 (dd) ppm was obtained in 9 h and 24 h samples which may be associated with the neighbouring proton of substituted benzophenone segment of Br-PEEK. The substitution in benzophenone segment of PEEK polymer was also reported by the Conceição et al. [18]. The DS in Br-PEEK was also determined by measuring the ratio of intensity of the distinct signal with integrated intensity of the signals corresponding to all the other aromatic hydrogens [10]. The DS obtained by the NMR was found lower in comparison to the DS obtained by the elemental analysis (EDAX data) (0.74 (3 h), 1.23 (6 h), 1.65 (9 h), 2.38 (24 h)).

3.2. Characterization of Phosphonated PEEK (P-PEEK)

3.2.1. FTIR Spectra of P-PEEK. P-PEEK was characterized by the FTIR spectrometer. The main reported absorption bands are as follows. González et al. [19] assigned the P=O stretching in the range of 1240–807 cm\(^{-1}\). Trotta et al. [20] assigned the P=O stretching at 1240 cm\(^{-1}\). According to Stuart [21] the characteristic infrared bands in phosphonated aromatic compounds are as follows: (1) aromatic P=O stretching in
between 1350–1430 cm\(^{-1}\), (2) aromatic P–C stretching in between 1450–1430 cm\(^{-1}\), and (3) phosphorus ester P–OH stretching in the region 1040–930 cm\(^{-1}\). The spectrum of pristine PEEK shows many absorption bands in the above mentioned region such as asymmetric stretching of diphenyl ether groups in the region of 1227 cm\(^{-1}\) and 1190 cm\(^{-1}\). Therefore, a clear identification of addition of phosphonate ester group was somewhat difficult. From the comparison of spectra of P-PEEK ester and PEEK (Figure 5), we found the new absorption band at 1250–1233 cm\(^{-1}\), 1470 cm\(^{-1}\), and doublet at 1036 cm\(^{-1}\) which might be due to the presence of P=O stretching, P–C stretching, and phosphorus ester P–OH stretching, respectively. All other characteristics band of PEEK such as presence of carbonyl group at 1651 cm\(^{-1}\) remained the same in P-PEEK derivatives.

### 3.2.2. Elemental Analysis by EDAX

The wt.% of different elements in P-PEEK ester derivatives were determined by EDAX (Figure 6) and also calculated theoretically by ignoring the hydrogen atom as like in Br-P-PEEK. Table 3 represented the calculated and measured wt% of different elements in monophosphonated P-PEEK ester. The wt% of phosphorus in different P-PEEK ester samples were found lower than the calculated wt% of monophosphonated PEEK (7.69 wt%). It was observed that P-PEEK samples have some bromine. The DS was calculated according to (1) whose values were ~0.17, 0.30, 0.45 and 0.71 in P-PEEK ester 5m, 10m, 15m and 20m respectively.

### 3.2.3. Solubility of P-PEEK Ester and P-PEEK Acid

The solubility of P-PEEK ester and P-PEEK acid were determined by visual inspection in various solvent at room temperature and also at high temperature >150°C. It was found that both are insoluble in almost all the organic solvents. NMP sparingly dissolved the P-PEEK acid and ester both only at high temperature. Further, addition of 2-3 drops of acid such as HBr or H\(_2\)SO\(_4\) fairly dissolved the both form of polymer (Table 4).

### 3.2.4. NMR Characterization of P-PEEK

Solubility of P-PEEK ester was not found in any normal available deuterated solvent. Therefore, characterization of P-PEEK in liquid stage was somewhat difficult. To resolve the problem of solubility, initially a concentrated solution of P-PEEK ester in NMP at higher temperature was prepared which was further utilized in DMSO-\(d_6\) to prepare a solution of P-PEEK ester—NMP/DMSO-\(d_6\) in the ratio of 1/3. The \(^1\)H NMR spectra of NMP and P-PEEK ester—NMP in DMSO-\(d_6\) were determined, respectively. NMP showed the signal at 3.4 ppm, 2.85 ppm, 2.37 ppm, and 2.30 ppm. The signal near 2.5 ppm was associated with DMSO-\(d_6\). These entire signals were also found in P-PEEK ester-NMP sample. P-PEEK ester gave signal in both aromatic and also in aliphatic regions (Figure 7) due to presence of aromatic protons and protons of ethyl ester at 4.46 ppm and 1.19 ppm. Aryl phosphonation effected a downfield shift of proton neighbouring to phosphonic ester group as well as a broadening and splitting of signals into a doublet of doublets [5]. The broadening, splitting of signal, and downfield shifting were also found in case of P-PEEK samples as the degree of phosphonation increases (Figure 7). The degree of phosphonation can be calculated from the signal ratio of the ethyl ester protons and the protons of aromatic region [4] which was observed 0.14, 0.25, 0.42, and 0.68 in P-PEEK ester 5m, 10m, 15m, and 20m, respectively. Phosphonation in PEEK polymer was also confirmed by the solid state \(^31\)P NMR spectrum of P-PEEK (Figure 8) which showed only a single signal at 12.52 ppm. Single peak was also reported by Bock et al. [5] in case of \(^31\)P NMR spectra of P-PSU acid.

### 3.2.5. Thermal Analysis of P-PEEK

P-PEEK (20 m) showed \(T_g\) 220°C and \(T_m\) ~ 381°C which was about 44°C higher than the PEEK polymer. It shows that P-PEEK exhibited higher thermal stability than PEEK polymer (\(T_g\) 152°C, \(T_m\) 337°C) (Figure 9). A significant wt. loss was found at 313°C which may be possible due to the conversion of phosphoric acid segment into anhydride (Figure 10). P-PEEK also showed the higher residual mass, which may be possible due to presence of incombustible phosphorus oxides.

### 3.2.6. Proton Conductivity P-PEEK

Proton conductivity of P-PEEK was determined by casting the film on Indium-tin oxide (ITO) coated glass sheet using the solvent NMP. Coated
**Figure 5:** FTIR of P-PEEK ester (20 m).

**Figure 6:** EDAX of P-PEEK ester (20 m).

**Figure 7:** $^1$H NMR of P-PEEK ester 5 m, 10 m, 15 m, and 20 m.

glass sheet was further dipped in water for 24 h. The thickness of polymer film was determined by taking the difference in glass sheet thickness before and after the coating. The polymer coated sheet was sandwiched with ITO coated glass sheet, and impedance was measured by varying the frequency
100 Hz to 32 MHz, AC voltage 50–500 mV in Impedance Gain Phase Analyzer (Solartron SL1260). Julabo S 25 was used for variation in temperature during the impedance measurement. Proton conductivity was calculated by the following equation $\sigma = L/R A$, where $L$, $R$, and $A$ are the distance between the two electrodes, membrane resistance, and cross-sectional area of the membrane, respectively [22–24]. The value of $R$ was determined by plotting the graph between the impedance of real and imaginary plot (Figure 12). The point of resistance was that where the imaginary part was found to be zero. Conductivity of the P-PEEK samples increases with temperature and degree of phosphonation. The proton conductivity P-PEEK-20m was found 0.0069 S cm$^{-1}$ at 25°C, 0.055 at 65°C, and 0.114 cm$^{-1}$ at 120°C (Figure 11 and Table 5). The Nafion membrane has been reported best ionic conductor at low temperature and high humidity [8, 25]. S-PEEK membrane showed comparable proton conductivity with Nafion at high degree of sulfonation and humidity. Both Nafion and S-PEEK membrane exhibited loss of conductivity and physical failure at temperature >100°C. The loss of conductivity was found greater in S-PEEK. Although conductivity of P-PEEK was found to be slightly lower than Nafion at >100°C but its thermal stability was found higher, and it is expected that P-PEEK will show better durability with acceptable proton conductivity in comparison to both Nafion and S-PEEK.

### 4. Conclusions

Commercial PEEK polymer can be brominated with only a small excess of bromine in H$_2$SO$_4$. However, no catalyst was used during the reaction. FTIR, EDAX, and $^1$H-NMR indicated that PEEK can be brominated readily. Further, conversion of Br-PEEK in to P-PEEK was carried out in presence of nickel-based catalyst. P-PEEK was characterized by various techniques, and it was found that P-PEEK showed high thermal stability in relation with PEEK polymer and solubility in NMP at higher temperature. The proton conductivity of P-PEEK was compared with Nafion at >100°C which showed slightly low value but thermal stability of P-PEEK was found good. Thus, it is expected that P-PEEK will show better durability with acceptable proton conductivity in comparison to both Nafion and S-PEEK at high temperature.

### Acknowledgments

One of the authors is thankful for financial support from the Ministry of Human Resource Development (MHRD), India,
and also for NCL Pune, India, for carrying out solid state NMR.

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