

Double cross-linked polyetheretherketone proton exchange membrane for fuel cell

Hongze Luo ^{a*}, Guntars Vaivars ^b, Mkhulu Mathe ^a

^a The Council for Scientific and Industrial Research, Pretoria, 0001, South Africa

^b Institute of Solid State Physics, University of Latvia, LV-1063, Latvia

Abstract

The proton exchange membrane based on polyetheretherketone was prepared via two steps of cross-linking. The properties of the double cross-linked membrane (water uptake, proton conductivity, methanol permeability and thermal stability) have been investigated for fuel cell applications. The prepared membrane exhibited relatively high proton conductivity, $3.2 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature and $5.8 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C. The second cross-linking significantly decreased the water uptake of the membrane. The performance of direct methanol fuel cell was slightly improved as compared to Nafion[®] 117 due to its low methanol permeability. The results indicated that the double cross-linked membrane is a promising candidate for the polymer electrolyte membrane fuel cell, especially for the direct methanol fuel cell due to its low methanol permeability and high stability in a methanol solution.

Keywords: cross-linked PEEK; water uptake; proton conductivity; proton exchange membrane; fuel cell.

* Corresponding Author: Tel: +27-12-8412389; fax: +27-12-8412135; E-mail: hongzee@gmail.com.

1. Introduction

Among the presently developed fuel cell technologies, the polymer electrolyte membrane fuel cells (PEMFCs) are the promising candidates for applications such as stationary power, low-emission vehicles and portable electronics ^[1, 2].

The proton exchange membrane is a key component of PEMFC, which has two roles of conducting protons and separating the fuel from oxidant. A polyperfluorosulfonic acid ionomer Nafion[®] (developed by *Dupont*) is the mostly used proton exchange membrane in PEMFCs, because of its high proton conductivity and excellent chemical stability ^[3, 4]. However, the high cost of Nafion[®] limits the large-scale commercialization ^[5]. The high methanol cross-over of Nafion[®] is another shortcoming when the methanol is directly used as the fuel in PEMFC, which is usually called direct methanol fuel cell (DMFC). The high methanol cross-over of Nafion[®] drastically reduces the performance of DMFC ^[6].

Over the last decade, the proton exchange membranes based on polyetheretherketone (PEEK) and derivatives have shown the considerable promises for PEMFC applications ^[7]. These membranes were found to possess good thermal stability, appropriate mechanical strength, and high proton conductivity, which depend on their degree of sulfonation. However, the mechanical properties of PEEK deteriorate progressively with sulfonation ^[8], which makes the long term stability of the highly sulfonated polymer questionable ^[9].

The non-cross-linked membranes based on highly sulfonated PEEK (SPEEK) deteriorate due to excessive water uptake (swelling), making questionable their long-term stability in PEMFC applications ^[10]. The cross-linked SPEEK membranes were found to be much less susceptible to swelling than that of non-cross-linked PEEK. Unfortunately, these membranes also have got many disadvantages, like low stability in a practical environment, such as acidic environment, at high temperatures. Besides that, synthesis of known cross-linked PEEK membranes is comparatively complex process, and requires using expensive materials.

In this work, the proton exchange membrane based on PEEK was prepared via two steps of cross-linking. The procedure did not involve the use of expensive materials. The properties of the double cross-linked membrane, such as water uptake, proton conductivity, methanol permeability and thermal stability have been investigated for fuel cell applications.

2. Experimental

2.1. Materials

The catalysts, platinum (40 %) on carbon black (cathode), platinum (30 %)/ruthenium (15 %) on carbon black (anode), Nafion[®] (5 %) solution, and carbon cloth were purchased from *Alfa Aesar*. Polyetheretherketone (PEEK), chlorosulfonic acid (98 %) was purchased from *Aldrich*. All other reactants and solvents were purchased from *Merck* and used without further purification.

2.2. Polymer synthesis and membrane preparation

10 g of PEEK was slowly added into 50 ml of concentrated chlorosulfonic acid under stirring at 60 °C for 1 h. After cooling down to room temperature, the mixture was precipitated in large excess of deionized ice-water. The precipitated polymer was washed with deionized water until pH = 7. Thereafter, the cross-linked sulfonated-sulfinated (CSsPEEK) was converted from the cross-linked sulfonated-chlorosulfonated PEEK (CSCPEEK) via a reduction in the sodium sulfite solution for 10 h at 80 °C, and then washed with deionized ice-water. The obtained CSsPEEK was dried in a vacuum oven at 60 °C.

The membrane was prepared via a second cross-linking. The cross-linker diiodomethane was added to the CSsPEEK solution (15 wt.%) in 1-Methyl-2-pyrrolidinone. After the solution was homogenized by stirring, the polymer solution was cast on a glass Petri dish. The solvent was then removed in a vacuum oven at 130 °C. The membrane was peeled off from the Petri dish. Thereafter, the membrane was treated in 10 wt.% of NaOH solution at 90 °C for 24 h,

then in 10 wt.% H₂SO₄ at 90 °C for 24 h and finally in water for 24 h at 90 °C. Figure 1 shows the preparing procedure of the double cross-linked PEEK membrane.

2.3. Characterizations

Fourier Transform Infrared (FTIR) spectra were obtained in a scanning range of 400 – 2000 cm⁻¹ on a PerkinElmer Spectrum™ 100 FTIR spectrometer. *Nuclear magnetic resonance (NMR)* spectrum was obtained with a Varian Gemini XR2000 NMR Spectrometer with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as the solvent. The thermal stability of the membrane was analyzed in an argon atmosphere by using Thermal Analyzer STA 1500 (CCI-3, *Rheometric Scientific*) in a temperature range from 20 °C to 550 °C at a heating rate of 10 °C min⁻¹.

The water uptake of the cross-linked membrane was determined by measuring the weight difference between the fully hydrated membrane and the dry membrane. The following equation was used:

$$\text{Wateruptake} = \frac{G_w - G_d}{G_d} \times 100\% \quad , \quad (3)$$

where G_w is the weight of the wet membrane, and G_d is the weight of the dry membrane.

The proton conductivity of the membrane was obtained from the impedance data. Impedance measurement was carried out using a potentiostat (*Autolab PGSTAT30*, Netherlands) in combination with the computer controlled frequency response analyzer over the frequency range from 1 Hz to 100 kHz. The proton conductivity σ was calculated, using the relationship:

$$\sigma = L/RS \quad , \quad (4)$$

where L , R and S is the thickness (cm), resistance (Ohm) and contact area of the membrane (cm²), respectively.

The methanol permeability (cross-over) was examined by using a diaphragm diffusion cell. The membrane was clamped in-between two compartments. The methanol concentration changes were measured using gas chromatography (Hewlett Packard 5890) at room temperature. The methanol permeability was calculated according to the following equation ^[11, 12]:

$$P = \frac{L}{A} \times \frac{V_B}{C_A} \times \frac{\Delta C}{\Delta t} \quad (5)$$

where, P is the methanol permeability, $\text{cm}^2 \text{s}^{-1}$; L is the membrane thickness, cm; A is the membrane area available for permeability, cm^2 ; V_B is the volume of the receiving compartment, M; C_A is the initial concentration, M.

DMFC performance at 70 °C was evaluated by using 1 M methanol solution on the anode at a flow rate of 1 ml min^{-1} , and oxygen on the cathode at 0.5 l min^{-1} . The membrane electrode assembly (MEA) was carried out by hot-pressing the electrodes on both sides of the membrane at 130 °C and 140 bar for 2 min. The geometrical area of both electrodes was 4 cm^2 . The catalyst loading on the carbon cloth was 1.5 mg cm^{-2} for both of anode and cathode.

3. Results and discussions

In our work, the sulfonation, chlorosulfonation and cross-linking between PEEK with the formation of SO_2 bridging moieties were observed, as demonstrated by ^1H NMR and FTIR. The ^1H NMR spectrum of the CSCPEEK (in Figure 2) shows a new resonance at 8.22 ppm, which is not presented in the spectrum reported for SPEEK prepared by sulfonation in concentrated sulfuric acid ^[13]. It is characteristic for hydrogen atom in the ortho position to a SO_2 group ^[14], demonstrating the occurrence of cross-linking ^[15]

The membrane as prepared directly from CSCPEEK is not suitable for fuel cell applications, because the swelling by water led to the gel formation. However, the water is needed to

provide the proton conductivity. The CSCPEEK was converted to CSsPEEK by reducing sulfonyl chloride group to sulfinate group. CSsPEEK has two types of functional groups - sulfonic group for proton exchange and the sulfinate group for cross-linking.

The absorption bands at 1020 and 1078 cm^{-1} in the both FTIR spectra (in Figure 3) were assigned to symmetric and asymmetric stretching vibration O=S=O due to the presence of sulfonic groups. The absorption band, which appeared at 1250 cm^{-1} was also assigned to the sulfonic group^[16]. The FTIR spectrum of CSCPEEK showed characteristic band of sulfonyl group (SO_2Cl) at 1375 cm^{-1} (SO_2 asymmetric stretching vibration)^[17], which is not presented in the spectrum of sulfonated PEEK^[13]. The S=O stretching, specifically, a symmetric stretching of the sulfinate group, is observed at 975 cm^{-1} in the spectrum of CSsPEEK^[18]. It verified that sulfonyl group was successfully converted to sulfinate group after the reduction of CSCPEEK.

The water uptake of proton exchange membranes is well-known to have profound effect on proton conductivity, mechanical strength and dimensional stability. However, too much water results in the excess swelling of the membrane and further loss of its mechanical properties^[19]. Therefore, the water uptake is very important for proton exchange membrane using in fuel cell.

The water uptake of the membranes without the second step of cross-linking was extremely high, because the membranes prepared directly from CSCPEEK and CSsPEEK gelified in water. The water uptake of the double cross-linked membrane was 25 % at room temperature and 38 % at 80 °C. The water uptake is increasing with temperature. This result indicates that the second cross-linking can significantly decrease water uptake of the membrane. The cross-linkages between the polymer chains in the membrane form a three-dimensional network, and prevent the polymer from swelling to infinity, in other words from dissolving. This is due to the elastic retraction forces of the network, which decreases the entropy of the chains^[20]. The

prepared double cross-linked PEEK membrane can be applied in a practical fuel cell due to its low water uptake.

The conductivity of the double cross-linked PEEK membrane was $3.2 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature and $5.8 \times 10^{-2} \text{ S cm}^{-1}$ at $80 \text{ }^\circ\text{C}$. The conductivity of CSCPEEK membrane was comparable with that of the Nafion[®] 117 ($9.7 \times 10^{-2} \text{ S cm}^{-1}$) measured under the same conditions. The methanol permeability of the double cross-linked PEEK membrane was $1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was almost ten times lower than that of the Nafion[®] 117 ($1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The comparative properties of the membranes are listed in Table 1.

Table 1. The comparative properties of the membranes measured at the same condition.

Membrane	Water uptake (%) at $20 \text{ }^\circ\text{C}$	Water uptake (%) at $80 \text{ }^\circ\text{C}$	Conductivity (S cm^{-1}) at $20 \text{ }^\circ\text{C}$	Conductivity (S cm^{-1}) at $80 \text{ }^\circ\text{C}$	Methanol permeability ($\text{cm}^2 \text{ s}^{-1}$) at $20 \text{ }^\circ\text{C}$
Double cross-linked PEEK	25	38	3.2×10^{-2}	5.8×10^{-2}	1.5×10^{-7}
Nafion [®] 117	20	27	6.2×10^{-2}	9.7×10^{-2}	1.4×10^{-6}

The thermal stability of the double cross-linked PEEK membrane was analyzed by TGA. The thermal stability of the membrane was analyzed by TGA. The TGA curve (in Figure 4) showed three subsequent steps of weight loss. The first weight loss from 20 to $150 \text{ }^\circ\text{C}$ was caused by removal of absorbed water from the membrane. The second weight loss from 250 to $400 \text{ }^\circ\text{C}$ can be associated to the decomposing of the sulfonic groups from the main chain of PEEK [13, 21]. The third weight loss is attributed to the decomposition of the membrane from $400 \text{ }^\circ\text{C}$.

The power curve (Voltage–current density, Figure 5) of a single DMFC exhibited a slightly better performance for double cross-linked membrane as compared with that of Nafion[®] 117. The DMFC operated at $70 \text{ }^\circ\text{C}$ temperature and 1 M methanol solution and oxygen was used

as a feed. It might be linked to lower methanol permeability and membrane thickness reduction. The thickness of the double cross-linked membrane was 80 μm , and Nafion[®] 117 - 185 μm .

4. Conclusions

The PEEK based membrane was successfully prepared via two steps of cross-linking. The double cross-linked PEEK membrane is characterized by relatively high proton conductivity ($5.8 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C) and by low methanol permeability ($1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). The DMFC test shows improved performance for double cross-linked PEEK membrane as compared to Nafion[®]. In the future work, the effect of the cross-linking degree will be studied.

References

- [1] M. Winter, R.J. Brodd, *Chemical Reviews*, 104 (2004) 4245-4270.
- [2] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chemical Reviews*, 104 (2004) 4587-4612.
- [3] X. Zhou, J. Weston, E. Chalkova, M.A. Hofmann, C.M. Ambler, H.R. Allcock, S.N. Lvov, *Electrochimica Acta*, 48 (2003) 2173-2180.
- [4] Z. Chen, B. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz, Yan, *Chemistry of Materials*, 18 (2006) 5669-5675.
- [5] K.D. Kreuer, *Chem. Mater*, 8 (1996) 610.
- [6] A. Heinzl, V.M. Barragan, *Journal of Power Sources*, 84 (1999) 70-74.
- [7] L. Carrette, K.A. Friedrich, U. Stimming, *ChemPhysChem*, 1 (2000) 162-193.
- [8] X. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, *British Polymer Journal*, 17 (1985) 4-10.
- [9] S.D. Mikhailenko, K. Wang, S. Kaliaguine, P. Xing, G.P. Robertson, M.D. Guiver, *Journal of Membrane Science*, 233 (2004) 93-99.
- [10] S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *Journal of Membrane Science*, 285 (2006) 306-316.
- [11] P. Mukoma, B.R. Jooste, H.C.M. Vosloo, *Journal of Membrane Science*, 243 (2004) 293-299.
- [12] H. Luo, S. Ji, G. Vaivars, B. Bladergroen, V. Linkov, *South African Journal of Chemistry*, 60 (2007) 85-90.
- [13] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *Journal of Membrane Science*, 229 (2004) 95-106.

- [14] M.J. Sumner, W.L. Harrison, R.M. Weyers, Y.S. Kim, J.E. McGrath, J.S. Riffle, A. Brink, M.H. Brink, *Journal of Membrane Science*, 239 (2004) 199-211.
- [15] M.L. Di Vona, D. Marani, C. D'Ottavi, M. Trombetta, E. Traversa, I. Beurroies, P. Knauth, S. Licoccia, *Chemistry of Materials*, 18 (2006) 69-75.
- [16] R.J.W. Cremlyn, *Chlorosulfonic Acid: A Versatile Reagent*, 1 ed., Royal Society of Chemistry, 2002.
- [17] M. De Carvalho Barcellos, A.P. De Aguiar, M.R.M.P. De Aguiar, L.C. De Santa Maria, *Polymer Bulletin*, 55 (2005) 61-70.
- [18] U. Zoller, *The Chemistry of Sulphonic Acids, Esters and their Derivatives*, Wiley, 1991.
- [19] Y.S. Kim, L. Dong, M.A. Hickner, T.E. Glass, V. Webb, J.E. McGrath, *Macromolecules*, 36 (2003) 6281-6285.
- [20] M. Elliott, in, *BASF Aktiengesellschaft, Ludwigshafen Germany*, 2004, pp. 5.
- [21] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *Journal of Membrane Science*, 173 (2000) 17-34.

Figure captions

Figure 1. The sulfonated PEEK membrane preparing procedure by double cross-linking.

Figure 2. NMR spectrum of CSCPEEK.

Figure 3. FTIR spectra of CSCPEEK (bottom) and CSsPEEK (top).

Figure 4. TGA of the double cross-linked PEEK membrane.

Figure 5. Voltage–current density plot of DMFC using the double cross-linked PEEK membrane and Nafion[®] 117 at 70°C with 1 M methanol as a feed and oxygen as an oxidant.

Figure 1
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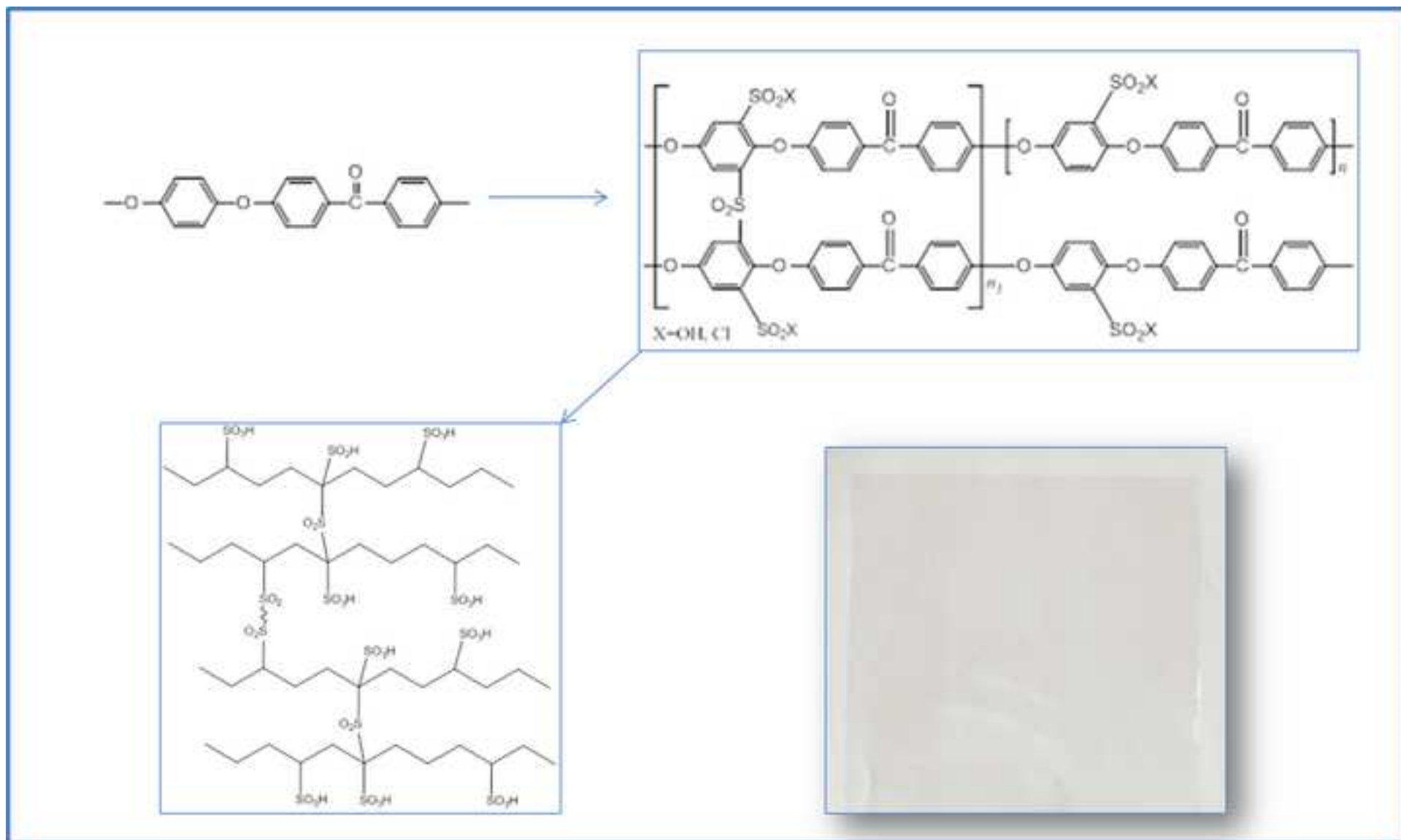


Figure 2
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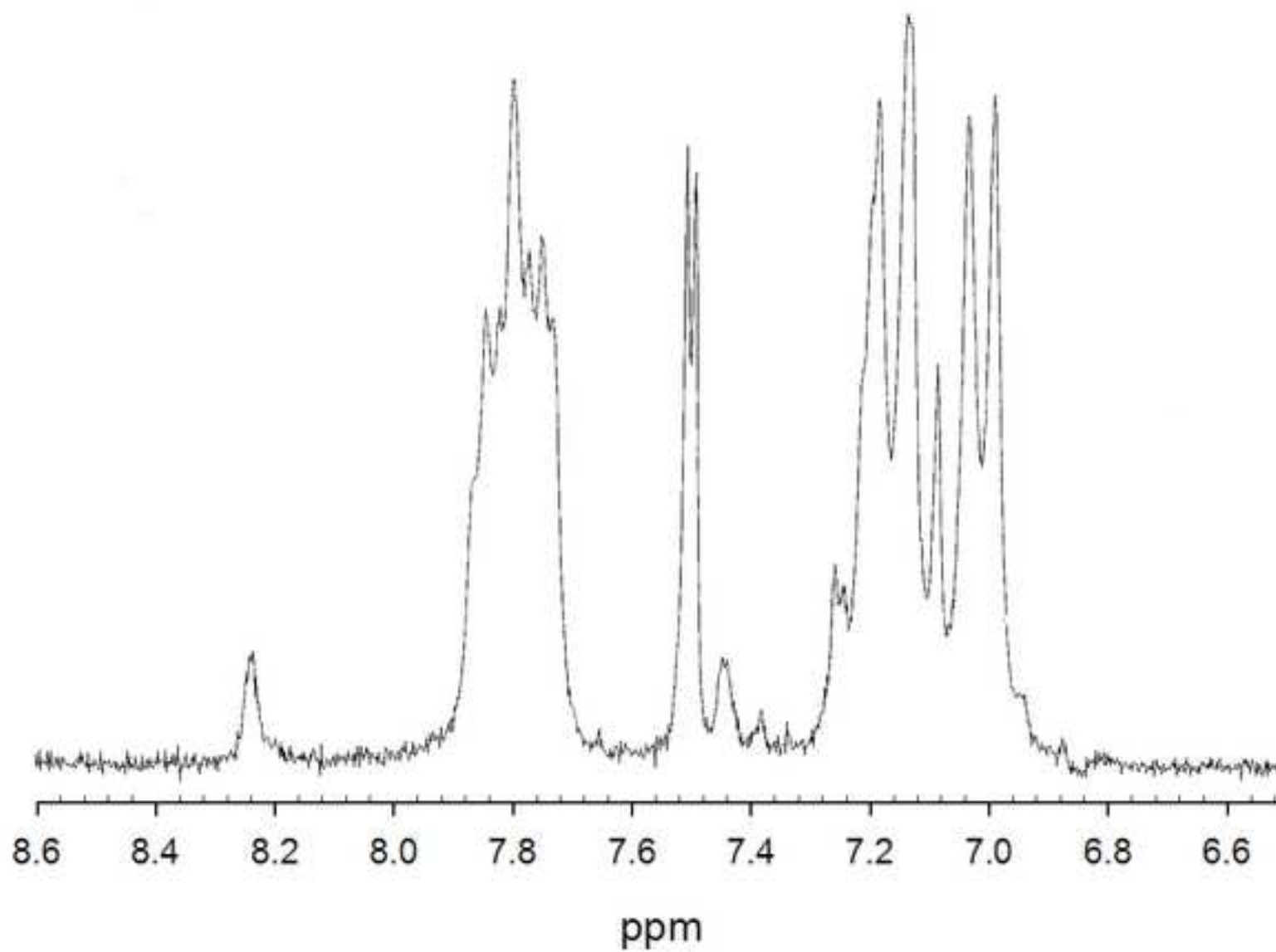


Figure 3
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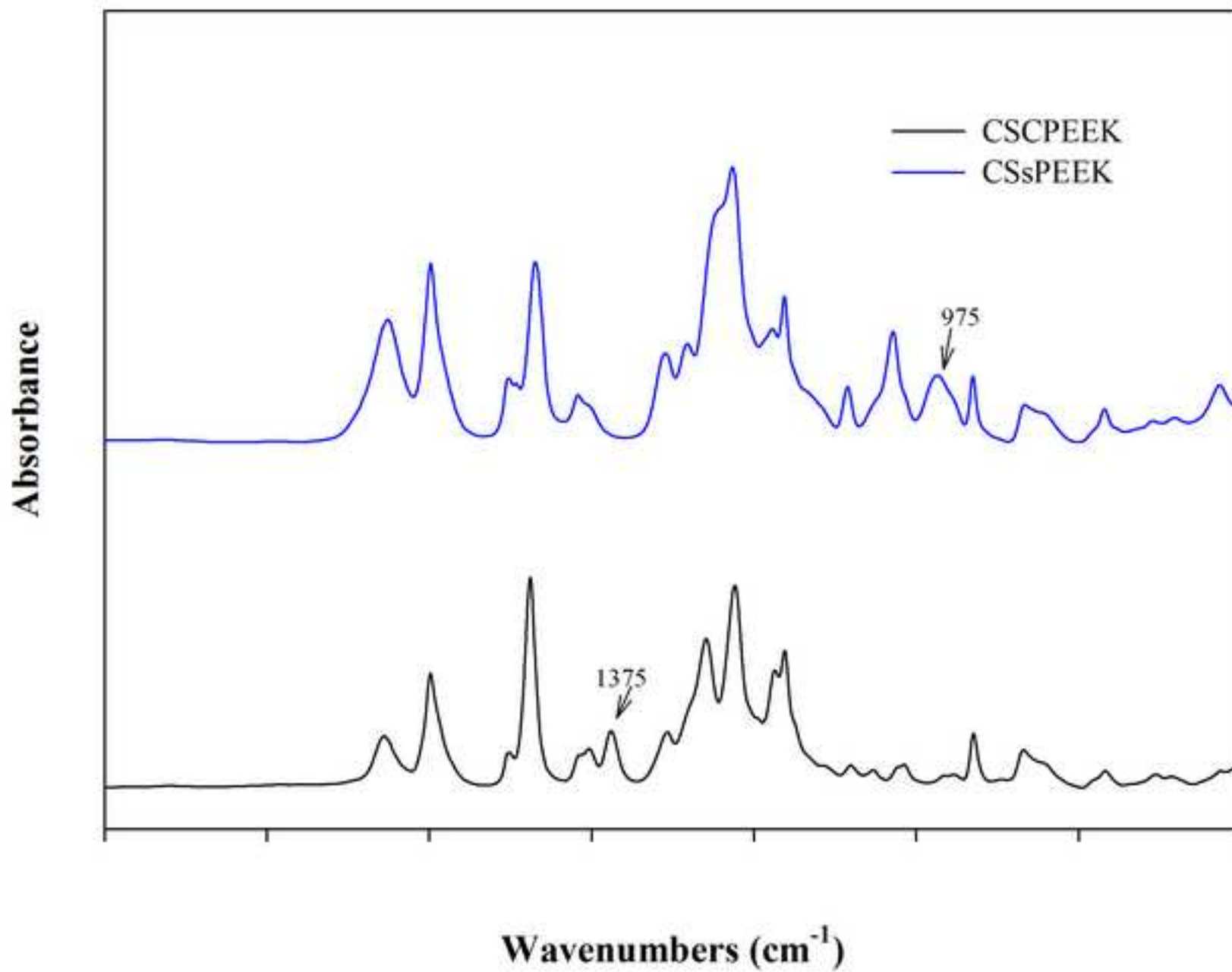


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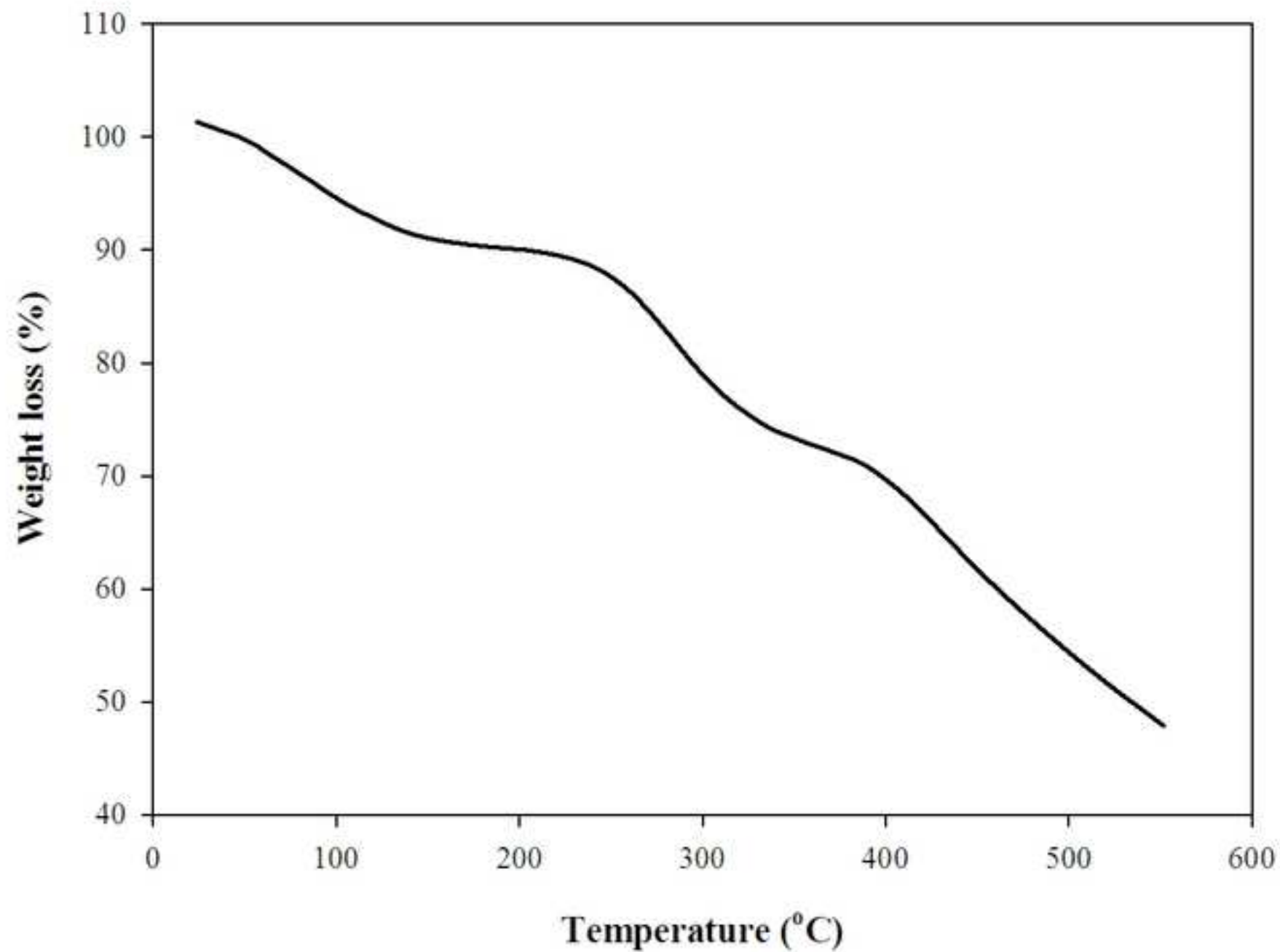


Figure 5
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