Stability of PVDF hollow fibre membranes in sodium hydroxide aqueous solution

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Abstract

The stability of PVDF hollow fibre membranes in sodium hydroxide (NaOH) aqueous solutions were investigated in this study. PVDF hollow fibre membranes were prepared from each of the three commercial raw PVDF materials (Kynar 761, Solef 1015 and Solef 6010) from two major suppliers (Atofina Chemicals Inc., USA and Solvay, Belgium) for comparison purposes. The effect of NaOH concentration, treatment time and temperature on mechanical properties, thermal properties and crystalline structure of the PVDF hollow fibre membranes were investigated through mechanical strength measurement, surface area analysis, XRD, FTIR and DSC analyses. The obtained results indicate that the reaction between PVDF and NaOH was initiated even at low concentrations of NaOH and was aggravated with the extended treatment time, resulting in the decrease in mechanical strength and crystallinity of PVDF hollow fibre membranes. The reaction was accelerated and intensified by increasing the concentration of NaOH and/or treatment temperature. At 70 °C, the mechanical integrity of the PVDF membranes was completely destroyed in 4 wt% NaOH solution within 24 h or in 10 wt% NaOH solution within 8 h. The deterioration of stability in NaOH solutions is considered universal for all PVDF employed in this study, irrespective of the raw materials or the corresponding hollow fibre membranes.

Keywords: PVDF Hollow fibre membrane Stability Chemical resistance Sodium hydroxide Mechanical strength

1. Introduction

PVDF is an excellent membrane material due to its outstanding thermal stability, mechanical strength, and also its distinctiveness in chemical resistance against a wide range of harsh chemicals such as halogens and oxidants, inorganic acids (apart from fuming sulphuric acid), as well as aromatic, aliphatic and chlorinated solvents (Lovinger, 1982; Yeow et al., 2003; Hashim et al., 2009). It can be categorised as an outstanding membrane material especially in waste treatment application where harsh chemicals are commonly involved.

However, PVDF is vulnerable to caustic environment, which has been proven fundamentally by a number of studies (Komaki and Otsu, 1981; Shinohara, 1979; Kise and Ogata, 1983; Wegener et al., 2006; Vigo et al., 1984). In actual applications, PVDF membranes are often exposed to caustic environments: for instance during the operations of chemical cleaning or soluble gas removal from waste gas streams (Li et al., 1999). Potential damage to the membranes caused by the caustics is unlikely to be avoidable. Early investigations reported the observation of brownish discoloration of PVDF after its exposure to a sodium hydroxide (NaOH) solution (Komaki and Otsu, 1981; Shinohara, 1979). The immersion of the irradiated PVDF film into the NaOH solution resulted in the development of fission tracks on the film, where the film became brittle with deep colour with a NaOH–ethanol solution and forms a brown colour deposit with the KMnO4 solution (Komaki and Otsu, 1981). Stress corrosion cracking of PVDF in the NaOH solution was investigated, and it was found that NaOH can chemically attack PVDF. The chemical attack is accelerated by increasing the temperature and by applying strain (Hoa and Ouellette, 1983).

In the recent years, by employing various modern analytical techniques such as Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS), the chemical reactions between PVDF and NaOH can be explained as a phenomenon of dehydrofluorination, in which the carbon–carbon double are formed as a result of the elimination of hydrogen fluoride (HF) units from the polymer (Kuhn et al., 1987; Marchand-Brynaert et al., 1997; Kise and Ogata, 1983). Depending on the degree of the dehydrofluorination, the colour change of PVDF from white to brown and then to black can be visually observed. Despite the fact that quite a number of work has been carried out on the stability of PVDF in caustic environment, it should be noted that most of the previous experiments have been carried out under very strong caustic conditions or with the assistance of catalysts, as the reactions might be slow under certain moderate conditions: such as at ambient temperature or low chemical concentration. Such experimental results provide not only important, but also fundamental information on the stability of PVDF material in the sodium hydroxide solution. However, a systematic evaluation of the stability of PVDF membranes in caustic environment is still lacking.

To date, only two publications have been found to be directly related to the evaluation of stability or chemical resistance of PVDF membranes.
against caustics: one of them is the long-term investigation on the effect of different types of strong oxidants, including NaOH solutions, on the membrane performance (Benninger et al., 1980). The employed PVDF membranes that have been prepared from Kynar PVDF raw materials do not show significant changes in terms of water flux and polyethylene glycol retention after being immersed in 1 wt% NaOH solution for 24 months or at 10 wt% NaOH solution for 1 month. Remarkable changes could only be observed after 3 months treatment with the latter.

Another study has focussed on the investigation of chemical stability of a sulfonated hydrophilic PVDF ultrafiltration membrane by storing the membranes in NaOH solution for 12 months, with the permeate flux being monitored over a certain period of time (Vigo et al., 1984). The flux reduction as a consequence of aging was observed to be relatively low in diluted NaOH solution compared to the ones stored in tap water. It is believed that the higher permeate flux may be attributed to the incipient deterioration of the membrane matrix as it is well known that NaOH chemically attacks PVDF. Nevertheless, these studies have been mainly focusing on the effect of long-term exposure of NaOH to PVDF membranes. To our knowledge, there have been no systematic studies that have reported on the short-term effect of NaOH solution on PVDF membranes, which is analogous to chemical cleaning processes of PVDF membranes. Besides, previous investigations have employed only one type of PVDF materials, whilst quite a number of PVDF materials have been produced by manufacturers. Moreover, up to now, the changes in mechanical strength of PVDF membranes caused by the caustic environment have not been mentioned elsewhere.

In this article, we will first report a systematic investigation on the effect of sodium hydroxide solutions with different concentrations on the stability of PVDF hollow fibre membranes. In general, the hollow fibre configuration is preferred over the flat sheet owing to its high surface area per unit volume, which is one of the crucial aspects in industrial membrane productions. The hollow fibre modules can be easily scaled up and provide easy maintenance through the use of industrial membrane productions. The hollow fibre modules can be used as membrane materials. The details of these materials are listed in Table 1. 1-methyl-2-pyrrolidone (NMP) was purchased from Rathburn Chemicals Ltd., UK. NaOH was purchased from VWR International for PVDF hollow fibre treatment.

### 2. Preparation of hollow fibre membranes and NaOH treatment

PVDF hollow fibre membranes were prepared and spun from different types of PVDF materials via a dry-jet wet spinning method. In this experiment, three different types of commercial PVDF materials labelled as Kynar 761, Solef 1015 and Solef 6010 were selected and investigated for comparison. The detailed preparation and spinning conditions are also tabulated in Table 1. In this experiment, small amount of lithium chloride (LiCl) was used as an additive in the spinning solution to aid the spinning process of PVDF membranes. Tap water was used as the external coagulant, while deionised water was used as the bore fluid medium throughout the spinning process. The spinneret with an inner diameter/orifice diameter of 0.72/2.0 mm was used. The temperature and relative humidity of spinning environment were 20 ± 2 °C and 65–70%, respectively. The fresh hollow fibres emerged from the tips of the spinneret were guided through two water baths at a take-up velocity (Meliflow Ltd, Excal) carefully adjusted to match the free-falling velocity. After spinning, the hollow fibre membranes were rinsed and stored in DI water for 3 days prior to the treatment with NaOH solution. Following that, the chemical stability of PVDF hollow fibre membranes were examined by using NaOH solutions with different concentrations: 1, 4 and 10 wt%. The aforementioned treatment was conducted at both sides of the hollow fibres at room temperature (20 °C) and in temperature controlled oven at 70 °C with different durations: 1, 4, 8 and 24 h. After the treatment, hollow fibre membranes were thoroughly rinsed with water to remove any residual NaOH in the membrane. Hollow fibres were pre-treated in ethanol solution for 1 h prior to membrane characterisations.

### 2.3. Raw materials and membrane characterisation techniques

The morphology of the surface and cross-section of the PVDF membranes prepared were examined by the Scanning Electron Microscope (SEM; JSM-5610LV, JEOL, Tokyo, Japan). The membranes were immersed in ethanol for 10 min, followed by liquid nitrogen for about 5–10 min. Subsequently, the membrane samples were fractured, and then flexed into a short sample with tweezers in order to maintain the original cross-sectional fracture of the membranes. These membrane samples were positioned on a metal holder, then sputter coated with gold under vacuum for 3 min. The micrographs of the surface and cross-section of the membranes were taken at various magnifications.

Tensile strength and elongation at break of the prepared hollow fibre membranes were measured by Instron 4466 tensile test machine.

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### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular weight (Dalton)</th>
<th>Density (g/mL)</th>
<th>Water absorption</th>
<th>Form</th>
<th>Supplier</th>
<th>Spinning dope</th>
<th>Spinning conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PVDF (wt%)</td>
<td>NMP (wt%)</td>
</tr>
<tr>
<td>Kynar 761</td>
<td>440,000</td>
<td>1.77–1.79</td>
<td>0.01–0.03</td>
<td>Fine powder</td>
<td>Atofina Chemicals Inc.</td>
<td>18</td>
<td>81</td>
</tr>
<tr>
<td>Solef 1015</td>
<td>573,000</td>
<td>1.78</td>
<td>&lt; 0.04</td>
<td>Granular powder</td>
<td>Solvay</td>
<td>18</td>
<td>81</td>
</tr>
<tr>
<td>Solef 6010</td>
<td>322,000</td>
<td>1.78</td>
<td>&lt; 0.04</td>
<td>Granular powder</td>
<td>Solvay</td>
<td>18</td>
<td>81</td>
</tr>
</tbody>
</table>
with a load cell of 1 kN, at a constant elongation velocity of 5 mm/min at room temperature (20°C). At least five sample fibres with 50 mm length were tested and the average data was taken from each sample. The deviation between the sample values and the average value is less than 5%.

Surface Area & Porosity Analyser TriStar 3000 (Micromeritics, UK) was used for the measurements of specific surface area of PVDF raw materials and hollow fibre membranes with Brunauer, Emmet and Teller (BET) adsorption method using nitrogen at 77.35 K. XRD-XPert PRO (PANalytical, The Netherlands) was used to determine the crystalline phases of PVDF hollow fibre membranes. PVDF hollow fibres were positioned on a sample holder loaded on the diffractometer, using CuKα radiation, with the generator working at 40 kV and 40 mA. The scanning range covers 10 < 2θ < 70 with a scanning step of 0.02°. The structure of PVDF raw materials and membranes, as well as structural changes due to NaOH treatment were analysed by using a Fourier Transform Infra-Red (FTIR) spectrometer (Perkin Elmer, Spectrum One equipped with an attenuated total reflection (ATR) attachment). The samples were placed on the sample holder and all spectra were recorded in the wavenumber range of 4000–600 cm⁻¹ by accumulating 8 scans at a resolution of 2 cm⁻¹. A differential scanning calorimeter (DSC Q2000, TA Instrument, UK) was used to obtained thermograms at a heating rate of 10°C/min for all the specimens, using the 0.5 mg samples. The melting point depression was also measured at a heating rate of 10°C/min.

3. Results and discussion

3.1. Morphology of PVDF hollow fibre membranes

The morphology and structure of the prepared PVDF hollow fibre membranes were examined using SEM analysis. Since the same spinning conditions were employed for all the three membrane

Fig. 1. SEM images of PVDF hollow fibre membrane: (a) overall cross-section, (b) partial cross-section, (c) outer surface (magnification of 1500 ×) (d) outer surface (magnification of 5000 ×) and (e) outer surface (magnification of 5000 ×: after treatment).
materials, similar structures were observed for all of them, hence only SEM images from one hollow fibre membrane were presented. Fig. 1(a) and (b) shows the SEM images of the overall and the partial cross-section, while Fig. 1(c) shows the image of the outer surface of Kynar 761 hollow fibre membrane. A typical asymmetric structure of hollow fibre was observed, which comprised of long finger-like voids near the inner surface accompanied by relatively shorter finger-like voids near the outer surface, with sponge-like structure sandwiched between them. The formation of the aforementioned fibre structure is attributed to the mechanism of the membrane coagulation process. During dry/wet spinning process, the inner layer of hollow fibres is initially in contact with water in comparison to that of the outer layer. In this study, a small amount of hydrophilic additive has been added into the spinning solution for the purpose of facilitating the spinning process of PVDF hollow fibres. The addition of additive could have promoted the water diffusion near the lumen side of the membrane, where rapid precipitation occurred and long finger-like structure was formed near the inner layer. On the other hand, the outer layer of the membrane experienced a relaxation of the polymer solution in the air gap region thus resulting in the relatively shorter finger-like structure. The membrane outer surface is a bit rough but no big defects are observed. It is worth mentioning that the crack formation observed in the membrane cross-section was occurred during the fracturing membrane sample in liquid nitrogen for SEM analysis. For the purpose of comparison, the SEM images of the membrane outer surface before and after treatment are demonstrated in Fig. 1(d) and (e) at a higher magnification of 5000 ×. Overall, it could be observed that there were no significant changes in the membrane outer surface after the NaOH treatment.

3.2. Mechanical stability

The mechanical properties of PVDF hollow fibre membranes prepared from different PVDF materials have been studied by the tensile strength and elongation at break measurements. Table 2 lists the tensile strength, elongation at break and Young’s modulus of PVDF hollow fibre membranes spun from Kynar 761, Solef 1015 and Solef 6010. It can be seen from Table 2 that the tensile strength of hollow fibre membranes prepared from different PVDF materials falls in the moderate range between 1.03 and 1.44 MPa, while the elongation at break values are between 84% and 183%. Among all, Solef 6010 exhibited the highest Young’s modulus of 57.82 MPa.

Table 2

Surface properties of raw materials and its membranes, and mechanical strength of PVDF hollow fibre membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Inner diameter (ID, mm)</th>
<th>Outer diameter (OD, mm)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s modulus (MPa)</th>
<th>BET measurement</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Surface area of</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>raw material (m²/g)</td>
</tr>
<tr>
<td>Kynar 761</td>
<td>1.05</td>
<td>1.55</td>
<td>1.03</td>
<td>174</td>
<td>24.89</td>
<td>10.42</td>
</tr>
<tr>
<td>Solef 1015</td>
<td>0.90</td>
<td>1.40</td>
<td>1.05</td>
<td>84</td>
<td>20.73</td>
<td>29.93</td>
</tr>
<tr>
<td>Solef 6010</td>
<td>1.20</td>
<td>1.80</td>
<td>1.44</td>
<td>183</td>
<td>57.82</td>
<td>12.51</td>
</tr>
</tbody>
</table>

In general, the mechanical properties depend on the polymer properties as well as the structure of the resultant hollow fibre membranes. Although the molecular weight of Solef 6010 raw material is the lowest among all, its corresponding hollow fibre membrane showed the highest tensile strength. This could be due to the fact that the Solef 6010 hollow fibre membrane exhibited the highest Young’s modulus, which corresponds to the material’s stiffness, and the highest degree of crystallinity compared to that of Kynar 761 and Solef 1015 hollow fibres, as shown in Table 3 (Section 3.6).

A series of experiments in regards to the stability of PVDF hollow fibre membranes against NaOH solutions have been conducted by immersing the membranes into NaOH solutions. The effects of NaOH concentration, treatment time and temperature on the mechanical properties of the membranes were investigated by measuring the changes of tensile strength and elongation at break under different treatment conditions. As broken fibre can be considered as the major cause of failure in membrane modules and operation of membrane system, the flexibility of hollow fibre membranes plays an important role in determining the extent of mechanical strength. Therefore, discussions on the mechanical properties will be made and focused solely on the elongation at break of the prepared hollow fibre membranes. The elongation values employed herein are normalised, by dividing the elongation of the hollow fibre membrane after NaOH treatment with the elongation of hollow fibre membrane before NaOH treatment. Fig. 2(a–c) illustrates the changes of the nominal elongation of PVDF membranes with different degrees of NaOH concentrations (1, 4 and 10 wt%) and treatment conditions.

Overall, the elongation of hollow fibre membranes prepared from different type of PVDF materials was observed to be instantly reduced by the treatment with NaOH solutions. Fig. 2(a: top) demonstrates the elongation changes of Kynar 761 hollow fibres using different concentrations of the NaOH solution at room temperature with different treatment times. While the reductions of elongation resulted from 1 and 4 wt% NaOH treatments are observed to be moderate, the effect of NaOH treatment at higher concentration of 10 wt% demonstrated a drastic reduction in the elongation of the hollow fibres. For instance, the elongations of the membranes were reduced to 75% for 1 wt% solution and 70% for 4 wt% solution in 1 h, and continued to decrease with further treatment time. After 24 h of treatment using 1 and 4 wt% NaOH solutions, the elongations of the hollow fibres were reduced to 40% and 30%, respectively. On the other hand, the hollow fibre membrane

Table 3

Melting temperature, melting enthalpy and degree of crystallinity of PVDF raw materials and untreated hollow fibre membranes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Kynar 761 Powder</th>
<th>Kynar 761 Hollow fibre</th>
<th>Solef 1015 Powder</th>
<th>Solef 1015 Hollow fibre</th>
<th>Solef 6010 Powder</th>
<th>Solef 6010 Hollow fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature, (T_m) (°C)</td>
<td>165.2</td>
<td>166.1</td>
<td>170.8</td>
<td>170.9</td>
<td>171.9</td>
<td>172.8</td>
</tr>
<tr>
<td>Melting enthalpy, (\Delta H_m) (J/g)</td>
<td>41.8</td>
<td>64.2</td>
<td>47.4</td>
<td>64.1</td>
<td>51.2</td>
<td>67.2</td>
</tr>
<tr>
<td>Degree of crystallinity, (\Delta X_c) (%)</td>
<td>40.0</td>
<td>61.4</td>
<td>45.4</td>
<td>59.2</td>
<td>49.0</td>
<td>64.3</td>
</tr>
</tbody>
</table>
treated with 10 wt% NaOH exhibits a sharp reduction in elongation to approximately 30% within 1 h treatment, and eventually lost its mechanical integrity after 8 h of treatment.

Fig. 2(a; bottom) shows the elongation changes of Kynar 761 hollow fibres with different NaOH concentrations and time at a higher temperature of 70 °C. It was observed that the hollow fibres could hardly withstand hot NaOH solutions, even at a lower concentration of NaOH solution. Membrane elongation declined sharply to 20% in 1 wt% NaOH solution in just 1 h at 70 °C, and the membrane became very fragile in 10 wt% NaOH solution. Once the membranes were immersed into any of NaOH solutions for more than 8 h at 70 °C, they became very fragile to allow the measurement of the elongation to be performed.

![Graphs showing elongation changes](image)

**Fig. 2.** Effect of NaOH treatment on nominal elongation of PVDF hollow fibre membranes made from (a) Kynar 761, (b) Solef 1015 and (c) Solef 6010 at room temperature (20 °C) and higher temperature (70 °C).

![Graphs showing XRD diffractograms](image)

**Fig. 3.** XRD diffractograms of PVDF (a) raw materials, and hollow fibre membranes prepared from: (b) Kynar 761, (c) Solef 1015 and (d) Solef 6010; (i) untreated membrane (ii) 10 wt% NaOH treated membrane at 20 °C and (iii) 10 wt% NaOH treated membrane at 70 °C.
An almost similar trend was observed on the elongation changes of hollow fibre membranes made of Solef 1015 at relatively lower NaOH concentrations. However, Solef 1015 showed a much smaller reduction in elongation in comparison with Kynar 761 under the same treatment conditions. Fig. 2(b) illustrates the nominal elongation of hollow fibre membranes treated with NaOH solution at room temperature and 70 °C. Referring to Fig. 2(b; top), the elongations of Solef 1015 hollow fibre membranes decreased to 80% and 65% after treatment with 1 and 4 wt% NaOH solutions, while the elongation of membrane treated with 10 wt% NaOH solution reduced to 26% after 24 h treatment at room temperature. This indicates that Solef 1015 hollow fibre membrane showed a higher ability to retain its elongation properties after being treated with NaOH, compared to Kynar 761 hollow fibre membrane. When the NaOH solution is heated to 70 °C, membrane elongation could be retained at 54% for 1 wt% solution and 27% for 4 wt% solution. The elongation of Solef 1015 hollow fibre was still measurable for treatment with high NaOH concentration of 10 wt% after 8 h, while the elongation of Kynar 761 hollow fibre has already dropped down to zero within 1 h under the same treatment condition, which further supports the fact that Solef 1015 showed a better stability against NaOH solution in comparison to Kynar 761.

Fig. 2(c) shows the nominal elongation of PVDF hollow fibre membrane made of Solef 6010 with a lower molecular weight compared to Solef 1015. With reference to Fig. 2(c; top), it was observed that the trend of elongation changes of Solef 6010 hollow fibre was almost similar to that of Solef 1015 at a lower NaOH concentration of 1 and 4 wt% solutions at room temperature. In fact, the retained elongation of Solef 6010 hollow fibre membrane is observed to be higher than the Solef 1015 and Kynar 761 at these lower concentrations of NaOH. This could be due to the higher degree of crystallinity exhibited by the Solef 6010 membrane compared to others, as illustrated in Table 3 (Section 3.6). However, when the NaOH concentration is increased to 10 wt%, the elongation of Solef 6010 hollow fibre membrane is dramatically reduced within 8 h treatment and levelled off with further treatment time. Compared to Solef 1015 hollow fibre, Solef 6010 hollow fibre may be less stable in more concentrated NaOH solution since the retained elongation after 24 h treatment in 10 wt% NaOH solution was much smaller than that of Solef 1015. This could be due to the fact that Solef 6010 material has a lower molecular weight and shorter polymer chains. Solef 6010 hollow fibre became very fragile when subjected to the treatment of hot NaOH solution at 70 °C, and it completely lost its mechanical integrity in both 4 and 10 wt% solutions, which is similar to that of Kynar 761 hollow fibre membrane; however, the former shows a slightly better stability in hot NaOH solution at a lower concentration of 1 wt%.

It is believed that the reduction in the membrane’s mechanical strength after the NaOH treatment could be due to the degradation of polymer as a result of the chemical reaction between PVDF and NaOH. The NaOH had chemically attacked PVDF membrane and caused the dehydroflourination in the polymer chain, where this phenomenon is further discussed in Section 3.5.

### 3.3. Surface area of PVDF raw materials and hollow fibre membranes

Chemical reaction usually takes place on the interface of the contacting objects. The reaction kinetics depends highly on the specific surface area of the material. The surface areas of both PVDF raw materials and hollow fibres were measured in order to investigate the relationship between the surface area and the stability of PVDF hollow fibre membranes. It is worth mentioning that the colour of the fabricated PVDF membranes changed from white to brown upon immersion into the NaOH solution, which generally indicates that chemical reactions happened between the membranes and the NaOH solution.

The specific surface area results of the three PVDF raw materials and their hollow fibre membranes obtained by the BET method are listed in Table 2. Among all the three raw materials, Solef 1015 possesses the largest surface area of 29.93 m²/g, while the surface area of Solef 6010 with 12.51 m²/g is slightly bigger than that of Kynar 761 (10.42 m²/g). However, the specific surface area of the raw materials is significantly changed after the formation of the hollow fibre membranes from the corresponding materials. Although the preparation conditions of the hollow fibres were almost identical, significant changes on the surface area were observed. As can be seen from Table 2, the surface area of Kynar 761 hollow fibre membrane is dramatically increased to 90.17 m²/g, while the surface area of Solef 6010 is increased to 35.91 m²/g. Only Solef 1015 hollow fibre membrane showed a decrease in surface area compared to its raw material. The obtained results may give an explanation of why the loss of mechanical strength of the Kynar 761 hollow fibre membrane was much quicker than the other two. The changes of Kynar 761 surface area were mainly due to the processing of raw material to the form of hollow fibre membrane during spinning and phase inversion process. It is of interest to further study the changes in the surface area of different raw materials caused by membrane fabrication; for instance, by determining the extent of homogeneity of membrane solution containing different PVDF materials.
3.4. XRD analysis

XRD analysis has been performed to examine the crystal structures and structural changes of PVDF after hollow fibre membranes formation and the effects of NaOH treatment on the membranes. Fig. 3(a) shows the XRD diffractogram of PVDF raw materials Kynar 761, Solef 1015 and Solef 6010. The spectra of all three materials are similar, with several strong diffraction peaks at 2θ = 17.9°, 18.4°, 19.9° and 26.5°. Each peak represents the reflection of a crystal structure with the majority of the peaks from α-phase (Gregorio and Ueno, 1999; Gregorio, 2006), suggesting that all the three PVDF raw materials exhibit α-phase crystals structure. The only difference between Kynar and Solef materials is that those major peaks of both Solef materials are relatively narrower than that of Kynar 761, indicating that the crystal size of both Solef materials may be bigger, more orientated or highly crystalline.

Fig. 3(b)–(d) illustrates the XRD diffractograms of the PVDF hollow fibre membranes made of Kynar 761, Solef 1015 and Solef 6010. It can be seen from the spectra that the previously observed diffraction peaks from the raw materials have all disappeared and have been replaced by a new strong diffraction peak at 2θ = 20.95°. On the basis of crystallographic data in the literature (Wang et al., 2009; Gregorio, 2006), the peak at 20.95° is attributed to the β-phase. Hence, this may suggest that most of the crystal phase in PVDF raw materials has been changed to β-phase during hollow fibre spinning, whereby the β-phase crystal structure becomes dominant with some transitions or mixtures of α and β phases.

Similar β-phase formation in the preparation of PVDF membranes via phase inversion method could be observed using XRD and FTIR in other studies (Lin et al., 2006; Buonomenna et al., 2007). On the other hand, no significant changes were detected by the XRD analysis on the crystal structure of PVDF hollow fibre membranes after NaOH treatment. Therefore, in this section only the spectra from the membranes treated under extreme conditions, for example, in a 10% NaOH solution for 24 h, which are also presented in Fig. 3(b)–(d). It can be seen that the spectra of both treated and untreated hollow fibre membranes were almost identical, although the treated hollow fibre membrane had totally lost their mechanical integrity. This indicates that XRD may not be sensitive to the changes in the crystalline structure caused by NaOH treatments, and it is also less effective in identifying the stability of PVDF hollow fibre membranes in such environment.

3.5. FTIR spectroscopy

Based on the XRD analysis as discussed above, the α-phase of the crystal structure of PVDF raw materials has been transformed into β-phase during hollow fibre formation. In this study, FTIR analysis has been performed for the determination of the crystal structure of both PVDF raw materials and hollow fibre membranes, as well as to investigate the effect of NaOH treatment on the PVDF hollow fibre membranes in terms of structural changes in chemical groups. From FTIR spectra, a number of major characteristic bands were observed in the range of 650 and 1850 cm⁻¹, which these peaks were believed
to be attributable to different crystalline structures and phases. It is worth mentioning that several other typical characteristic bands that fall within the range 400 and 600 cm$^{-1}$ were not detected due to the limitations of the equipment used in this experiment.

FTIR spectra of PVDF raw materials and hollow fibre membranes are illustrated in Fig. 4(a) and (b). As can be seen from Fig. 4(a), characteristic bands appeared at 765, 796, 859, 874, 976, 1070, 1148, 1180, 1206, 1383 and 1423 cm$^{-1}$, which were similar to the bands observed for PVDF film containing mainly $\alpha$-phase, while several other peaks were observed at 840, 1275 and 1404 cm$^{-1}$ could be attributed to $\beta$-phase (Gregorio, 2006; Bachmann, 1979; Boccaccio et al., 2002). Small differences were observed between Kynar 761 and Solef PVDF materials, where the intensity of the characteristic bands at 840 and 1404 cm$^{-1}$ of Kynar 761 spectrum were observed to be relatively stronger than that of both Solef materials. On the other hand, Solef materials exhibited stronger characteristic bands at 1148, 1206 and 1383 cm$^{-1}$ attributable to $\alpha$-phase. Several other weak bands are observed at 677, 1330 and 1453 cm$^{-1}$, which could be due to the polymer chain defects caused by the head-to-head and tail-to-tail linkages (Kuhn et al., 1987; Lovinger, 1982; Boccaccio et al., 2002).

Fig. 6. DSC curves of PVDF materials and untreated hollow fibre membranes.

![DSC curves of PVDF materials and untreated hollow fibre membranes.](image)

Fig. 7. DSC curves of NaOH untreated and treated PVDF hollow fibre membranes at 20 °C with different treatment times: (a) 1 h and (b) 24 h.
However, the characteristic bands at 796, 976, 859, 1206 and 1383 cm\(^{-1}\) assigned to the \(\alpha\)-phase (as stated above) of PVDF raw materials disappeared after the hollow fibre membranes formation, as illustrated in Fig. 4(b). The characteristic band at 765 cm\(^{-1}\), attributable to \(\alpha\)-phase also became very weak. According to the literatures (Gregorio, 2006; Bachmann, 1979; Boccaccio et al., 2002), the appearance of several stronger or new peaks specifically at 840, 1074, 1172, 1275 and 1432 cm\(^{-1}\) are attributable to \(\beta\)-phase. This indicates that a significant transition has occurred in PVDF materials from \(\alpha\)-phase to the majority of \(\beta\)-phase with a mixture of \(\alpha\) and \(\beta\) phase formations. Furthermore, no significant difference could be observed on the three PVDF hollow fibre membranes from the FTIR spectra. The results from FTIR analysis are further confirmed with the observations from XRD diffractograms as described above.

The changes in the functional groups of PVDF membranes caused by the NaOH treatment are studied by FTIR. Fig. 5(a) and (b) shows the IR spectra of NaOH treated membranes at room temperature (20 °C) and at higher temperature (70 °C). From these figures, both membranes treated at 1 and 24 h exhibited similar IR spectra, though the differences between these membranes could be spotted from a relatively narrower scanning range between 1850 and 1450 cm\(^{-1}\). From Fig. 5(a), a shoulder at around 1595 cm\(^{-1}\) in the spectrum of Kynar 761 membrane was observed, after being treated with the NaOH solution for 24 h. The reaction between NaOH and PVDF Kynar 761 might have occurred during treatment resulting in the formation of carbon–carbon double bond (\(-\text{CF}^-\text{CH}^{\text{3}}\)), caused by the dehydrofluorination on the surface (Kise and Ogata, 1983; Wegener et al., 2006). The shoulder around this peak is not very clear for Solef 1015 and Solef 6010 membranes. However, the shoulder at 1595 cm\(^{-1}\) became stronger and further developed into a peak in the IR spectra of the 10 wt% NaOH treated membranes at a higher temperature of 70 °C as shown in Fig. 5(b), suggesting that more carbon–carbon double bonds have been formed due to the dehydrofluorination caused by the NaOH treatment.

3.6. Thermal analysis using DSC

3.6.1. PVDF raw materials and hollow fibre membranes

Further investigation on the stability of PVDF in NaOH has been carried out by measuring the melting temperature and melting enthalpy using DSC. Fig. 6 illustrates the thermograms of both PVDF raw materials and hollow fibre membranes. Based on the DSC thermograms, the values of the melting temperature (\(T_m\)) and the melting enthalpy (\(\Delta H_f\)) were obtained and are tabulated in Table 3.
It can be seen from Table 3 that the hollow fibre membranes show a slightly higher melting temperature and significantly higher melting enthalpy compared to that of the raw materials. This indicates that more crystals have been formed during the spinning of hollow fibres, where the major crystal structure has been verified by the XRD and FTIR analysis as the β-phase. In comparing the raw materials, the melting temperature and melting enthalpy of Kynar 761 were relatively lower than those of Solef materials, possibly because of the differences in crystal size, crystalline organisation, or population of the α and β crystals. This is consistent with the XRD analysis results discussed in the previous section. Significant difference also could be observed on the melting temperatures among the three hollow fibre membranes, for which Kynar 761 remained the lowest. However, the melting enthalpies among all membranes were observed to be more or less the same.

The degree of crystallinity, \( \Delta X_C \), was measured as the ratio between \( \Delta H_f \) and \( \Delta H_{100} \), where \( \Delta H_{100} \) is the melting enthalpy of totally crystalline PVDF material (\( \Delta H_{100} = 104.5 \) J/g for α-phase and \( \Delta H_{100} = 103.4 \) J/g for β-phase (Lanceros-Mendez et al., 2001; Nakagawa and Ishida, 1973)) by using the equation as below:

\[
\Delta X_C = \frac{\Delta H_f}{\Delta H_{100}} \times 100
\]

The obtained degree of crystallinity of PVDF raw materials and hollow fibre membranes are also tabulated in Table 3. It can be seen that the degree of crystallinity significantly increased after the hollow fibre membrane formation. Solef 6010 shows the highest degree of crystallinity among all, which could be due to its small molecular weight and the ease of crystallisation.

### 3.6.2. Effect of NaOH treatment on PVDF hollow fibre membranes

The effect of NaOH treatment on the thermal properties of PVDF hollow fibre membranes has been further investigated using DSC. Figs. 7 and 8 demonstrate the changes of melting peak of PVDF hollow fibre membranes immersed in different concentrations of NaOH solution at 20 °C and at 70 °C, respectively. Based on the calculations, the melting temperatures, melting enthalpies and the degree of crystallinity are listed in Table 4.

<table>
<thead>
<tr>
<th>Hollow fibre</th>
<th>Kynar 761</th>
<th>Solef 1015</th>
<th>Solef 6010</th>
</tr>
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<tr>
<td>NaOH treatment time</td>
<td>1 h</td>
<td>24 h</td>
<td>1 h</td>
</tr>
<tr>
<td><strong>Melting temperature (°C)</strong></td>
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<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>165.5</td>
<td>163.1</td>
<td>169.6</td>
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<tr>
<td>10 wt% NaOH</td>
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<td>161.6</td>
<td>169.5</td>
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<tr>
<td>70 °C</td>
<td>158.4</td>
<td>147.9</td>
<td>162.3</td>
</tr>
<tr>
<td>4 wt% NaOH</td>
<td>158.8</td>
<td>153.5</td>
<td>160.5</td>
</tr>
<tr>
<td>10 wt% NaOH</td>
<td>161.1</td>
<td>153.5</td>
<td>164.4</td>
</tr>
<tr>
<td><strong>Melting enthalpy (J/g)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>63.1</td>
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<td>52.1</td>
<td>61.0</td>
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<tr>
<td>70 °C</td>
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<td>26.6</td>
<td>50.15</td>
</tr>
<tr>
<td>4 wt% NaOH</td>
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<td>20.6</td>
<td>40.9</td>
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<tr>
<td>10 wt% NaOH</td>
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<td>50.15</td>
</tr>
<tr>
<td><strong>Degree of crystallinity (%)</strong></td>
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<tr>
<td>10 wt% NaOH</td>
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<tr>
<td>70 °C</td>
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<tr>
<td>10 wt% NaOH</td>
<td>47.5</td>
<td>25.7</td>
<td>48.4</td>
</tr>
</tbody>
</table>

From Fig. 7, it can be observed that the melting peaks of the hollow fibres do not significantly change except that they shift towards a relatively lower temperature with the increase of NaOH concentration or treatment time. A shoulder could be spotted on the DSC curve of the treated Solef 1015 membrane, which can be interpreted as the melting of two crystalline phases that coexists (Nakagawa and Ishida, 1973).

On the other hand, remarkable changes in the melting peaks were observed from the PVDF hollow fibre membranes when the treatment temperature was increased to 70 °C. Fig. 8 demonstrates that the melting peaks had rapidly shifted to the lower temperature and the area of the peak was significantly reduced with the increase of NaOH concentration or treatment time. The melting peaks of PVDF membranes became smaller in 4 wt% NaOH solution and almost disappeared in 10 wt% after 24 h treatment. Such changes in the melting enthalpy demonstrated the reduction in the crystallinity of hollow fibre membranes and suggest that the crystals of the hollow fibre membranes can be easily destroyed by the hot NaOH solution. Similar changes of the melting temperatures and melting enthalpies could be observed on all the three types of membranes that were treated with the hot NaOH solution. Nevertheless, it is noted that Solef 1015 membranes retained a better melting enthalpy in comparison with that of Kynar 761 and Solef 6010 under the strongest treatment condition of 10 wt% NaOH solution at 70 °C for 24 h. While the melting enthalpy of the Solef 1015 treated membrane was 28.4 J/g, the Kynar 761 and Solef 6010 treated membranes exhibited melting enthalpies of 20.6 and 18.0 J/g, respectively, (refer to Table 4). Comparing these melting peaks with the ones before treatment (refer to Table 3), Solef 1015 showed the smallest reduction from the original one (64.2 J/g) among all the three types of membranes. This might help to explain why the Solef 1015 is more stable than Kynar 761 or Solef 6010 especially at higher temperature or in a concentrated NaOH solution, and this finding is consistent with the results of mechanical stability as discussed in the Section 3.2.

Based on the DSC results, it can be concluded that the PVDF hollow fibre membranes had been attacked by the NaOH solution under all tested conditions, which led to a decrease in the melting temperature, melting enthalpy and crystallinity. Furthermore, the decrease was accelerated at a high temperature or in a concentrated NaOH solution. The degree of crystallinity of the PVDF hollow fibre membranes was reduced over the course of the NaOH treatment.

### 4. Conclusions

The stability of PVDF hollow fibre membranes against NaOH solution has been systematically studied. The effect of NaOH concentration, treatment time and temperature on the membrane properties, such as mechanical properties, thermal properties and crystalline structure of three different commercialised PVDF materials namely Kynar 761, Solef 1015 and Solef 6010 were investigated and compared using various analytical techniques. The obtained results show that PVDF hollow fibre membranes were instantly attacked by the NaOH solutions resulting in the decrease of elongation and crystallinity. The decrease was found to be accelerated either by increase in the NaOH concentration or elevating the treatment temperature. All three different types of membranes generally follow similar trends, though the detailed conclusions could be made as follows:

- The mechanical strength of the membranes was further reduced, with an increase in concentration and/or temperature of NaOH solutions. PVDF membranes totally lost their mechanical integrity in very short time under harsh treatment conditions. Membranes made from Kynar 761 showed an inferior stability in NaOH solution than those prepared from Solef, mainly due to the extremely high
specific surface area formed after the Kynar raw material was processed into the hollow fibre membranes.

- According to XRD and FTIR analysis, PVDF raw materials contain mainly α-phase crystals, while the PVDF hollow fibre membranes contain mainly β-phase crystals. It is believed that most of the α-phase crystals have been transformed into the β-phase crystals during hollow fibre spinning.
- From DSC analysis, the melting temperature and melting enthalpy of the PVDF hollow fibre membranes were reduced after NaOH treatment, because of a direct decrease in the crystallinity. The trend of crystallinity changes is consistent with that of the mechanical strength changes, though the changes in mechanical strength may not be only from the crystalline phase but also the amorphous phase or others.

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References


