

HYDROPHOBICITY ENHANCEMENT OF POLY (VINYLIDENE FLUORIDE-*co*-HEXAFLUORO PROPYLENE) FOR MEMBRANE DISTILLATION

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ABSTRACT

Poly (vinylidene fluoride-*co*-hexafluoropropylene), (PVdF-*co*-HFP) hollow fibre membrane was prepared by phase inversion method using different concentrations of PVP as a pore former additives in the dope solution. Surface modification was done using a formic acid through immersion technique. It was observed that the contact angle for all membranes increased due to the surfaces modification (10% of hydrophobicity increment). Based on SEM and FTIR analysis the study found that the hydrophobicity of (PVdF-*co*-HFP) hollow fibre membrane can be enhanced via formic acid surface modification process.

Keywords: contact angle; membrane distillation; PVdF-*co*-HFP membrane; surface modification;

INTRODUCTION

Having clean drinking water is a major problem for developing countries all over the world. Improvement in the efficiency and cost of water treatment is a great challenge to overcome the shortage of drinking water. Various membrane separation methods have been used for water purification, including micro filtration (MF), ultrafiltration (UF), nano-filtration (NF), reverse osmosis (RO) and membrane distillation (MD). UF and MF are sophisticated techniques used for water handling, whereas RO is widely used for sea water desalination and purification. MD is a new advanced technology and it has high possibilities for the desalination of high salinity water. The membranes play a major role in water treatment processes based on membranes and they determine the technological and economic efficiency of the technologies mentioned above; in fact, improving the membrane can significantly leave an impact on the performance of the existing technology [1,2]. MD is a separation process that is driven thermally which enables separation due to phase alteration. Hydrophobic membrane shows an impediment to the liquid phase, allowing the vapour phase (such as water vapour) to pass through pores of the membrane.

However, disadvantages associated with the MD process are the fluxes are lower than in other membrane processes for industrial applications. It is because the material of MD production is so sensitive to the surface tension and undesirable wetting of the membrane pores [3,4].

Formic acid is the simplest carboxylic acid, is an organic compound that contains a carboxyl group (COOH), a polar organic solvent. It consists of hydrogen-bonded dimers rather than individual molecules. The modification using formic acid is a very hassle-free method to eliminate fluorine (F) atom. A carboxylic acid is an organic compound that contains a carboxyl group, where the carboxylic acids are polar by nature. As both hydrogen-bond acceptors (the carbonyl -C=O) and hydrogen-bond donors (the hydroxyl -OH), they also take part in hydrogen bonding, alongside the hydroxyl and carbonyl group that forms the carboxyl functional group. The surface hydrophobicity modification on the PVdF-*co*-HFP thus makes the hollow fibre membrane is feasible as it is treated with formic acid, which can impart the hydroxyl groups onto the membrane surface. The hydroxyl and carbonyl in the form of carboxyl functional group are formed on the polymer chain. The possible reaction of formic acid onto the PVdF-*co*-HFP membrane surface is shown in **Fig. 1**.

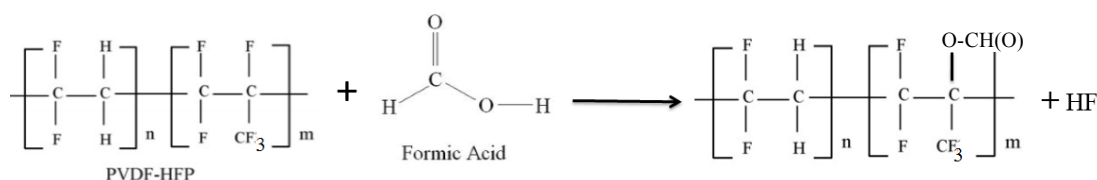


Fig. 1 Reaction of PVdF-*co*-HFP membrane with formic acid

Many of previous researches in this field have pointed out that the polymeric additives are appropriate and miscible with the base material, which indicates that these materials may be advantageous in various applications. It can form some highly hydrophilic membranes with highly effective resistance to protein adsorption using several functional groups, such as sulfonated, and carboxylated groups, and this is due to the creation of highly hydrophilic membranes. By using some of the inorganic materials it could lead to improving the flow within the membrane, and produce membranes with anti-fouling properties. Moreover, the mechanical properties are generating new functional membranes for defined applications. The flux strength can be achieved by improving the features of the modified membranes, hydrophilicity, roughness, structure, membrane thickness and attributes of the surface. Improvement of the membrane permeability, the structural attributes and the surface properties can be guaranteed by the additive modifications [5]. In this research, a simple and sustain method of surface modification was studied to enhance the hydrophobicity of membrane which is very important in membrane distillation application.

EXPEREMENTAL

Materials

PVdF-*co*-HFP hollow fibre membranes were fabricated in our lab. Poly(vinyl pyrrolidone) (PVP) purchased from Sigma-Aldrich Co. Germany was used as a pore forming additives ranged from 0 to 9 wt.%. Formic acid (HCOOH, 46.03 g/mole) was purchased from R&M Chemicals UK.

Membrane Preparation

The spinning condition of the membrane is as listed in **Table 1**; PVdF-*co*-HFP and PVP were dried in a vacuum oven (Model 282A, Thermo Fisher Scientific Inc.) at 50 °C. PVP was first dissolved in dimethylacetamide (DMAC) in a glass flask. PVdF-*co*-HFP was then added to the mixture at 50 °C. The dope solution was kept under magnetic stirring until a homogeneous dope was obtained. The homogeneous dope solution was transferred to a vertical stainless steel reservoir.

Membrane Surface Modification

To modify a new hydrophobic membrane, a method has been carried out via immersing the membrane samples in (0.5 N, 95.0 %w/w) formic acid for five to seven hours. After that the samples were washed with distilled water and then completely dried.

Table 1 Spinning condition of the PVdF-*co*-HFP hollow fibre membranes

Parameter	Operating conditions
Spinneret dimension	o.d. =2.0 mm, i.d. = 1.0 mm
Dope solution pressure (bar)	1
External coagulation temperature (°C)	45
Internal coagulation temperature (°C)	40
Bore flow rate (mL/min)	4
Air gap (cm)	6
Take-up speed	Free falling velocity
Ambient temperature (°C)	25
Room humidity (%)	77%
Coagulation composition	Tap water

Contact Angle Measurement

Contact angles of outer surfaces were measured through the surface tension effects on the membrane as shown in **Fig. 2**. While measuring, a copper wire was inserted through the lumen side, where part of the fibre was soaked in water, and silicon sealant was found helpful to seal the submerged end of hollow fibre and fix the end of copper wire on the lumen side wall, so that water could not get into the fibre lumen.

Following the surface tension effect, the mass weighed by an accurate balance will decrease. Contact angle of the PVdF-*co*-HFP hollow fibre can be calculated by equations (1), (2) and (3) [6,7]:

$$\Delta m = F \cos \frac{\theta}{g} \quad (1)$$

$$\theta = \frac{1}{\cos} \left(\frac{\Delta m}{F} \right) \quad (2)$$

$$F = \pi \gamma \cdot D_o \quad (3)$$

where: Δm (kg) is a mass difference, F (N) is the force from surface tension, θ ($^\circ$) is the contact angle between the solution and the membrane surface which depends on the hydrophobicity of the membrane, γ (N/m) is the surface tension of the solution, D_o (m) is the membrane outer diameter, g (m/s^2) is the acceleration due to gravity.

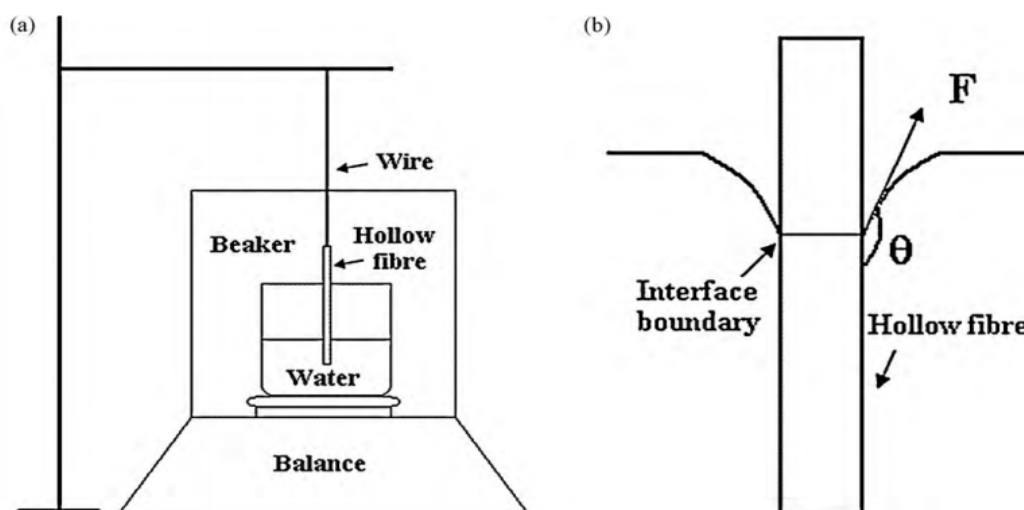


Fig. 2 Contact angle measurement for outer surface. (a) Measurement schematic for outer surface. (b) Force balance at interface boundary

However, the mass value shown on the balance decreased continuously throughout the measurement period, because the instrument is an open system and water evaporated. Hence, it was difficult to determine the mass reduction caused directly by the surface tension, and it is necessary to know the evaporation rate of the water. During the measurement, the recorded temperature in the laboratory only varied in the ranged of $20 \pm 1^\circ\text{C}$, therefore it is reasonable to assume the water evaporation rate was constant.

RESULTS AND DISCUSSION

The morphology of the prepared PVdF-co-HFP hollow fibres was studied by observing the effect of different concentrations of PVP in the polymeric dope solution. Membrane characteristics and features can be modified by adding the additives into polymer dope solutions, PVP is commonly used as a pore former in the membrane fabrication.

Fig. 3 illustrates the morphology of the PVdF-co-HFP hollow fibre membranes. Finger-like pores and cavities have provided the most cross-section of the fibre with PVP as an additive, while a sponge-like structure take a considerable part of the cross section without PVP in the dope solution.

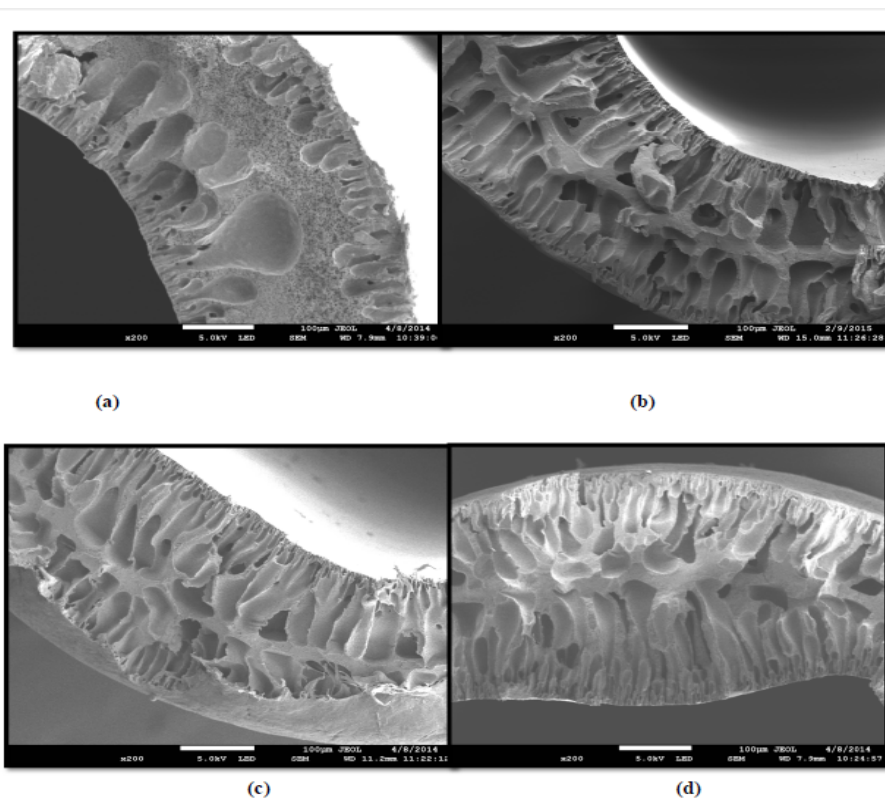


Fig. 3 FESEM images of PVDF-HFP hollow fibre membranes prepared with: (a): 0% PVP, (b): 5% PVP, (c):7% PVP, (d):9% PVP

Adding 5 wt. % PVP into the dope, the size of cavities developed from the inner side was much bigger, however, the average size of the cavities decreased with increasing amount of PVP to 9 wt. %.

The hydrophobicity of both the treated and untreated PVdF-*co*-HFP membranes was assessed with the aid of the water contact angle measurement. The mass changes with the time for contact angle measurement prior to the unmodified PVdF-*co*-HFP membrane exhibited in **Fig. 4**. It is discovered that the weight loss has decreased with increasing PVP content in the dope solution. This implies that the contact angle was decreased with increasing PVP content in the blend membrane [8]. It is possible to observe that similarly, the weight losses versus time decreases with the increasing PVP percentage in the dope solution for the modified PVdF-*co*-HFP hollow fibre membrane **Fig. 5**. It is evident that the values of weight losses for all types of hollow fibre membrane were higher than that for membrane prior to the modification process. This is clear from the value of the slope for weight loss of modified membranes have a higher tendency than other unmodified membranes. This sheds light on the fact that the hollow fibre membrane contact angle had increased after the modification process. As has been discussed, it is conclusive that the modification process altered the membrane wettability to the point that it became more hydrophobic.

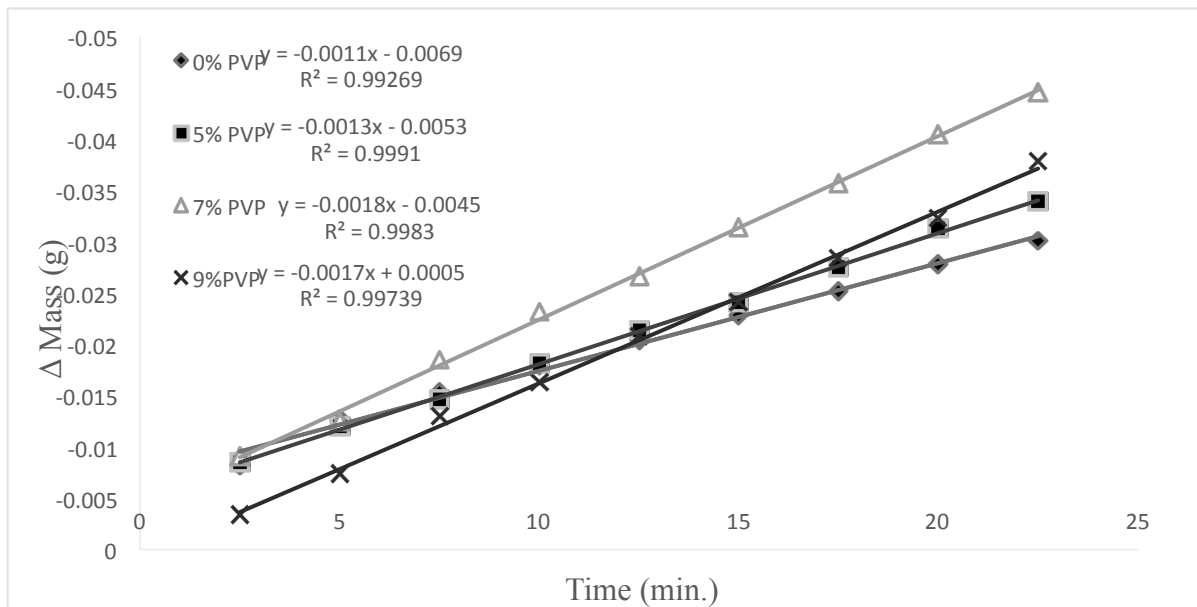


Fig. 4 Mass change against the time in contact angle measurement for unmodified PVdF-co-HFP membrane

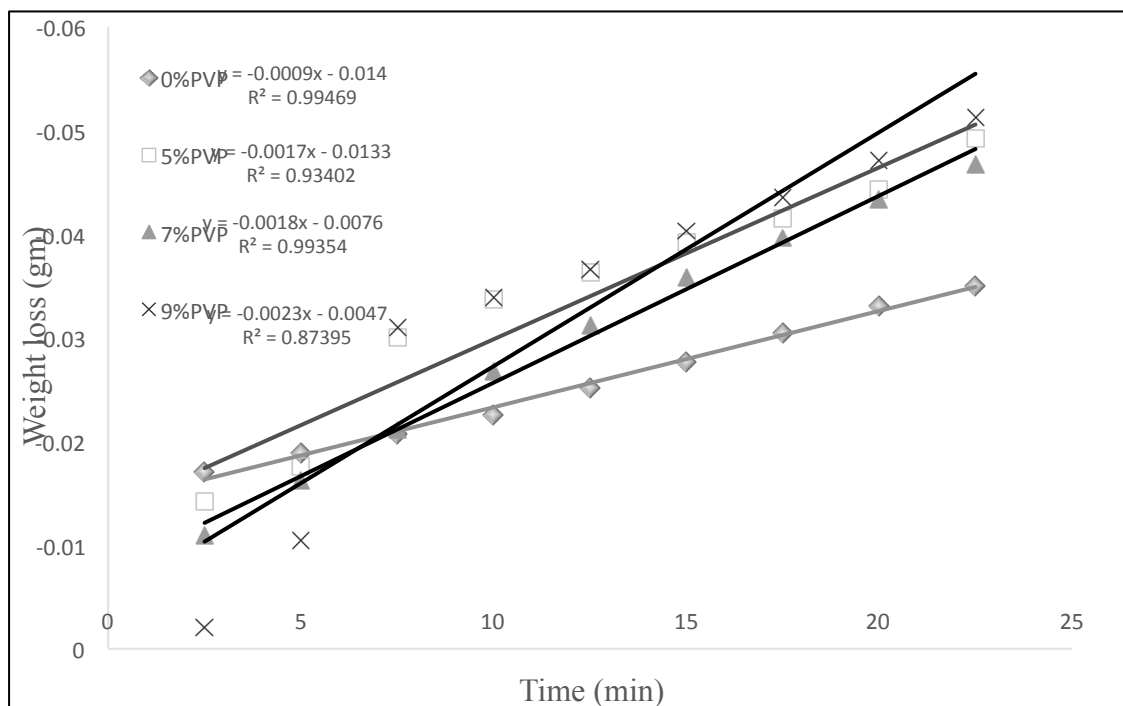


Fig. 5 Mass change against the time in contact angle measurement for modified PVdF-co-HFP hollow fibre membrane

Obviously, the modification process is very efficient when the concentration of the PVP additives were between 0 to 5 % (**Fig. 6**). The presence of PVP in the dope solution for quantities more than 5% will lower the effectiveness of the modification process. This may be due to the dope solution has high concentration of PVP and the solvent/non-solvent exchange can be stalled. This counterbalances the PVP's thermodynamic effect, and the membranes' skin layer became denser with the increase in the amount of PVP added.

This is harmonious with the reports by Chuang et al. [9]. As suggested by Bumsuk et al. [10], the growth of the top layer simply increases as the PVP is added. Nonetheless, the top-layer thickness does not vary at low concentration of PVP. Based on the aforementioned, it can be concluded that the dense top layer gives major resistance to the permeation of formic acid through or on the membrane surface.

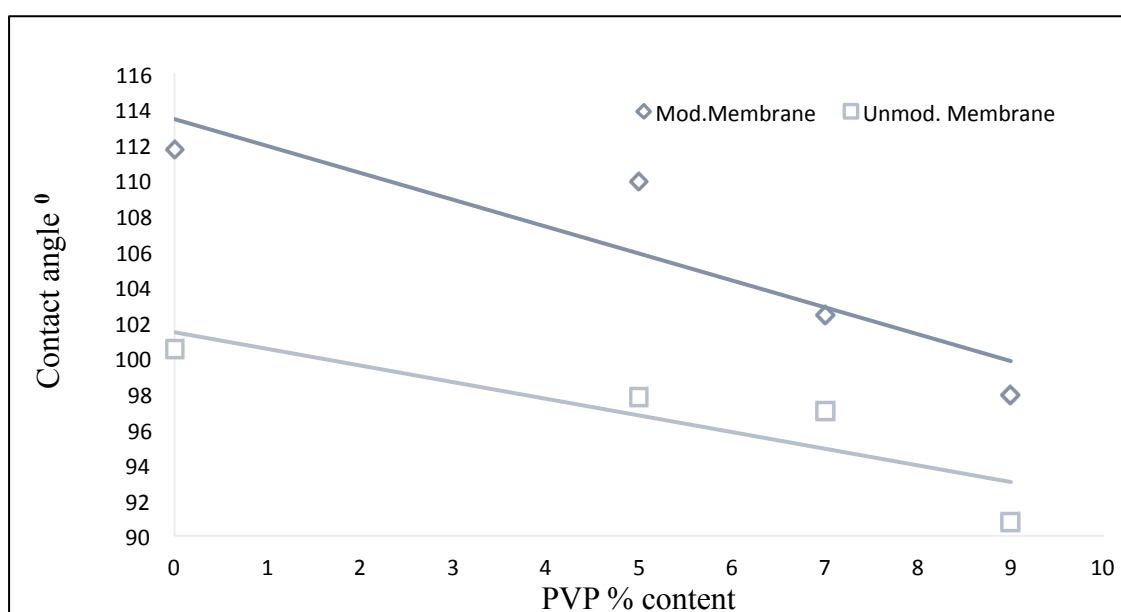


Fig.6 Contact angle for modified and unmodified membranes with different percentage of PVP added

FTIR analysis is a strong technique to determine the type and nature of bonding and the functional groups present in a specimen by observation the levels energy vibration for the molecules, which are especially the fingerprint of various molecules. FTIR analysis was conducted to emphasize the chemical reaction between PVdF-co-HFP and formic acid on membrane surface. As illustrated in **Fig. 7** and **Fig. 8** for modified membrane and unmodified membrane, respectively, both hollow fibres have almost similar infrared absorption bands at the wave number range of 600-1400 cm^{-1} . The resemblance of the infrared spectra on this range indicates that the membranes have the same basic structure. After modification with formic acid, the infrared absorption bands at 1650 cm^{-1} and 1742 cm^{-1} were appeared. These two bands are attributable to the stretching vibrations of C-H or the so called CH stretching and C=O respectively. On the other hand, they were not distinct bands in unmodified PVdF-co-HFP hollow fibre membrane. It is likely to be the appearance of the C=O band is due to the effect of

carboxyl group, which indicates that the reduction modification by formic acid has occurred effectively. In addition it has been found that between 2850 cm^{-1} and 3023 cm^{-1} , a broad peak has been decreased and became clearer after modification process, these peaks are attributable to -OH group for modified PVdF-co-HFP hollow fibre membrane.

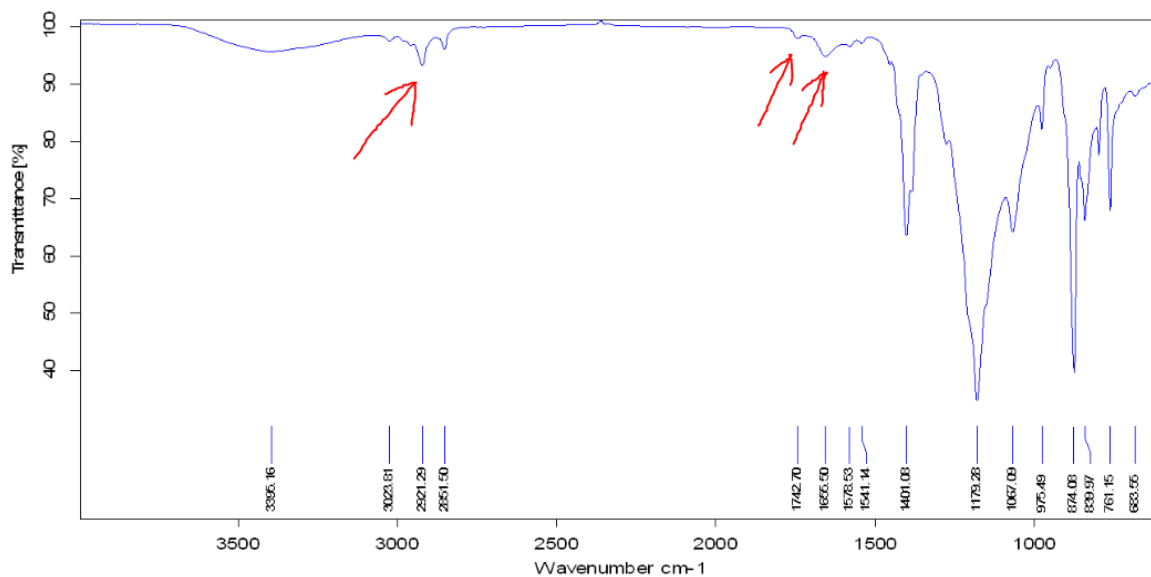


Fig. 7 FTIR spectrum of the modified PVdF-co-HFP hollow fibre membrane

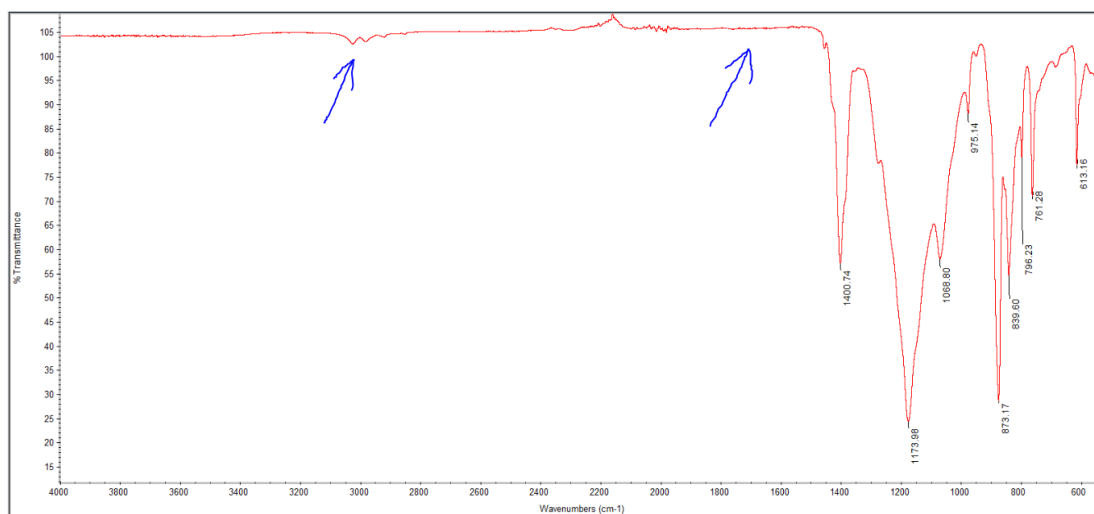


Fig. 8 FTIR spectrum of the unmodified PVdF-co-HFP hollow fibre membrane

CONCLUSION

This study offers a simple and effective way to improve the hydrophobicity of the PVDF-co-HFP hollow fibre membrane using acid formic. The alteration of the membrane hydrophobicity was analyzed in terms of the contact angle. It is also seen in the study that the hydrophobicity represented by contact angle for all modified membranes studied with formic acid was higher than that of the original PVdF-co-HFP hollow fibre. High contact angle (good hydrophobicity) could be obtained via the modification process for the membrane prepared using 0 % & 5 % PVP as additives. The contact angle increased from 100 to 111.7° and 97.8° to 109.9° for PVP content 0 % and 5 % respectively. The results of the present work show that the modification process for PVdF-co-HFP hollow fibre with a formic acid was efficient.

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