

## Thermal Stability of Hollow Fibers in Olefin/Paraffin Distillation

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### Abstract

In this study, hollow fiber membranes, made from polypropylene, polysulfone, polyvinylidene fluoride, and mixed ester, are used as structured packing materials in olefin/paraffin distillation. The stability of these hollow fiber membranes saturated in olefin/paraffin environments was investigated. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted for fresh and treated samples. The swellability of these membranes in different solvents and at different temperatures is discussed.

### Introduction

A unique feature of micro-porous membranes in hollow fiber form is its large surface area within a small volume, normally more than  $3000 \text{ m}^2/\text{m}^3$ <sup>1-3</sup>. This large mass transfer area typically offers 30 times more area than is achievable in conventional gas absorbers<sup>4</sup> and 500 times more than is available in liquid/liquid extraction columns and results in a remarkably low height of a transfer unit (HTU  $\sim 3 \text{ cm}$ )<sup>5</sup>. Specific to the olefin/paraffin distillation, when hollow fibers are used as structured packing materials in a distillation column, the liquid and the vapor flow counter-currently on the opposite sides of hollow fibers. Therefore, the column packed with the hollow fibers can operate above the normal flooding and below the normal loading limits of the conventional packing materials<sup>6, 7</sup>. For the propane/propylene distillation, our previous work demonstrated an increased rate of mass transfer at least 10 times that of conventional trays and structured packing materials<sup>8, 9</sup>.

In this report, as a continuation of the previous work on the olefin/paraffin distillation using hollow fibers<sup>8, 9</sup>, we investigate the thermal stability and swellability of fibers after they have been saturated in light hydrocarbon liquids (e.g. pentane and propane/propylene mixture) for different times. The TGA and DSC results suggest that the polypropylene (PP), polyvinylidene fluoride (PVDF), polysulfone (PS), and mixed ester (ME) are stable materials in the olefin/paraffin environment under 100 °C. The separation efficiency is preserved after several months of exposure.

### Experimental

#### 1. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric data was obtained from a thermogravimetry analyzer (NETZSCH STA 449C and TASC 414/4 controller) performed under dry nitrogen atmosphere (at 30 ml/min flowrate) over a temperature range of 25 – 500 °C at a heating rate of 10 °C/min. For experimental convenience we used pentane (HPLC grade, Aldrich) as a surrogate for liquid propane and propylene (hereafter called C<sub>3</sub> liquid) to soak these fibers at room temperature for different times. The treated fibers were dried at ambient condition before testing. The sample mass was 5 -10 mg. For the purpose of comparison, the fresh samples were also analyzed. PVDF and PP fibers collected from both Module 3 and Module 4, which were tested in the C<sub>3</sub>

distillation for several months<sup>7,8</sup>, were also analyzed. Before testing, the sample chamber was held under vacuum for a few minutes at room temperature (~22 °C). The weight loss/temperature curve was measured.

Differential scanning calorimeter (NETZSCH DSC 404C and CC200L controller) was used for the investigation of the glass transition temperature variation of hollow fibers after they have been soaked in pentane for a period of time. The CC200 liquid nitrogen supply system was used for controlling the sub-zero temperature study. The fiber samples with the same treatment were tested under helium purge from -70 to 300 °C at a heating rate of 5 k/min. The He purge flowrate was 30 ml/min. To ensure good contact between fiber samples and the aluminum pan, the samples were cut into very small pieces and a minimum mass of 5 mg. To minimize the hysteretic effect, the fiber samples were cooled and heated through two cycles between -80 and 100 °C, prior to recording the DSC data.

## 2. Swellability Test

In order to determine the swellability of hollow fibers in light hydrocarbon liquid, we used pentane to conduct experiments at different temperatures. The fiber samples with a length of ~ 150 mm were placed inside Wilmad NMR test tubes (5 mm x 229 mm ID x length) and filled with pentane. The length of the soaked fiber was measured after the fiber was immersed in the pentane for a few hours. The swellability is determined by the length change against that of the fresh samples. The tubes were also immersed in the thermal bath at different temperatures for at least 3 hours. The length of temperature-treated fiber was recorded to determine the effect of temperature on the swellability. The length change of these temperature-treated fibers is calculated against the length of the soaked fiber at 5 °C.

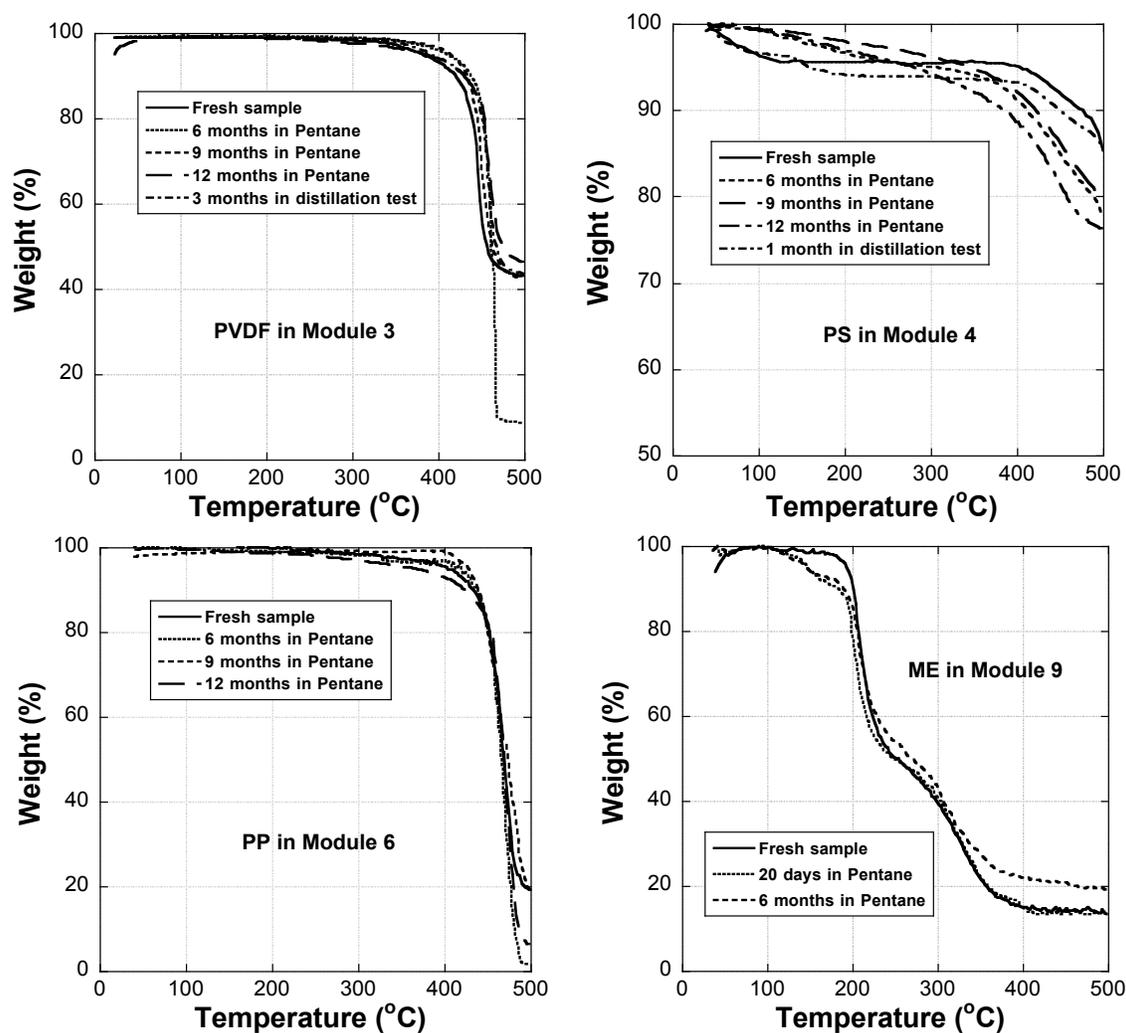
## Results and Discussion

### 1. Thermal Stability

The thermal stability of hollow fibers soaked in light hydrocarbon liquid is one of the concerns for their application in the olefin/paraffin separation. TGA is commonly used to study the thermal stability of polymers. Figure 1 presents the TGA results for the fresh and the soaked fiber samples. Among these four fiber samples, ME fiber is only stable up to 100 °C. Three ME fibers decompose at ~ 210 °C. When it decomposes, ME fibers lose up to 80% of their original mass. At the low temperature range (100 – 200 °C), the TGA results for ME fibers show that the soaking treatment changes the weight loss behavior compared to that of its fresh fiber. This difference may be due to a small amount of glycerin (its boiling point is ~ 290 °C) trapped in the fresh ME sample. However, in the ME fibers, the boiling point of the low molecular weight ester can be as low as < 150 °C. For the fresh ME sample, the existence of glycerin can more or less stabilize some low molecular weight ester because of the interaction between glycerin and polymer molecules. However, in the soaked fibers, since glycerin was washed away, the interaction between glycerin and ester is lost. Therefore, the esters with a low molecular weight start to lose their weight notably after 150 °C.

Among these four fiber samples, PS sample loses the least weight (< 20 mass%) within the temperature range between 25 and 500 °C. There are some differences between the fresh/one-month distillation tested samples and the pentane soaked samples. The former ones show about 5 % weight loss before 150 °C. This weight loss corresponds to the small amount of

residual solvents trapped inside PS fibers. Even after one month testing in the propane/propylene system, the TGA result is almost the same as the fresh sample at temperature < 150 °C. It suggests that the residual solvent inside PS fiber is difficult to wash away. Since the residual solvents possess hydrophilic properties and are difficult to remove, they will decrease the wettability of PS fibers in alkylated solvents, such as olefin/paraffin and pentane. However, the 6, 9, and 12 month soaked samples give very similar TGA results, which are different from the fresh one. These results suggest that after 6 months soaking in pentane, the residual solvent is removed.



**Figure 1.** Effect of soaking time in pentane and C<sub>3</sub> liquid on the weight loss behavior of 4 hollow fiber samples.

The weight losses of PVDF and PP samples are quite stable up to 300 °C. However, both of them start to decompose and largely lose their weight when they are heated above 400 °C. Similar TGA results for the fresh and soaked fibers suggest that there is not an appreciable amount of residual solvents in both PVDF and PP fibers.

DSC analysis is another important method used to determine the stability of polymer materials. Since we are mainly interested in the stability of the polymeric fiber below 300 °C, the DSC test was conducted between – 70 to 300 °C. Figure 2 presents the DSC results collected from the fresh and the soaked samples. The melting temperature and glass transition temperature of the tested samples are summarized in Table I.

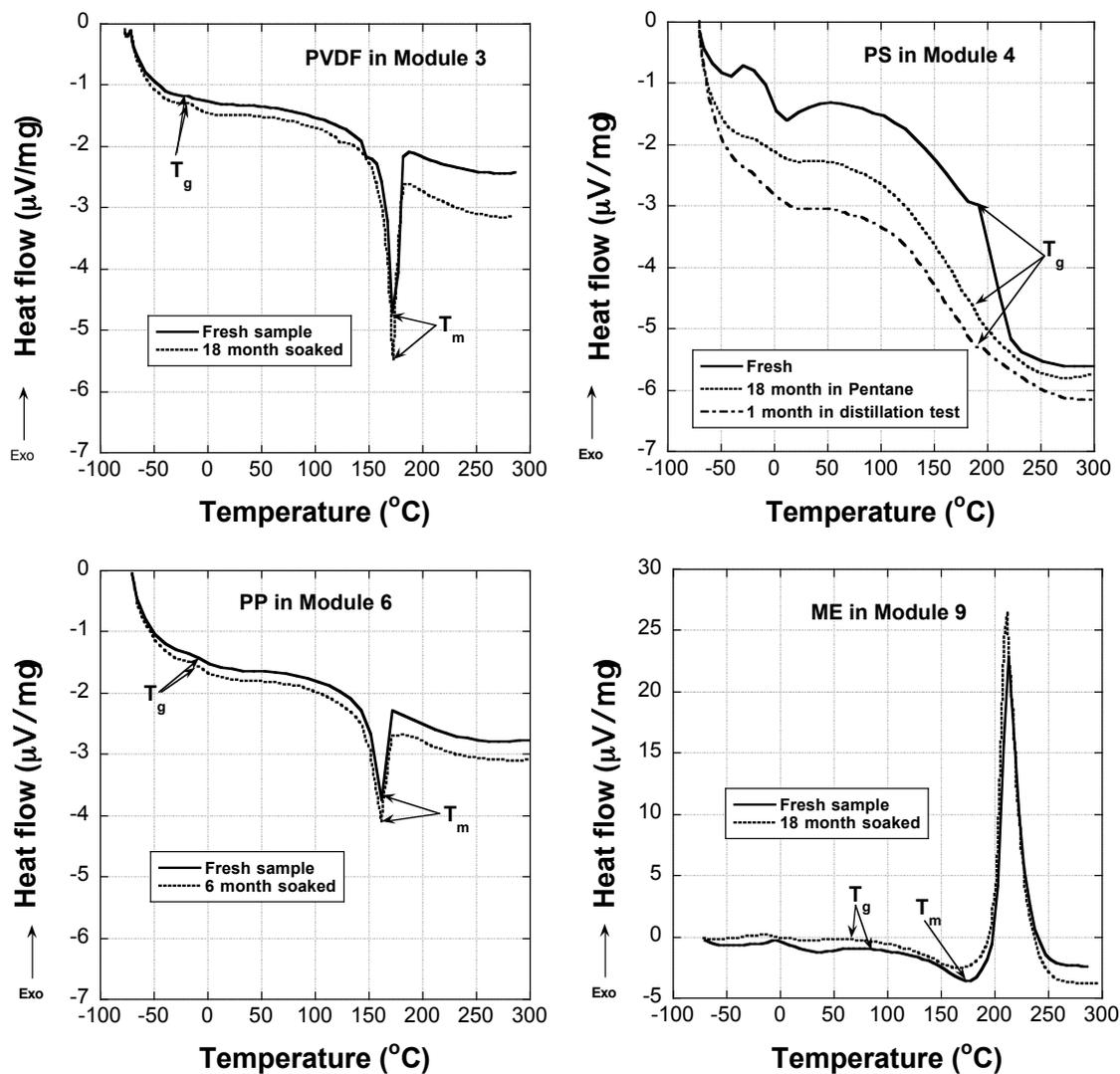


Figure 2. DSC results of fresh and soaked hollow fiber samples packed inside four modules.

Again, both PS and ME fibers have different DSC results between their fresh and the soaked samples. The residual solvents trapped inside the fibers are responsible for the difference and the slight shift of both  $T_m$  and  $T_g$  of these two polymers. On the other hand, similar to the TGA results, both PVDF and PP samples have similar DSC results between their fresh and the soaked samples.

**Table I. Summary of DSC results for four fiber samples.**

Polymer	Module #	$T_m^{1)}$ (°C)		$T_g^{2)}$ (°C)		
		Fresh sample	Soaked in pentane	Fresh sample	Soaked in pentane	After 1 month tested in C <sub>3</sub> liquid
PVDF	Module 3	173.9	173.4	-26.8	-25.8	
PS	Module 4	~283	~278	191.5	185.5	189.7
PP	Module 6	161.6	161.3	-7.1	-7.6	
ME	Module 9	213.3 <sup>3)</sup>	211.1 <sup>3)</sup>	85.2	66.3	

<sup>1)</sup>:  $T_m$  is melting temperature.

<sup>2)</sup>:  $T_g$  is glass transition temperature.

<sup>3)</sup>: ME decomposes at ~210.0 °C right after its melts. The melting point of the ME fibers is hard to determine ([http://physchem.ox.ac.uk/MSDS/CE/cellulose\\_acetate.html](http://physchem.ox.ac.uk/MSDS/CE/cellulose_acetate.html)).

Among these four hollow fibers, PS fiber has the highest  $T_g$  since it contains aromatic groups in its main chain. Hence, PS fiber has the least flexibility. The board peak between 100 and 300 °C suggests that the PS structure changes within this temperature range. Therefore, the stable operational temperature range for this fiber is below 100 °C.

The  $T_g$  of both PVDF and PP is below zero. Due to the low  $T_g$ , both fibers are more flexible than the ME and PS fibers. Both PVDF and PP have a sharp melting peak around 160 and 175 °C, respectively, and decompose above 400 °C.

For the ME fiber, the value of  $T_g$  depends on the molecular weight. For the soaked sample, the  $T_g$  is around 66 °C. A large exothermic peak is observed at ~210 °C. Together with TGA results, we conclude that this exothermic peak corresponds to the polymer decomposition. However, prior to this exothermic peak, a smaller endothermic peak is observed around ~175 °C, which is due to the melting of the ME polymer.

Combining TGA and DSC results, we conclude that these four polymers are stable in a light hydrocarbon environment below 100 °C. However the fibers will go through structural changes, melting, and/or decomposition when they are heated above 100 °C.

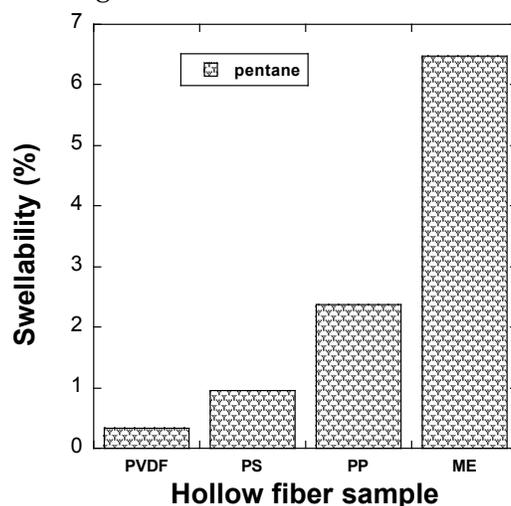
### 3. Swellability of Hollow Fibers

Polymeric membranes swell when they are soaked in wetting solvents. In order to test the swellability of these hollow fibers, we used pentane to conduct the experiments at different temperatures. Although the swelling behavior of these fibers in propane/propylene liquid may not be the same as in the pentane, we assume that the relative trend should be the same because the similarity of physical properties between the pentane and propane/propylene. Theoretically speaking, when the polymeric fibers are soaked in a wetting solvent, the swelling can occur in both longitudinal and radial directions. Due to the small diameter of the fibers and low boiling point of pentane, it is hard to accurately measure changes in the diameter of the soaked fibers. Therefore, only a quantitative swellability in the longitude direction is reported in Figure 3. The related parameters of the fibers are listed in Table II.

**Table II. The parameters of tested hollow fibers**

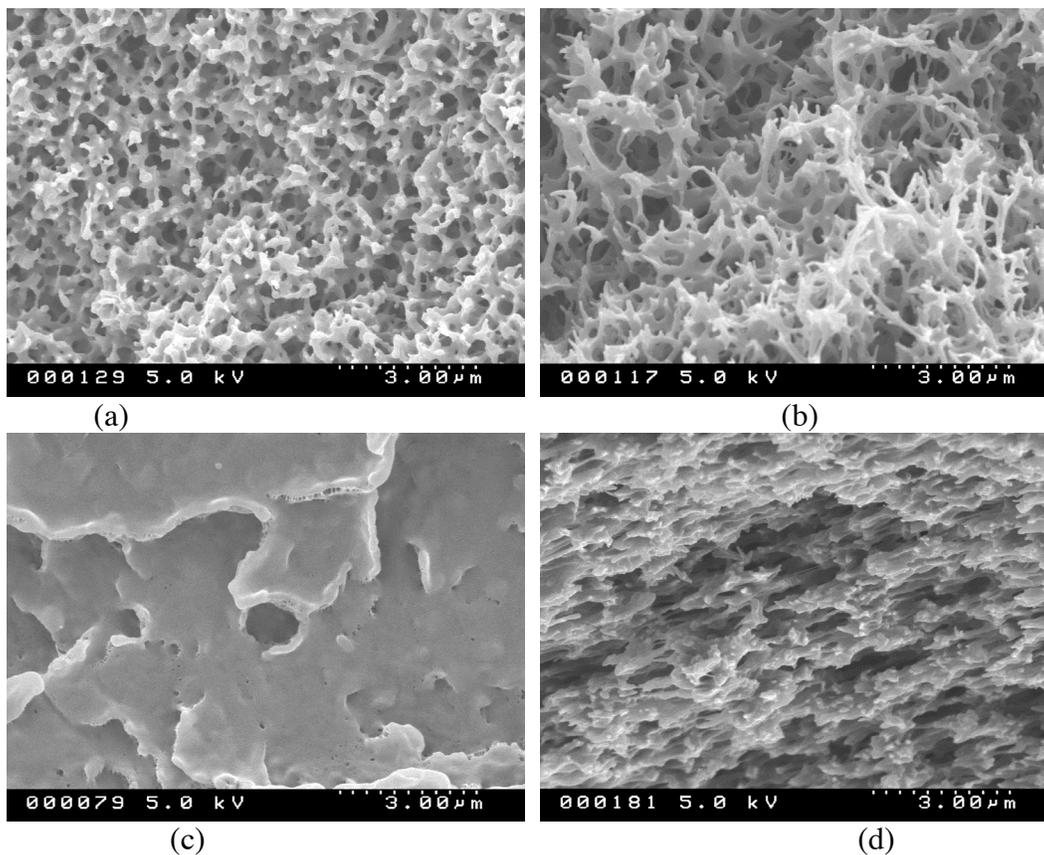
Module label	Module 3 (M3)	Module 4 (M4)	Module 6 (M6)	Module 9 (M9)
Fiber material	Polyvinylidene Fluoride (PVDF)	Polysulfone (PS)	Polypropylene (PP)	Mixed Ester (ME)
Fiber company	Pall AccuSep <sup>®</sup>	Spectrum <sup>®</sup>	Celgard <sup>®</sup>	Spectrum <sup>®</sup>
Fiber ID ( $\mu\text{m}$ )	626	480	240	680
Fiber OD ( $\mu\text{m}$ )	1200	630	300	850
Thickness ( $\mu\text{m}$ )	288	75	30	85

The experimental observation shows that PP and ME can be wetted easily in pentane compared to PVDF and PS. Among these four hollow fibers, ME fiber extends the most. When it is soaked in pentane at room temperature, its length can potentially extend up to 6.5%, but the PVDF extends the least ( $< 0.5\%$ ). Although it is hard to accurately measure the swellability in the radial direction, we estimate that the PVDF has the least swelling in the radial direction ( $< 0.5\%$ ) while the ME has the largest swelling ( $< 4\%$ ).



**Figure 3. Swellability in longitude direction of hollow fibers packed in four different modules in pentane at room temperature (Due to highly curved feature, the extension of PP may be under estimated. Therefore, the swellability of PP may be larger than the value reported here, but still less than that of ME fiber).**

Both wettability to solvent and morphology of hollow fibers should contribute to the swellability behavior. First, we will discuss the morphology effect. Figure 4 illustrates the SEM images of the porous structure of these four hollow fibers. Among these four samples, PVDF, PS, and ME membranes fill with well-connected pores with a large surface area across membrane wall. Pentane can easily access this large surface area and interact with the polymer to cause swelling. Therefore, the swellability of PVDF, PS, and ME would be larger than that of PP if the wettability of these fibers were the same in pentane.



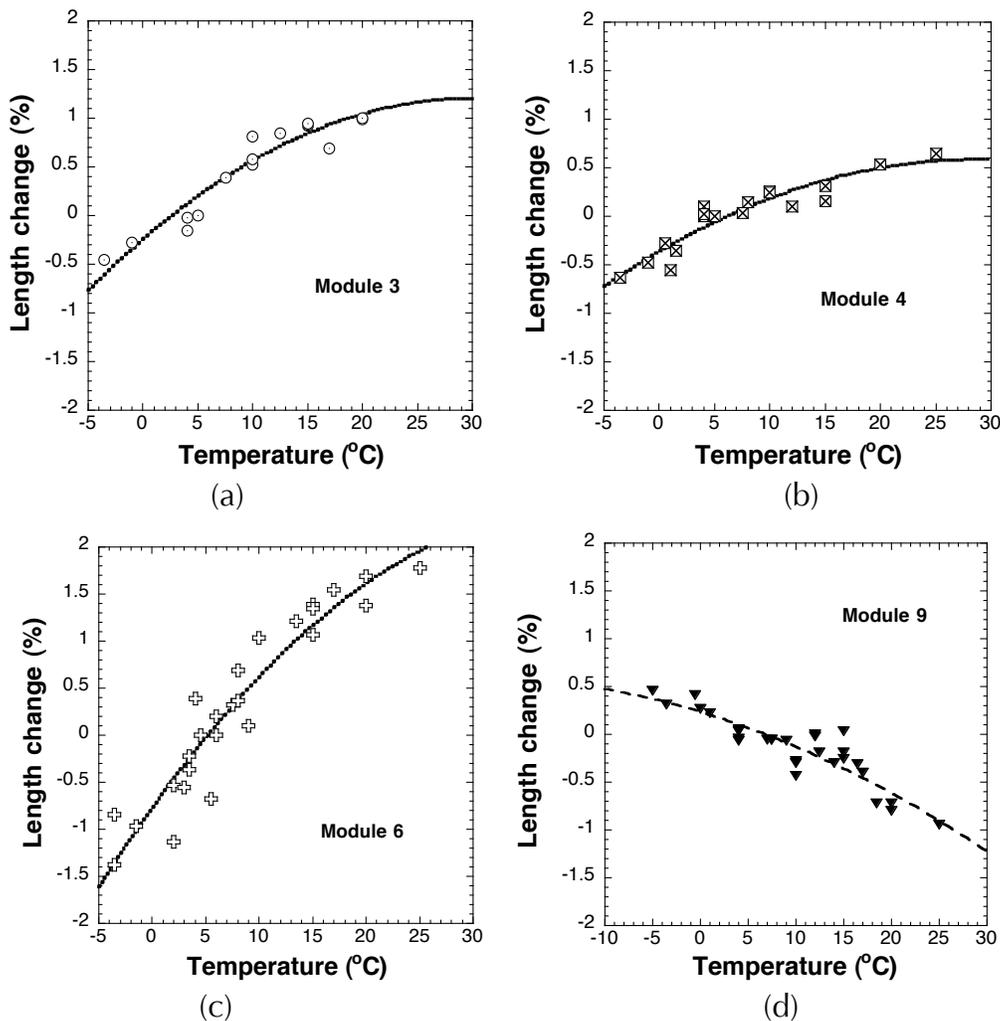
**Figure 4. SEM images of porous structure on the surface for PVDF in Module 3 (a), PS in Module 4 (b), PP in Module 6 (c), and ME in Module 9 (d).**

However, the wettability of these fibers must not be the same. Among these four hollow fibers, PP should have the best wettability due to the chemical similarity to pentane. This may explain why PP shows a large swellability even though it is a relatively dense membrane. Although ME and PS fibers are naturally hydrophobic, the Spectrum® ME and PS fiber was spun from the polymer dope solutions that contained hydrophilic solvents, and thus the resulting fibers are hydrophilic. From the above TGA and DSC results, we know that the hydrophilic solvents are easily removed from ME fiber but not from PS fiber. Therefore, washed ME fiber possesses hydrophobic properties. With its open structure, ME fibers show the largest swellability among these four fibers. On the contrary, the hydrophilic affinity inside PS fiber can reduce its wettability and thus its swellability in pentane even though PS fiber has the open porous structure. The least swellability of PVDF suggests its wettability is the poorest among these four polymers. Therefore, combining the effects of morphology and wettability, ME has the largest swellability whereas PVDF has the least among these fibers.

After the fibers were potted in the polycarbonate to fabricate hollow fiber modules, we used pentane to flush the fiber several times and tried to remove any residual solvents as much as possible. During this washing step, the wetted ME and PP extended inside the module and became curved along the tube. On the other hand, there was no apparent change of PVDF fiber. The PS fibers showed some degree of extension but not as significant as ME and PP fibers do. This observation is in line with the reported results presented in Figure 3.

#### 4. Temperature Effect on Swellability

To explore the effect of temperature on the separation efficiency of these modules<sup>9</sup>, the operation temperature was varied from 2 to 25 °C. Along the same line of thought, we investigated the effect of temperature on the swellability of these fibers. The tested results are given in Figure 5. The effect of temperature has the largest impact on PP fibers (packed inside Module 6), but the total change is less than 4% over a 30 °C temperature range. The length of PVDF, PS, and PP fiber changes slightly with increasing temperature. Interestingly, the length of ME fiber (packed in Module 9) even slightly decreases with increasing temperature. Overall, the temperature effect on the length of the soaked fibers is not significant. Any impact of the length change due to temperature on the separation efficiency is secondary. Rather, the effect of temperature on the physical properties of olefin/paraffin has the greater influence on the separation efficiency<sup>8</sup>.



**Figure 5.** The effect of temperature on the length change of the hollow fibers packed inside four modules (the fiber length at 5 °C is the base to calculate the change at different temperature).

## Conclusion

The TGA and DSC study shows that PVDF, PS, PP, and ME fibers are stable in the light hydrocarbon environment. However, due to structural changes, melting, and/or decomposition that occurs above 100 °C, the stable operation temperature should be below 100 °C. Both PVDF and PS fibers have been tested in the distillation experiments for several months, the separation efficiency does not decrease significantly.

In this report, we also evaluated the swellability of these fibers in the pentane. Among these four fiber samples, ME extends to the largest degree (~ 6.5%) whereas PVDF has the smallest extension. Although the length extension can increase the surface area, it also has potential to cause channeling. We suspect that this may be one of reasons for a lower HTU (> 10 cm) value than we had expected<sup>8,9</sup>.

It is expected that the swellability will change the specific area of the hollow fiber modules and the spacing between the fibers. Although the swollen fiber gives a larger mass transfer area than that calculated based on the dry fiber's geometry, the curved fibers also increases the possibility of the contact between fibers and thus increase channeling problem. The two factors are contradictory to each other. The overall impact on the separation efficiency needs to be determined from experiments. The effect of temperature on the length change is insignificant.

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