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Transport properties of gases through integrally skinned asymmetric composite membranes prepared from date pit powder and polysulfone

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ABSTRACT: Studies were conducted on transport properties and separation performance of date pit/polysulfone composite membranes for CO_2, CH_4, N_2, He, and H_2 gases. Date seeds were obtained and processed into powder. Asymmetric flat sheet membrane was prepared by solvent casting method with 2–10 wt % date pit powder. Membrane characterization was done using high pressure gas permeation, X-ray diffraction, thermogravimetric, and scanning electron microscope analyses. The separation performance and the plasticization resistance property were evaluated in terms of gas permeability, selectivity, and plasticization pressure, respectively. Time dependent performance properties were evaluated up to a pressure of 40 bar for 75 days. Results obtained showed the highest selectivity values of 1.54 (He/H_2), 3.637 (He/N_2), 2.538 (He/CO_2), 2.779 (He/CH_4), 3.179 (H_2/N_2), 3.907 (H_2/CO_2), 1.519 (CH_4/N_2), 1.650 (CO_2/N_2), and 1.261 (CO_2/CH_4) at 10 bar and 35 °C feed pressure and temperature, respectively. The resulting composite membrane showed about 39.50 and 66.94% increase in the selectivity of He/N_2 and CO_2/CH_4, respectively, as compared to the pure polysulfone membrane. Thus, the membrane composites possess some potentials in membrane gas separation. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43606.

INTRODUCTION

The increasing need of various gases for industrial and domestic purposes has resulted in an aggressive search for energy efficient and low cost gas separation technology. Membrane gas separation technology is one of the commonly investigated technologies that have attracted industrial and academic interests for this purpose. This is due to its simplicity, high energy efficiency, small foot prints, and simplified process operations and maintenance.[1] Gas separation by selective transport through polymeric membranes is an important separation technology commonly employed in natural gas sweetening, fuel cell system, food packaging, hydrogen recovery, air purification and oxygen enrichment, biogas purification, enhanced oil recovery and hydrocarbon separation.[2–4] Membrane material is a very vital component of membrane gas separation system. The use of renewable materials in conjunction with energy efficient separation systems such as membrane based gas separation technology is one of the ways to ensure the sustainability of industries that need these gas separation processes. Till date, varieties of methods and materials have been investigated with respect to improving the membrane materials that are currently used in gas separation industries.

Polysulfone is one of the most investigated glassy polymers for gas processing. This is due to its availability, excellent mechanical property, chemical resistance, and low cost.[5] On a general note,

the performance of polymeric membrane for gas separation can be improved by incorporating functional group with high affinity to CO_2. Some of these functional groups include oxygen ether, hydroxyl, amine, and nitrile.[6] Such incorporation can be by physical mixing (blending) or chemical method such as grafting. The use of blending method to prepare composite membranes has attracted a lot of research attention due to its simplicity and cost effectiveness in scaling up. In the present study, date pit powder was used to prepare a composite membrane using polysulfone as a base polymer.

Naturally occurring composites commonly known as green composites are new set of materials that are generating both industrial and academic interests in varieties of applications[7,8] including gas separation and barrier properties in packaging.[9] An example of such material is the date seed powder. Date fruits, which are botanically called *Phoenix dactylifera L.*, are well known staple food in the Northern part of Africa and the Middle East. Date pit, also known as date seed, is an integral part of date fruit. It constitutes about 6–14 wt % of the total weight of the fruits. Research work on the chemical composition of date revealed that it contains 98.89 wt % polyols compounds of cellulose, hemicelluloses, and lignin.[10,11] The presence of cellulose, lignin and hemicellulose can constitute varieties of advantages that are beneficial to membrane gas separation processes.[12] For example the hydrogen bond and
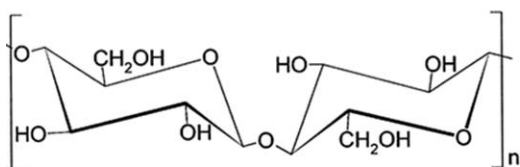
Figure 1. Chemical structure of cellulose.

Figure 3. Chemical structure of lignin.

other linkages in cellulose provide necessary strength and stiffness for membrane composites.[13] Moreover, one of the major issues with oil field chemicals is that of environmental issues. The presence of lignin and hemicellulose enhances the biodegradability of membranes that are made from such date pit based nanomaterials[13] after disposal. In addition, cellulose molecules are composed of reactive hydroxyl groups[14] which can enhance the performance of its composite in varieties of mixture separation.

The chemical structures of the compounds that are contained in date pits are shown in Figures 1 to 3 below. The presence of poly hydroxyl and oxygen ether groups is known to increase the transport properties of gas such as CO_2.[15–17] This is due to the interaction of CO_2 with the OH functional groups of the date pit. This special feature makes the date pit powder a good filler that is expected to improve the gas transport property of the membrane composite made out of this pit.

Therefore, the objective of this research is to investigate the synergistic effect of adding a date pit powder on the physicochemical properties of a glassy polysulfone polymer membrane. Moreover, the data presented here is expected to serve as preliminary results on the potential of date pit based composite membranes in natural gas processing and other gas separation processes.

Membranes were fabricated using solution casting method. Properties which include gas permeability and permselectivity, thermal, physical aging, and morphology were investigated. In addition, the performance and dynamic behaviors of the membrane at high feed pressure were also evaluated. The outcome of these investigations will enhance our understanding into the potential of multicomponent membrane materials made from naturally occurring composites (such as date pit) in gas separation processes.

EXPERIMENTAL

Materials
The polysulfone (PSF) used in this study is Udel-P1700 which was supplied by Amoco Chemicals. Date pit used was collected from date processing industry at Al Hassa, Eastern Province of Saudi Arabia. The 1-methyl-2-pyrrolidone (NMP), and methanol (MeOH) supplied by Merck, and hexane was bought from Sigma–Aldrich. The PSF was oven dried overnight before being used. Solvent and other organic reagents were used as received.
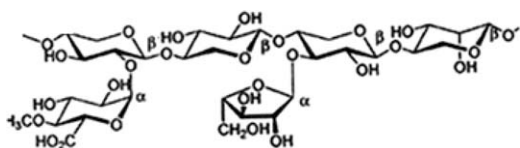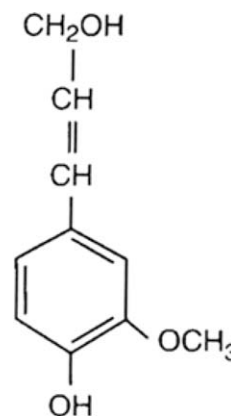

Figure 2. Chemical structure of hemicellulose.

Date Pit Processing
Detailed explanation of date pit processing has been reported elsewhere.[11] The date seed were soaked in water, washed by sonication, and dried. The dried seeds were ground to powder and de-oiled using Soxhlet apparatus with n-hexane solvent. The de-oiled powder was dried in vacuum oven at 100 °C until constant weight was obtained.

Particle Size Analysis
The particle size analysis of the de-oiled powder was performed using Analysette 22 MicroTec plus from Fritsch. This test has been performed to know the range of the sizes of the date pit and their effect on the composite membrane performance.

Preparation of Date Pit Composite Membranes
Composite membranes were prepared by solution casting using a modified form of the method described in Ismail and Lai.[18] PSF was dissolved in a blend of solvents (NMP and THF) and stirred for 24 h. A predetermined quantity of date pit was then added into the polymer solution while stirring continuously. The stirring was done for another 24 h. The solution was casted on a glass plate using a doctor blade. Casted samples were allowed variety of free standing periods of time (10, 30, and 60 s) before being immersed into water and left for 24 h at 25 °C. The free standing periods of time were varied to control the surface morphology of the membrane active layer. Membrane samples were later immersed in methanol for 2 h followed by air drying for 48 h. Membrane samples with 30-s free standing time were used for further characterization. This is because other membrane samples have poor selectivity, which is a very important performance requirement in membrane separation.

Scanning Electron Microscopy (SEM)
Membrane microstructure and morphology were examined using scanning electron microscopy (SEM, JEOL JSM – 6610L). Membrane samples were broken in liquid nitrogen and then sputtered with a thin layer of gold. The cross sectional as well as surface morphology of the membranes was examined.

Gas Permeation Measurement
Gas permeability was measured by a constant pressure/variable volume apparatus. The apparatus is composed of a permeation cell, a mass flow controller on the upstream side, and soap-film bubble flowmeter on the downstream side. The permeation cell
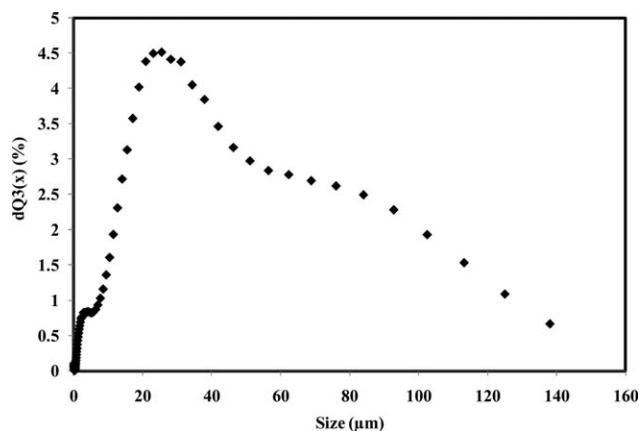
Figure 4. Date pit size distribution.

was housed in an oven whose temperature was kept at constant value of 35 °C. The active permeation area was 2.974 cm^2. The measurement time used was in the range of 3–593 s.

Permeate flow rate was measured using a bubble flowmeter. At steady-state condition, gas permeability was calculated using the following equation:

$$P = \frac{22,414}{A} \frac{l}{(p_2 - p_1)} \frac{p_1}{RT} \frac{dV}{dt} \qquad (1)$$

where A is the membrane area (cm^2), p_2 and p_1 are feed or upstream and permeate or downstream pressures, respectively, R is the universal gas constant (6236.56 cm^{3}cmHg/molK), T is the absolute temperature (K), $\frac{dV}{dt}$ is the volumetric displacement rate of the soap - film in the bubble flowmeter (cm^3/s) and 22,414 is the number of $cm^3(STP)$ of penetrant per mole.[19,20]

In addition, time dependent permeability was also examined to evaluate the long term stability of the membrane performance. The time dependence permeability experiment was conducted at various feed gas pressures between 5 and 40 bar. The permeation system was run for about 75 days with at least 15 days at each of the feed pressure.

RESULTS AND DISCUSSION

The main purpose of the present investigation is to evaluate the physico-chemical properties of the membrane composites made using date pit powder. Results obtained from varieties of evaluations are described as follows:

Particle Size Analysis

The results obtained from the size analysis of the pit were displayed in Figure 4. From this figure it was observed that the date pit particle of the size around 20 μm constitutes the largest percentage of the pits that were used in this experiment. Also, the results from the figure revealed that the largest particle were about 141 μm in size while the smallest is 0.09 μm. The distribution is expected to affect the performance of the membrane as will be explained in subsequent sections.

Morphological Studies using Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD)

Generally, the mode of permeation and separation of a particular membrane is dictated by its morphology.[14] In the present

study, nonporous integrally skinned dense top selective layer and the porous supports were probed using SEM. The micrograph images of the powder are shown in Figure 5. The results on Figure 5 showed a similar distribution with the results of the particle size analysis in Figure 4. In addition, the SEM image revealed that some of the large sized particles are actually agglomerates which were formed during date pit processing. Investigations into the agglomeration issues and its prevention are part of our future research work.

The micrographs of membrane composites are shown in Figures 6 and 7 for the surface and cross-section respectively. In Figure 6, surface of the pure PSF and the composites are compared. The SEM images of the surface displayed in this figure for the pure PSF revealed a continuous defect-free surface with no detectable micro pores. However, the SEM images DP-PSF 5 and DP-PSF 10 revealed few small potholes on the surfaces. The sizes of these potholes increase with increase in the loading of the date pit. This is in line with the observation from the results of the cross section micrographs.

SEM micrographs of the cross section of the membrane composites were shown in Figure 7 at 100 μm. The figure reveals two distinct morphologies for the top layer and the porous support. Also, the microstructure of the support revealed a spongy-like uniformly distributed pores with few finger-like macro voids. The population of the finger-like macro-pores was observed to increase with increase in the percent loading of the date pit. Moreover, the distribution of the date pit particles was also revealed in one of the macro voids as shown in Figure 7(b). It was observed that the date pit particles are well uniformly dispersed.

The X-ray diffraction was used to investigate the crystalline nature of the membrane composites. Figure 8 shows the X-ray diffraction spectra of the composites. The reflection peaks associated with the amorphous as well as the crystalline regions of the pure PSF and DP-PSF composites were observed on this figure. It was observed that the pure sample show a mixture of amorphous halo and crystalline peaks. At higher loading of date pit particles such as 5 wt %, the sharp crystalline was found to be disappearing. The resulting spectra of this composite revealed DP-PSF-5 to be more amorphous than the pure PSF. At 2 wt % date pit loading (DP-PSF-2), there were two obvious spectra of both amorphous halo and sharp crystalline peaks. Thus, DP-PSF-2 sample was observed to be more crystalline than the pure PSF (DP-PSF-0). This observation corresponds well with the results of gas permeability which will be discussed in later section.

Gas Permeation Measurement

Effect of Date Pit Loading on Permeability and Selectivity. Table I contains the results of permeability of He, H$_2$, N$_2$, CH$_4$, and CO$_2$ through the composite membranes. There was a drastic drop in the gas permeability of the membranes for 2 wt % loading while at higher loading the permeability begin to increase. At 10 wt % loading, the permeability is about two times the permeability of the pure PSF membrane for all the gases. The reduction of permeability as observed for the 2 wt % loading is in agreement with the results reported for many mixed matrix/composite membranes. For nonpermeable dispersed phase, it is often observed that lower loading of particles reduces the permeability
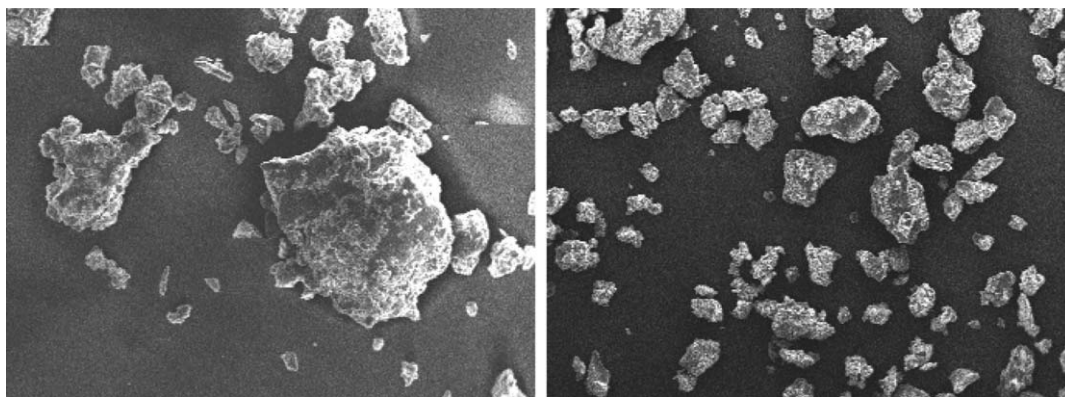
Figure 5. Date pit power 100 μm.

due the creation of tortuous path which lengthens the distance that the gas molecules will need travel through to permeate the membranes.[21–24] For porous dispersed phase such as date pit, such phenomenon can be observed due to the orientation of the particles as dispersed within the polymer matrix. At higher loading, the premeability was found to incease with increase in the percentage loading of the date pit powder. Possible explanation for such increase in permeability has been made in literature. For example, Matteucci et al.[23] and Merkel et al.[21] explained that dispersed particles can inhibit the efficient segmental chain packaging in polymers thereby increasing free volume in the polymer phase which consequently increases the permeability. Moreover, in heterogenous polymer systems such PSF-Date Pit powder,

voids at polymer–particle interface or between particle aggregates must have caused permeability to be greater in the composites than in unfilled polymers. In addition, the observed increase in gas permeability due to the addition of higher wt % of date pit is expected since date pit has been reported to be a porous material.[25,26]
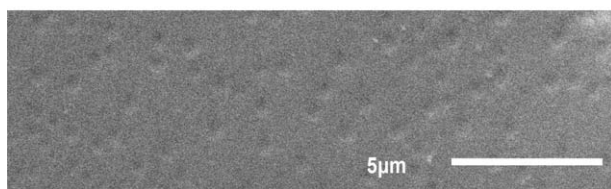
Moreover, the permeability results followed the same trend as the results of the X-RD as shown in Figure 8. The results displayed on this figure showed that DP-PSF-5 (with 5 wt % date pit) is more amorphous than DP-PSF-2. Consequently, the permeability DP-PSF-5 is higher than that of DP-PSF-2.
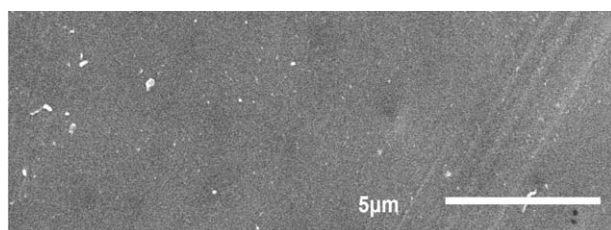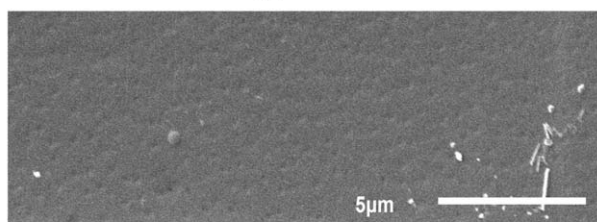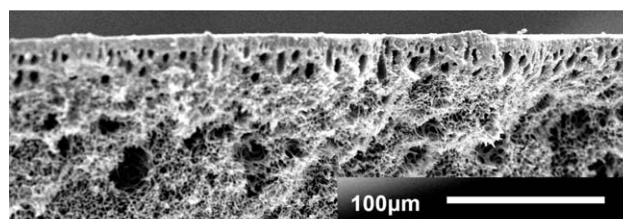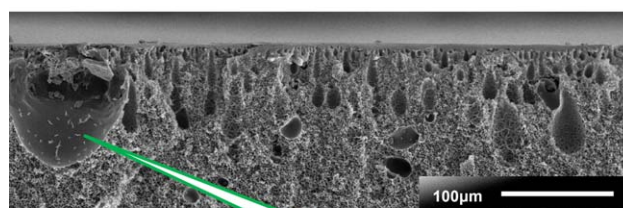

Figure 6. Date pit composite membrane surface SEM.
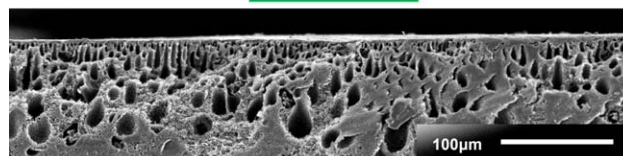
Figure 7. Date pit composite membrane cross section. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
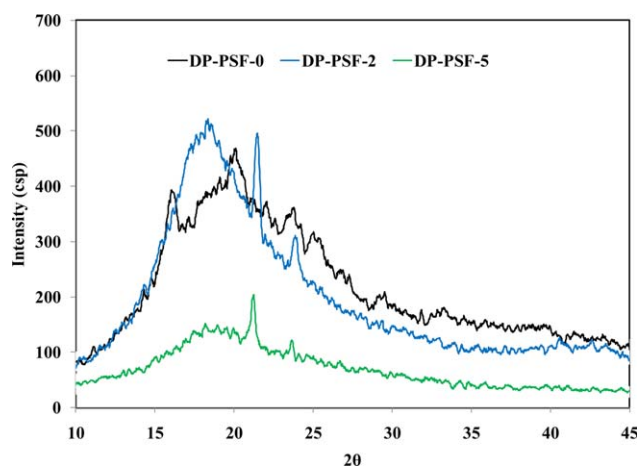
Figure 8. XRD spectra of the membrane composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results of the selectivity are displayed in Table II. Unexpectedly, the selectivity behaviors are a bit different from the permeability results in Table I. It is expected that a decrease in permeability should be accompanied with an increase in selectivity in line with the Robeson upper bound curve.[27] However, this is not the case for some of the samples in Table II. For example, the permeability of He and H_2 decrease while 2 wt % DP was added to the pure PSF. The selectivity of He/H_2 also decreased accordingly. An increase in %wt loading from 2 to 5 and then 10 showed a corresponding increase in both the permeability as well as the selectivity of He/H_2. The selectivity of He/N_2 was found to increase at 2 wt % loading. This was later followed by a decrease in selectivity with increasing wt % loading. A detailed evaluation of the results in this table shows four types of behaviors, namely: Nonpolar gases with close molecular diameter, nonpolar gases with large difference in molecular diameter; polar and nonpolar gases with close molecular diameter and polar and nonpolar gases with large difference in molecular diameter. To obtain a better picture of the gas transport behaviors, Table III has been included.

Nonpolar Gases with Close Values of Molecular Diameters. Examples of such are between CH_4 and N_2 and between He and H_2. In comparing the samples, it was observed that the permeability as well as the selectivity dropped at 2 wt % loading and then increased as the wt % loading was increased from 2 to 5. For non-polar gases, the permeability as well as selectivity is more of a function of the diffusivity than solubility. Thus, both the kinetic diameter and the shape

of the gas molecules are expected to play important roles. Because He is smaller than H_2, it tends to have higher permeability. Thus, the membrane is more selective to He than H_2 at higher %wt loading. Unfortunately, this concept does not apply to CH_4 and N_2, possibly due to shape of the gas molecules. Generally, the phenomenon observed with respect to the membrane performance for separating nonpolar gases with close values of molecular diameter is a complex one. Future work needs to be done to present more explanation of the phenomenon. This scenario will be captured in our future work.

Nonpolar Gases with Large Difference in Molecular Diameters. For this category, examples include between He and N_2 and between He and CH_4. For all the results of the selectivity for this class of gases, the selectivity was found to increase on adding 2 wt % DP but decreased with increase in the wt % loading above 2 wt %.

Polar and Nonpolar Gases with Close Values of Molecular Diameters. The selectivity behaviors between quadrupolar CO_2 and nonpolar N_2 and CH_4[28,29] (CO_2/N_2 and CO_2/CH_4) was observed to increase at 2 wt % DP loading. Above 2, the selectivity dropped. The permeability of polar gases like CO_2 has been reported to be very sensitive to the polymer structure.[30] Also, the polarity has been found to contribute the increase in selectivity in the presence of some functional groups such as ether,[31] hydroxyl,[29,32] carbonyl,[30] and others. As shown in previous section, the DP contains both ethers as well as hydroxyl groups that can enhance the selectivity of CO_2. However, the molecular sizes of the gases, as well as the diffusivity also contribute to the selectivity. The increase selectivity at 2 wt % DP as compared to pure PSF can be attributed to the presence of hydroxyl and ether functional groups that are present in DP. In addition, the decrease in the selectivity is due to the corresponding increase in macro voids due to increase in wt % DP loading as explained earlier. The increase free volume seems to be dominating the control of the permeability. This is in line with the fact that the diffusion coefficient is the primary factor in determining gas permeability in polymers.[30] This is also possible owing to the size distribution of the DP particles as shown in Figure 4.

Polar and Nonpolar Gases with Large Difference in Molecular Diameter. For this category, similar explanation as for polar and non-polar gases with close values of molecular diameters above also applies. The selectivity of He/CO_2 and H_2/CO_2 were observed to decrease at 2 wt % despite a decrease in the permeability. The selectivity of H_2/CO_2 was found to increase once the % loading increased from 2 to 5. This increment continued

Table I. Permeance at 10 Bar and 35 °C

Sample	wt %	He	H_2	N_2	CH_4	CO_2
DP-PSF-0	0.00	600.454	633.873	230.309	318.229	240.292
DP-PSF-2	2.00	30.768	20.339	8.461	11.072	13.957
DP-PSF-5	5.00	151.264	213.773	76.165	115.697	94.949
DP-PSF-10	10.00	1130.918	1741.240	547.787	705.246	445.658
Range of σ	–	0–0.015	0.001–0.039	0–0.021	0–0.005	0–0.006

σ is the standard deviation.

Table II. Selectivity at 10 bar and 35 °C

Sample	wt %	He/H$_2$	He/N$_2$	He/CH$_4$	He/CO$_2$	H$_2$/N$_2$	H$_2$/CH$_4$	H$_2$/CO$_2$	CH$_4$/N$_2$	CO$_2$/N$_2$	CO$_2$/CH$_4$
DP-PSF-0	0.00	1.056	2.607	1.887	2.499	2.752	1.992	2.638	1.382	1.043	0.755
DP-PSF-2	2.00	0.661	3.637	2.779	2.205	2.404	1.837	1.457	1.309	1.650	1.261
DP-PSF-5	5.00	1.413	1.986	1.307	1.593	2.807	1.848	2.251	1.519	1.247	0.821
DP-PSF-10	10.00	1.540	2.065	1.604	2.538	3.179	2.469	3.907	1.287	0.814	0.632

as the loading was increased from 5 to 10%. However, the selectivity of He/CO$_2$ was observed to further dropped as the % loading was increased from 2 to 5 and then increased when wt % loading increased to 10 wt %. Due the large size difference, the selectivity is most likely going to continue to increase with increase in the wt % loading. Thus, the main contribution to the selectivity increase here is the diffusion coefficients.[33]

Clearly, the results above showed that the membrane composite can serve both as gas barrier in gas pipelines (at low DP wt % loading) and as gas separation membrane at higher loading of the DP. It is particularly a potential material in separation of polar and nonpolar gases with large difference in molecular diameter.

Effect of Upstream Pressure on Permeability of CO$_2$. High pressure gas separation has been suggested as a means of improving the efficiency of membrane gas separation.[4] Unfortunately, plasticization is a painful phenomenon that usually occurred while membrane is used at high feed pressure.[25] Thus, one of the analyses performed in this work is high pressure evaluation of the membrane composites performance. The high pressure permeability was performed for pure CO$_2$ so as to evaluate the plasticization property of the membrane. In this regards, permeability test was performed on the membrane of 2 wt % DP loading at high pressure up to 45 bar. This sample was chosen based on its selectivity for CO$_2$/CH$_4$. Results obtained are displayed in Figure 9. This figure shows the results of CO$_2$ permeability as a function of feed gas pressure. The permeability of CO$_2$ was observed to decrease with increase in pressure from 10 to 35 bar. This is typical of the behaviors of glassy polymers in the absence of plasticization phenomenon.[4,34] It also means that, the membrane did not show any sign of plasticization up to a pressure of 35 bar. Above 35 bar, the permeability was found to increase which is an indication of plasticization phenomenon.[5] Thus from this experiment the plasticization pressure of the membrane is around 35 bar.[34]

Time Dependent Permeability and Physical Aging. The dynamic behavior of membrane separation process is very

Table III. Kinetic Diameter for Various Gases

Molecule	Kinetic diameter (Å)
He	2.69
H$_2$	2.89
N$_2$	3.64
CO$_2$	3.3
CH$_4$	3.87

important in evaluating the long term behavior of membranes. It is also necessary for investigating the extent of physical aging and the plasticization of the membrane. In the present study, a separate set of membranes was used to investigate the time dependency of the membrane performance. Permeation tests were performed at various pressures between 5 and 40 bar for a total period of 75 days. Samples with 2 wt % date pit loading were used. The results obtained from the time dependent permeability experiment are shown in Figure 10. On this figure the CO$_2$ permeability was plotted against the time. One sample was used throughout the experiment. Experiment was performed at incremental feed pressure of 5, 10, 20, 30, and 40 bar. The feed pressure was increased after 15 days of continuous gas permeation for each of the pressures.

The plasticization pressure of the sample that was used for the dynamic study was observed to be around 35 bar. On a general note, the performance of the membrane was found to be stable. At 5 bar, the permeability was found to fluctuate slightly from the beginning of the experiment to the end after 15 days. At 10 bar, the permeability is more stable than at 5 bar. This trend continues to the highest feed pressure. The stability of the membrane is maintained up till the highest pressure of 40 bar. Between the feed pressure of 5 and 30 bar, the permeability was observed to decrease with increase in pressure. Above 40 bar, the permeability was observed to increase from 24GPU at 30 bar to 27 GPU at 40 bar. The decrease in permeability as observed in these results is often associated with various reasons such as polymer aging, absorption of impurities, and membrane compaction.[35–38] The increase in permeability is due to plasticization.[4] Moreover, the results of CO$_2$ permeability as depicted in Figure 10 also reflect that of selectivity of CO$_2$ with respect to other gases used in this work. This is because selectivity is
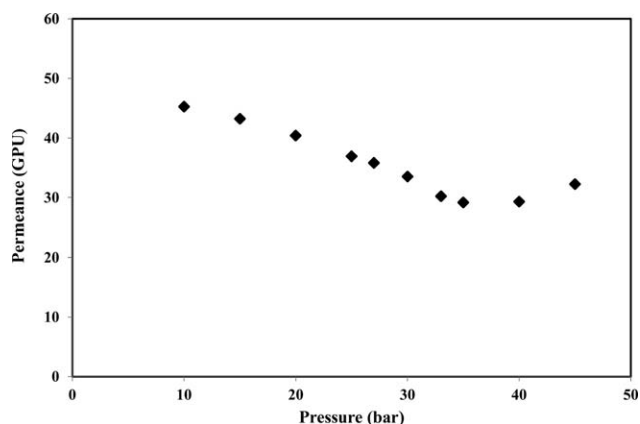
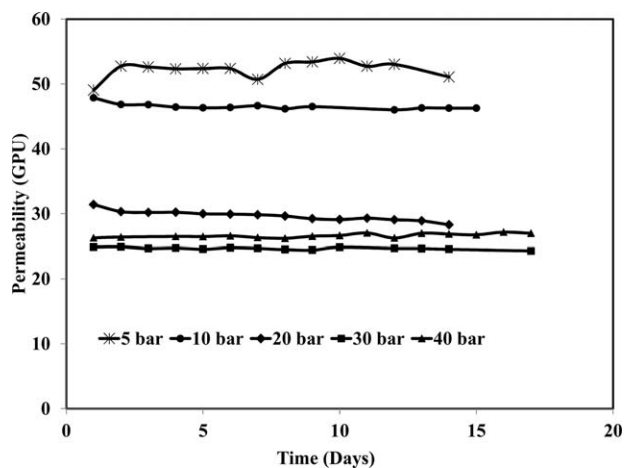**Figure 9.** Permeance of CO$_2$ as function of upstream pressure.

Figure 10. Time dependent CO_2 permeability of the composite membrane.

the ratio of permeabilities of the gases involved. Among the gases tested in this work, only CO_2 was known to have the possibility of causing plasticization.[5,25,39] Therefore, it is the only whose permeability may change with time. This implied that the stability of the membrane in terms of selectivity can also be maintained up to the highest pressure of 4o bar.

In general, the phenomenon observed during the time dependent permeation tests is explained using the two competing phenomena of physical aging and plasticization.[40,41] The effects of these two opposing phenomena have been identified for some polymers; however, literature reports on the long term permeation experiments are not common. In the present case none of the phenomenon (physical aging and plasticization) was detectable at 10 bar and above over the experimental period of 75 days. On another hand, it can be argued that both the physical aging and the plasticization phenomenon have counterbalanced each other throughout the experiment. Similar arguments have been proposed by some other authors.[40,42]

Thermogravimetric Analysis

TGA was performed in order to investigate the effect of date pit loading on the thermal properties of the composite membrane.
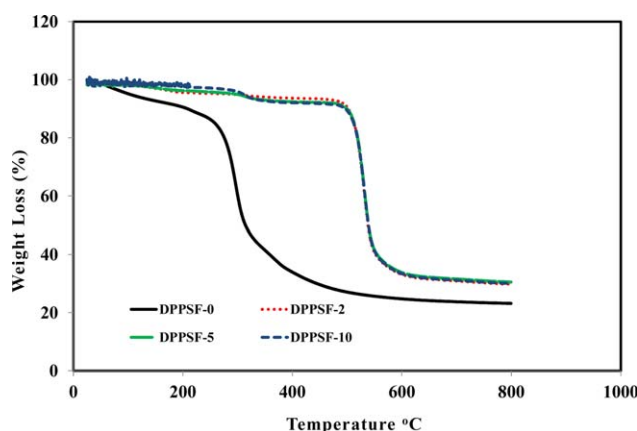

Figure 11. Thermal properties of composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

As shown in Figure 11, there was a distinct difference in the thermal properties of the date pit particles (DP-PSF-0) and the composite membranes. For the date pit, a major change in weight loss began to appear at around 250 °C while for the composite it appeared at 480 °C. The TGA spectral observed for the composite membranes is typical of the spectra reported for polysulfone in the literature.[43] The decomposition temperatures are almost similar for all the membranes. Thus, the addition of the date pit particles up to 10 wt % has no significant effect on the thermal properties of the composites.

CONCLUSIONS

Polysulfone composite membranes containing date pit powder at different weight percent loadings were prepared via solution casting. The composite membranes were evaluated for their gas separation potentials. Transport properties and plasticization behaviours of the composite membranes were evaluated. Time dependent properties were evaluated up to a pressure of 40 bar for 75 days. Values for single gas permeability of CO_2, CH_4, N_2, He, and H_2 were measured. The results of the performance measurements revealed that the date pit composite membranes possess some potential for gas separation. The result also revealed that date pit membranes are good candidates for high pressure application with resistance to plasticization and physical aging.

ACKNOWLEDGMENTS

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