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LIQUID PERMEATION AND WATER VAPOUR TRANSMISSION PROPERTIES OF A TEMPERATURE-SENSITIVE PVDF-g-NIPAAM BARRIER MEMBRANE

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ABSTRACT

Both liquid chemical permeation rate of n-hexane and water vapour transmission rate (WVTR) of temperature sensitive polymer membranes made from N-isopropylacrylamide (NIPAAM) grafted Poly(vinylidene fluoride) (PVDF) copolymer (PVDF-g-NIPAAM) were studied in order to evaluate its potential utility as a smart barrier layer in chemical protective clothing. It is found that the breakthrough time in the chemical permeation test decreased when the copolymer membrane were produced in the mass ratio of NIPAAM:PVDF increased from 1:100 to 1:1, and the WVTR of the copolymer membranes made from higher concentrations of NIPAAM (i.e., 1:1 and 1:10 for the mass ratio of NIPAAM:PVDF) at the environmental temperature (40°C) higher than the LCST of NIPAAM (32°C) was markedly greater than that at the environmental temperature (20°C) lower than the LCST of NIPAAM, it is believed that such characteristics is related to both the porous structure of the and the proportion of NIPAAM in the copolymers.

Key Words: *PVDF, NIPAAM, temperature sensitivity polymer, water vapour transmission rate, permeation rate*

1. INTRODUCTION

Barrier membranes used in impermeable chemical protective clothing are required to resist the permeation of liquid chemicals. Ideally, the membrane used in a semi-permeable chemical protective clothing will have both the capability of resisting permeation of liquid chemicals as well as moisture management properties. In this case, it is desirable to have a smart membrane whose moisture management properties change with the environmental temperature or with body temperature, while maintaining the required liquid chemical permeation properties.

N-isopropylacrylamide (NIPAAM) has a low critical solution temperature (LCST) around 31-32°C in an aqueous environment [1]. Below the LCST of NIPAAM, the NIPAAM polymer exhibits a hydrophilic and expanded state and exhibits a hydrophobic and shrunken state above its LCST [2]. İt is therefore capable of responsive change in different environmental temperatures and is widely used in smart membrane applications.

Poly(vinylidene fluoride) (PVDF) is a type of fluoropolymer having well-known chemical resistance, mechanical strength and piezoelectric properties [3]. It is widely used as a chemical liquid barrier material as well as in sensors. NIPAAM grafted with PVDF *via* the thermally induced graft copolymerisation method produces porous PVDF-g-NIPAAM membranes [4], wherein the pore structure can be manipulated to provide the necessary pore size distribution according to the environmental temperature. Whilst, this is useful in terms of controlling the moisture vapour transmission rate, the liquid permeation properties of non-porous PVDF-g- NIPAAM membranes have not so far been reported.

In this research, a PVDF-g-NIPAAM polymer is synthesised via thermally induced graft copolymerisation and a non-porous membrane is produced by applying high pressure and heat slightly below the melting point of the PVDF porous membrane [5]. The grafting effect of NIPAAM on the PVDF-g-NIPAAM was examined by means of FTIR and ToF-SIMS, and the microstructure of the resultant non-porous membrane was examined by SEM and mercury porosimetry. The liquid chemical permeation and water transmission properties of the non-porous membranes were evaluated in relation to their microstructural characteristics.

2. EXPERIMENTAL

2.1 Materials

PVDF Hylar® 301 powder was obtained from an industrial source (Solvay & Solexis). NIPAAM with 99% purity (Fisher Scientific Ltd.) was purchased and recrystallised in n-hexane before use. N-methyl-2-pyrrolidone (NMP) 99%+ (purity) and N,N-dimethylformamide (DMF) were obtained from VWR International and Sigma Aldrich respectively.

A 500-µm gap knife casting (K-Bar) and a glass plate of 30x30 square centimers were used to cast membranes prior to heat treatment and evaluation. A heat press system was used (Stewart-Buchanan, Glasgow, UK) that can be adjusted to apply the required levels of pressure and temperature to the PVDF-g-NIPAAM porous membranes.

2.2 Ozone treatment of PVDF material

The PVDF polymer in NMP solution at a concentration of 75 g dm^{-3} was oxidised ready for copolymerisation with NIPAAM through a continuous stream of O_2/O_3 flow at room temperature for 24 hours. The ozone flow has a concentration of 3000 mg hour^{-1} and is generated from an ozone generator model TCB-Y913GA2C (Trump XP Company, China).

2.3 PVDF-g-NIPAAM copolymerisation and membrane preparation

Both ozone activated PVDF polymer and NIPAAM polymer monomers in a certain mass ratio were introduced into NMP solution in a three-neck round-bottom flask. The copolymerisation was carried out in nitrogen atmosphere at 60°C for 6 hours. The resultant PVDF-g-NIPAAM copolymer solution was cooled in an ice bath and precipitated in excess of distilled water and further purified by stirring in distilled water for 48 hours, before being filtered and dried. The mass ratio of NIPAAM monomer and PVDF polymer is shown in Table 1.

Table 1. Copolymerisation of NIPAAM and PVDF in different mass ratios

Sample no.	Mass ratio (NIPAAM:PVDF)	%NIPAAM in PVDF/NIPAAM solutions
A1	1:1	50
A2	1:10	9.1
A3	1:100	1

The resultant PVDF-g-NIPAAM polymer was made into porous membranes following the procedure described as follows. 2 g of PVDF-g-NIPAAM copolymer material was re-dissolved in 10 ml of DMF at 60°C for 6 hours and left at room temperature for 12 hours to be degased. The copolymer solution was then cast on the glass plate using a 500-µm gap casting knife (K-Bar) and the membrane obtained was immediately immersed in distilled

water for 2 minutes to be solidified. The membrane was then dried at 40°C for 12 hours ready for further processing.

In order to obtain PVDF-g-NIPAAM copolymer membranes with reduced porosity, each PVDF-g-NIPAAM porous membrane was compressed in a Stewart-Buchanan heat press system at 150°C and 150 kPa for 60 minutes.

2.4 Methods for the characterisation of microstructure and properties of resultant PVDF-g-NIPAAM membranes

The chemical compositions and micro- and nano-porous structures of the resultant PVDF-g-NIPAAM copolymer membranes were characterised, and their liquid permeation and moisture transmission properties were measured, the linkage between the structure and properties of the PVDF membranes were examined.

2.4.1 Characterisation of the chemical compositions

The surface chemical compositions and the active groups of the resultant PVDF-g-NIPAAM were examined. The surface chemical composition of the resultant PVDF-g-NIPAAM was characterised by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in an IoN-Tof 'TOFSIMS IV' system at the Intertek Wilton laboratory, UK. The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the active groups throughout the resultant PVDF-g-NIPAAM polymer powder was characterised in a Perkin- Elmer spectrum BX spectrophotometer.

2.4.2 Examination of porous structures

The micro- and nano- porous structure of the resultant PVDF-g-NIPAAM copolymer membranes were characterised using both Scanning Electron Microscopy (SEM) and mercury porosimetry. The surface structure morphology of the PVDF-g-NIPAAM membranes was investigated at a magnification of 2000 times (Jeol JSM-6610LV scanning electron microscope).

Both the pore size distribution and surface area of the pores in the range of 5µm to 2nm in the PVDF-g-NIPAAM membranes obtained was examined by mercury injection porosimetry (Micromeritics Instrument Corporation, University of Leeds).

2.4.3 Liquid chemical permeation test

An open-loop chemical permeation test system consisting of a liquid permeation cell (Pesce Lab Sales Ltd, USA) and a multifunction PID gas detector (iBrid MX6 from Scientific Instrument Inc. USA) was built up based on the standard EN ISO 6529:2001. The testing was carried out at ambient temperature in the range of 20°C to 25°C. N-hexane was used as a challenge chemical using the ambient gas as the collection medium at a flow rate of 250 ml min^{-1}, which is slightly higher than the standard method.

The real-time dynamic change of the concentration of the challenge chemical permeating through the sample membrane was monitored and recorded by the multifunction PID gas detector. The dynamic permeation rate of the challenge chemical through the sample was calculated by using equation 1 [6];

$$\varphi_i = \frac{c_i q_v}{A} \tag{1}$$

Where,

φ_i is the permeation rate at t_i, (μg cm^{-2} min^{-1})

i is an indexing number to indicate the specific concentration c_i that was measured at time t_i

t_i is the time elapsed beginning with the initial chemical contact and end with the measurement of concentration c_i (min)

c_i is the concentration of test chemical in collection medium (μg dm^{-1})

q_v is the flow rate of fresh collection medium through the cell (dm min^{-1})

A is the area of the material specimen contacted (cm^2)

2.4.4 Water vapour transmission rate (WVTR)

The water vapour transmission rate (WVTR) of the PVDF-g-NIPAAM membranes was measured using a modified measurement method based on the standard BS 7209:1990. In the standard test (BS7209:1990), the temperature of the water used for the testing was maintained at 20°C throughout the test. However, in order to compare the results of the WVTR below and above the LCST, the WVTR of each PVDF-g-NIPAAM membrane were measured at two water temperatures: 20°C and 40°C. The testing procedure is described as follows. The membrane sample was cut into pieces and conditioned in a temperature of 20±2°C and a relative humidity of 65±2% at least 1 hour before testing. Glass cups with fitted cover rings were filled with distilled water to give a 10±1 mm deep layer of air between the surface of water and the sample covering on top. In the case of the experiment at 40°C, the distilled water was heated to 40°C before filling the cups. Then, the area of the membrane fitted on the edge of the cups were examined and sealed with extra silicon additives in case of cracks formed in the membrane during the membrane fitting, the assembled cups were placed into an environment chamber which was set the air velocity at 0.1 m s^{-1} in order to avoid the formation of still air layer above the cups. A relative humidity in this chamber was also adjusted at 65±2% with the temperature was set at 20°C and 40°C, respectively. The weights of the cup before and after a certain period of time were obtained for the calculation of the WVTR based on the equation (2) [7];

$$WVTR = \frac{G \times 24}{A \times t} \qquad (2)$$

Where,

$WVTR$ is the water vapour transmission rate (g m^{-2} day^{-1})

G is the weight change of the cup (g) before and after a certain period of time, t.
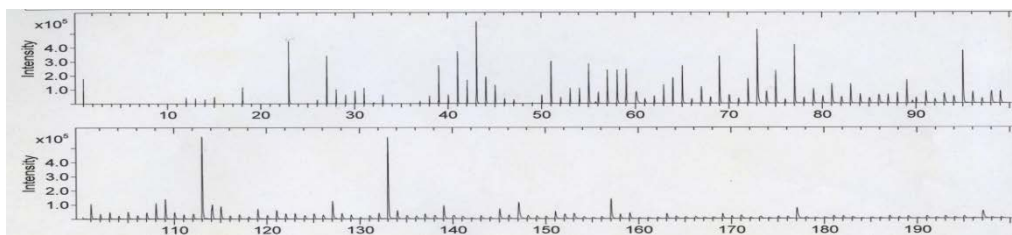
A is the effective area of the membrane specimen exposed to the water cup (m^2)

t is the measuring time (hour)

3. RESULTS AND DISCUSSIONS

3.1 The presence of NIPAAM in the NIPAAM-PVDF material

The surface analysis of the PVDF-g-NIPAAAM sample was examined by ToF-SIMS as shown in Figure 1.

Figure 1. Positive ion ToF-SIMS spectra (0<m z^{-1}<300) of A1

The positive ions in the ToF-SIMS spectra of the PVDF-g-NIPAAM membrane made from 1:1 of NIPAAM:PVDF as a result of the copolymerisation are indicated in Figure 1. The prominent signal for NIPAAM is observed at 58 m z^{-1} and relates to the protonated dimethylamine ((CH_3)$_2$$NH_2^+$) in the polymer [8]. This suggests that NIPAAM was present in the NIPAAM-g-PVDF membrane and that it may be a result of copolymerisation of PVDF and NIPAAM. The high intensity peaks of monomer fragments at 114 m z^{-1} can be attributed to the $C_6H_{12}NO^+$ fragments in the NIPAAM polymer [9], suggesting copolymerisation of NIPAAM and activated PVDF had successfully occurred. Based on spectra, it was reasoned that NIPAAM had been grafted on to the PVDF backbone.
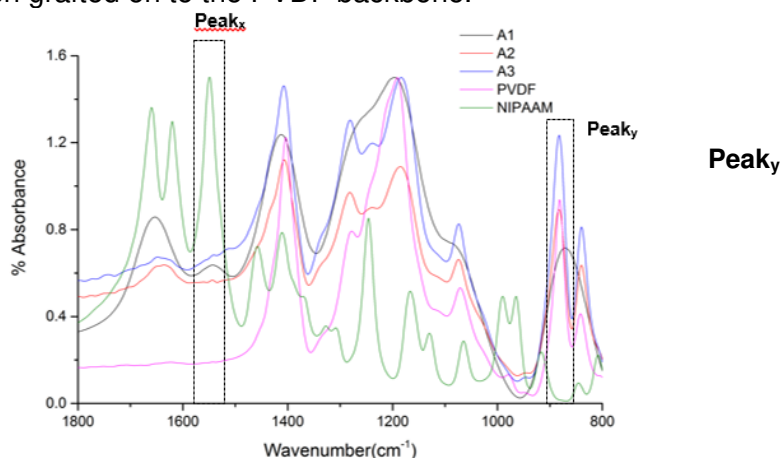
Figure 2. FTIR spectrums of the PVDF powder, NIPAAM and the three PVDF-g-NIPAAM membranes

The active groups of the PVDF-g-NIPAAM copolymer material before preparation of the membrane were further analysed by evaluating their FTIR spectra, as shown in Figure 2. The absorption bands at 1680-1642 cm^{-1} and 1550-1538 cm^{-1} were associated with the amide II group as a result of the C=O stretching and N-H stretching of NIPAAM respectively [10, 11]. The absorption peak of 1175-1290 cm^{-1} is attributable to the CF_2 functional groups of the PVDF and the absorption peak at 884 cm^{-1} and 840 cm^{-1} were respectively assigned to CH_2 rocking and CF_2 asymmetric stretching [12]. The absorbance spectra of the three different NIPAAM concentrations, the PVDF powder and the NIPAAM were measured as indicated in Figure 2.

With an increase in the mass ratio of NIPAAM to PVDF from 1:100, 1:10 to 1:1, the intensity of the absorption bands at 1680-1642 cm^{-1} and 1550-1538 cm^{-1} (amide II group) was found to substantially increase in comparison to pristine PVDF powder.

In studying the effect of NIPAAM concentration in the NIPAAM:PVDF solutions on the proportion of NIPAAM grafted onto the PVDF, the increase of grafted NIPAAM in the copolymers can be represented by the ratio of the amide II group at 1546 cm^{-1} from NIPAAM and the alkene peak at 884 cm^{-1} from the PVDF (Table 2). The proportion of NIPAAM grafted in the copolymer increased as the mass ratio of NIPAAM:PVDF increased.

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Table 2. The proportion of NIPAAM grafted onto the PVDF-g-NIPAAM materials

Sample no.	Mass ratio of NIPAAM:PVDF	Intensity of the peaks from Figure 2		Ratio of intensity of Peak$_x$:Peak$_y$ in grafted copolymer
		Peak$_x$ At 1546 cm^{-1}	Peak$_y$ At 884 cm^{-1}	
A1	1:1	0.64	0.67	0.95:1
A2	1:10	0.57	0.89	0.64:1
A3	1:100	0.68	1.23	0.55:1

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3.2 Microstructure and surface morphology of resultant PVDF-g-NIPAAM non-porous membranes

SEM images of the three different copolymer membranes are shown in Figure 3. Porous structure was evident in the surface of the PVDF-g-NIPAAM membranes, and two different areas could be distinguished, distributed across the surface, translucent areas and transparent areas, which can be linked to the heat treatment used during manufacture. It appeared that the porous structure was confined mainly to the translucent areas.

(a) Translucent area	(b) Transparent area
(c) Translucent area	(d) Transparent area
(e) Translucent area	(f) Transparent area
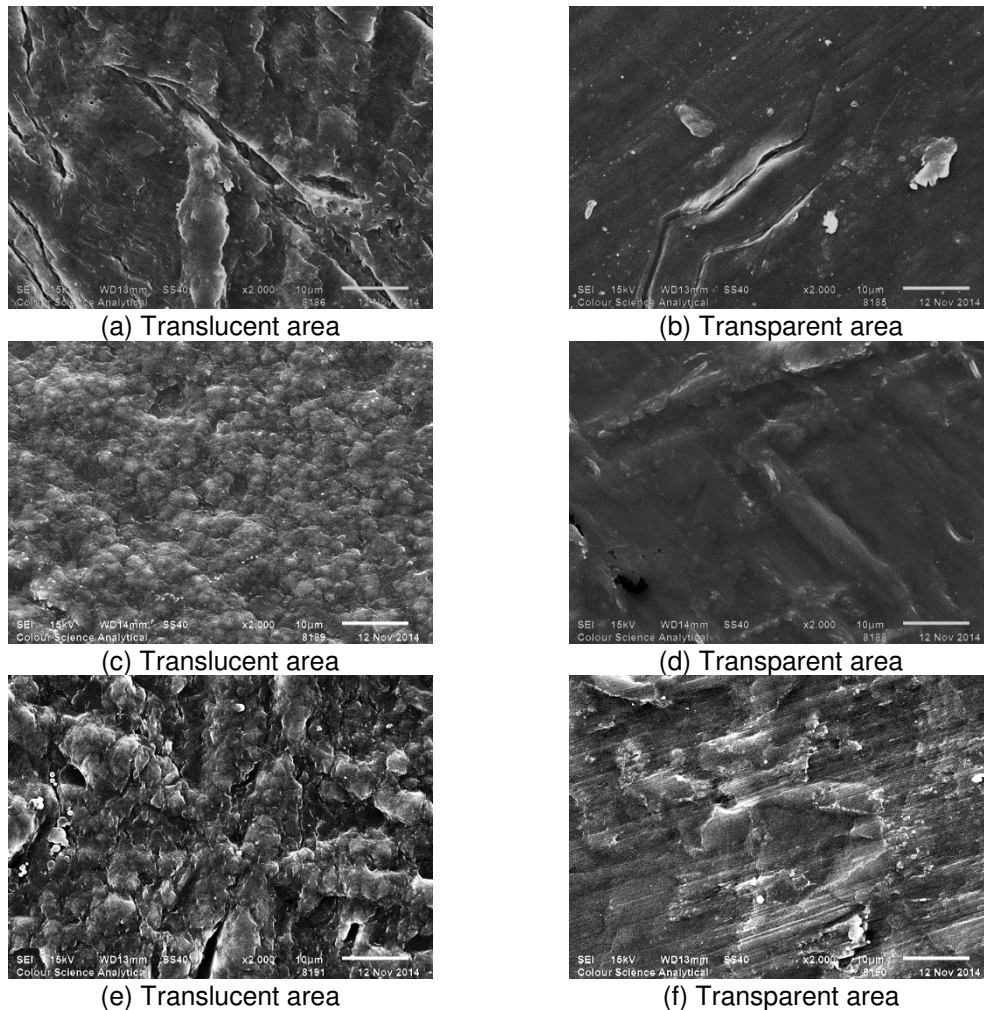
Figure 3. SEM micrographs of translucent and transparent areas in the PVDF-g-NIPAM membranes: (a, b) A1, (c, d) A2 and (e, f) A3

Differences in spatial composition of the PVDF-g-NIPAAM membranes were explored using EDX tool, as summarised in Table 3. It was expected that all the PVDF-g-NIPAAM membranes would contain oxygen, which is one of the elemental components of both NIPAAM and the ozone-oxidised PVDF. Interestingly, only the transparent area of 1:1 mass ratio of NIPAAM:PVDF indicated the presence of oxygen on the surface, which may be due to the amount of oxygen being too small. In summary, the porous structure was mainly associated with the NIPAAM component in the PVDF-g-NIPAAM membranes.

Table 3. Elemental composition of PVDF-g-NIPAAM membrane surfaces as determined by EDX

Membranes		C%	F%	O%
A1	Translucent area	34.6 ± 0.5	64.0 ± 0.5	1.4 ± 0.2
	Transparent area	35.0 ± 0.5	65.1 ± 0.5	-
A2	Translucent area	34.1 ± 0.6	65.9 ± 0.6	-
	Transparent area	33.0 ± 0.4	67.0 ± 0.4	-
A3	Translucent area	33.1 ± 1.1	67.0 ± 1.1	-
	Transparent area	33.0 ± 1.2	67.0 ± 1.2	-

3.3 Characteristics of the membrane porous structure

The characteristics of the porous structures, specifically, the pore size distribution and the average pore diameter, of the PVDF-g-NIPAAM membrane were investigated using mercury porosimetry as shown in Figure 4. The volumetric pore size distributions of the three PVDF-g-NIPAAM membranes made from different NIPAAM concentrations were in the range of 0-5 microns, and most of the pores in terms of the pore volumes were macropores, which relates to pores larger than 50 nm (or 0.05 microns) in diameter. However, there was also a large proportion (0.27, 0.29 and 0.46 cm^3 g^{-1} in membranes A1, A2 and A3 respectively) of mesopores, which are pores between 20nm~50nm (or between 0.002 and 0.05 microns in Table 4). The average pore diameters of the PVDF-g-NIPAAM membranes were 0.38, 0.32 and 0.25 microns for the A1, A2 and A3 membranes respectively, which means the pore volumes tended to increase as the mass ratio of NIPAAM in the copolymer increased.
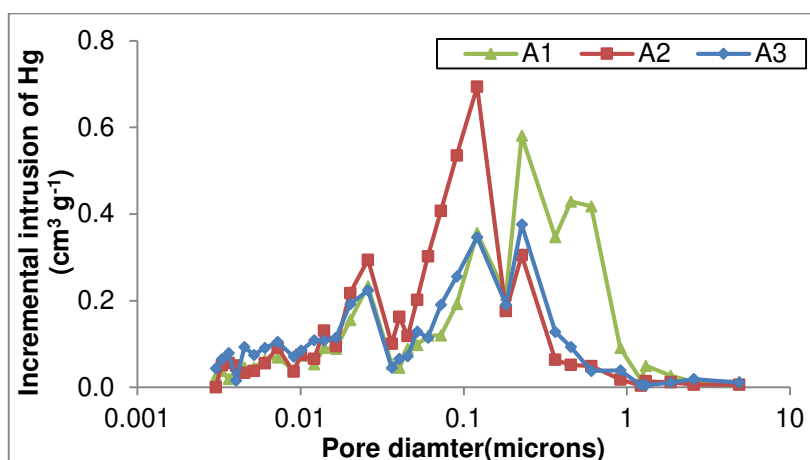

Figure 4. Pore size distribution of the PVDF-g-NIPAAM membranes

Table 4. Average pore diameter and pore volume of the PVDF-g-NIPAAM membranes

| Property		A1	A2	A3
Average pore diameter (microns)		0.38	0.32	0.25
Mesopores	Pores volume (cm^3 g^{-1})	0.27	0.29	0.46
	Percentage (%)	6.3	6.3	12.8
Macropores	Pores volume (cm^3 g^{-1})	4.07	4.23	3.15
	Percentage (%)	93.7	93.7	87.2
Total pores volume (cm^3 g^{-1})		4.35	4.52	3.61

3.4 Liquid permeation rate

The liquid chemical permeation rate in the PVDF-g-NIPAAM membranes was determined based on the method described in the section 2.4.3. The permeation rate and the breakthrough time of the three membranes of different concentration of NIPAAMs in the copolymer membrane are shown in Figure 5. The permeation rate at 0 µg cm^{-2} min^{-1} is not possible to include in such a logarithmic curve.
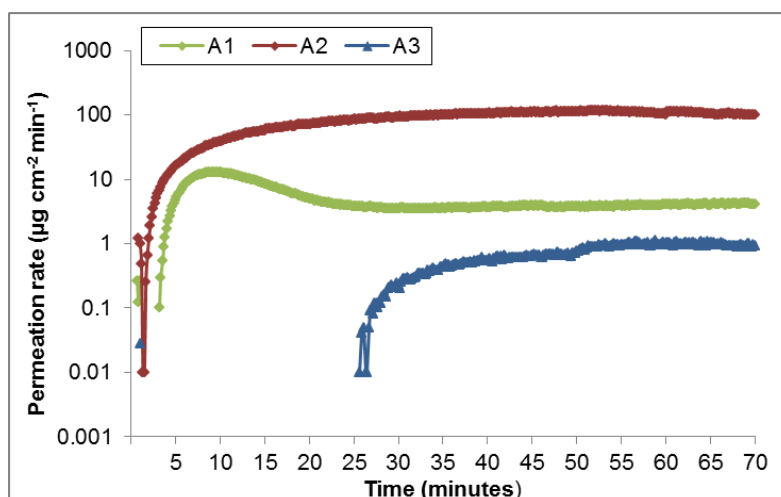
Figure 5. The dynamic liquid chemical permeation rate of the three PVDF-g-NIPAAM membranes

There are two possible mechanisms for the liquid permeation through this temperature sensitive polymer membrane. The first one is the presence of the hydrophilic NIPAAM polymer in the copolymer membrane, the NIPAAM polymer tends to form into amorphous structure and to let liquid chemicals easily diffusion through in comparison with crystallised PVDF polymer region; thus the more NIPAAM contained in the co-polymer, the smaller breakthrough time of the copolymer membrane. In Figure 5, the PVDF-g-NIPAAM membrane made from a smaller proportion of NIPAAM (1:100 for A3) shows the breakthrough time of 56 minutes at the permeation rate of 1 µg cm^{-2} min^{-1}, this is near to the performance of commercial impermeable membranes and the pristine nonporous PVDF membrane, while the other two copolymer membranes made from greater mass ratios of NIPAAM:PVDF (1:1 for A1 and 1:10 for A2), exhibit much shorter breakthrough time (4 and 1 minutes respectively) and ultimate greater permeation rate.

The second mechanism is the liquid chemicals flowing through the pores in the copolymer membranes; the velocity and the amount of the liquid transporting through the porous membranes depends on both the amount and the sizes of the pores formed in them. As shown in Figure 6, the greater permeation rate and smaller breakthrough time corresponds to the smaller average pore volumes in these membranes , and the greater pore volumes is also related to the smaller breakthrough time.

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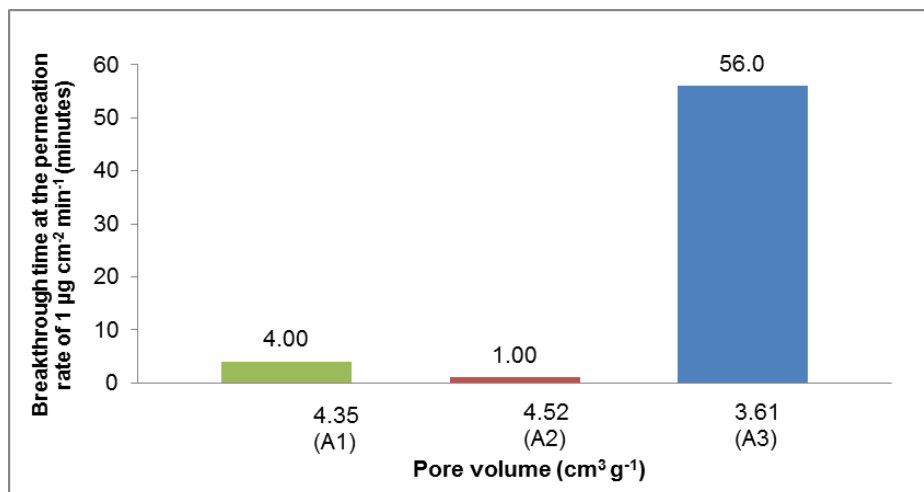
Figure 6. The breakthrough time at 1 µg cm^{-2} min^{-1}of the in PVDF-g-NIPAAM membranes

### 3.5 The water vapour transmission rate

The water vapour transmission rate of the three PVDF-g-NIPAAM membranes (A1, A2 and A3) were examined at two different temperatures, 20°C and 40°C, using the method described in section 2.4.4. Comparisons of the WVTRs of the three membranes at the two different temperatures are shown in Figure 7, and the influences of the pore volumes of the membranes on the WVTRs are indicated in Figure 8.
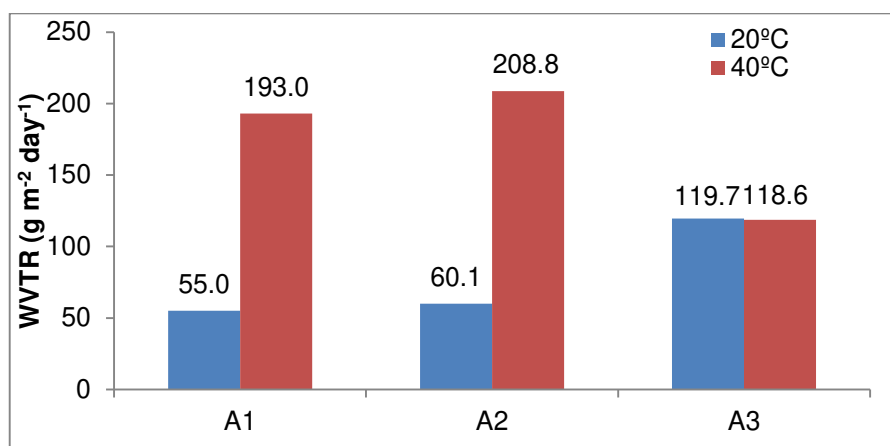
Figure 7. The effect of the proportion of NIPAAM in PVDF-g-NIPAAM membranes on their water vapour transmission rate (WVTR)

It was found that the WVTR of the membrane made from smaller mass ration (1:100) of NIPAAM:PVDF is hardly affected by the temperature irrespective of whether it is below or above the LCST of NIPAAM. However, the WVTR of the copolymer membranes made from higher concentrations of NIPAAM (mass ratio of 1:1 and 1:10 for NIPAAM:PVDF) exhibited higher WVTR when the environmental temperature changed from 20°C to 40°C. For the copolymer membranes containing a higher proportion of NIPAAM (1:1 and 1:10 in mass ratio of NIPAAM:PVDF), their WVTR at the environmental temperature (40°C) higher than the LCST of NIPAAM (32°C) is as approximately 3.5 times as that at the environmental temperature (20°C) lower than the LCST of NIPAAM.

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The two mechanisms for liquid permeation through this temperature sensitive polymer membrane also apply to the water vapour transmission through it, i.e., the water vapour diffusion through both the hydrophilic NIPAAM polymer region and the pores in the copolymer membranes. When environmental temperature changes, it appears that, regardless of whether or not it is grafted to the PVDF, the NIPAAM polymer contained in the PVDF-g-NIPAAM copolymer membrane is in a swollen state when the environmental temperature is lower than the LCST of NIPAAM. This means that, when the temperature is below the LCST, the NIPAAM grafted in the copolymer membrane will be in the swollen state, which leads to smaller pore sizes. When the environmental temperature is higher than the LCST of NIPAAM, the NIPAAM grafted in the membrane will be in a shrunken state, which leads to larger pore sizes in the copolymer membrane [11]. This could also explain why, for the PVDF-g-NIPAAM membranes containing large amount of NIPAAM (prepared in a solution where the mass ratio of NIPAAM:PVDF is greater than 1:10), its WVTR in an environmental temperature above the LCST of NIPAAM is greater than that at a temperature below the LCST of NIPAAM.
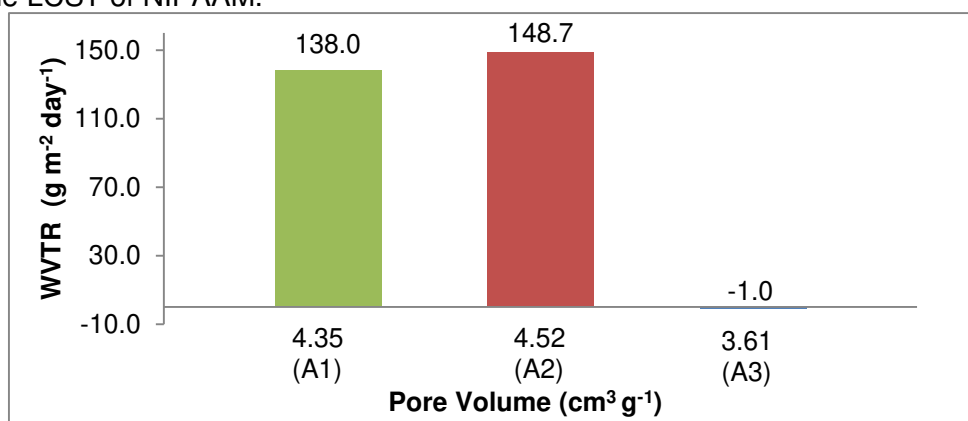
Figure 8. The WVTR differences between 20°C and 40°C against the pore volume of the PVDF-g-NIPAAM membranes

The relationship between the pore volumes in the membrane and the change of the WVTRs between 40°C and 20°C was indicated in Figure 8. The membrane having greater pore volumes (A2) measured in 20°C have slightly greater change of the WVTRs between 40°C and 20°C in comparison with the membrane having less amount of pores (A1).

4. CONCLUSIONS

PVDF-g-NIPAAM membranes produced by thermally induced graft copolymerisation to deliver temperature-sensitive materials have the potential to be applied as a smart barrier membrane in chemical protective clothing. The presences of the NIPAAM in the PVDF-g-NIPAAM copolymer and the porous structure of its membranes were examined by using various tools including ToF-SIMS, FTIR and SEM. The liquid chemical permeation rate and the water vapour transmission rate of the temperature sensitive membranes were studied. And the mechanisms for both liquid permeation and water vapour transmission through the temperature sensitive polymer membranes are attributed to both the amorphous hydrophilic NIPAAM polymer regions contained in the PVDF-g-NIPAAM copolymer and the pores formed in its membranes. It is found that the breakthrough time at a permeation rate of 1 µg cm^{-2} min^{-1} for the copolymer membranes made in a smaller mass ratio of NIPAAM:PVDF at 1:100 is much greater (60 minutes) in comparison with a smaller breakthrough time (4 minutes) for the membrane made in a greater mass ratio of NIPAAM:PVDF at 1:1. Also, PVDF-g-NIPAAM membrane containing greater pore volumes also exhibit smaller breakthrough times. The WVTR of PVDF-g-NIPAAM membranes containing NIPAAM of certain levels at an environmental temperature of 40°C, which is above the LCST of

NIPAAM, was markedly higher than that at a temperature of 20°C, which is lower than the LCST.

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