Utilization improvement of PDMS and fluoropolymers by mutual application

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Abstract. We investigated about the utilization improvement of the PDMS and fluoropolymers by mutual application in environmental analysis. We were conducted the direct fluorination with mild condition on the PDMS films and analyzed its surfaces before and after fluorination. The results of FTIR and SEM analysis on the PDMS films showed that the film surfaces were fluorinated without irreversible deformation by the fluorination. During the fluorination, the measured contact angles of water and several alcohols on the PDMS films decreased with time and that of most alcohols decreased to 0 after 30 minutes. The surface energy of fluorinated PDMS films has increased by 2 times. Also, we investigated the influence factors on the change of permeation rate of water through PDMS tubes with time. It was observed that the change of permeation rate of water through PDMS tube was affected by temperature, water phase and spatial distribution of water. From these results, we could verify the principal causes of the decrease of permeation rate of water through PDMS tube with time and proposed a new experimental setup for reducing the variation of permeation rate of water less than 2%.

Keywords: PDMS; fluoropolymers; direct fluorination; permeation rate; PDMS permeation tube.

1. Introduction

Silicone polymers and fluoro polymers are one of the most widely used polymeric materials in environmental analysis. Fluoro polymers have superior chemical and thermal stability, gas selectivity of gas separation membranes and barrier property (Garcia-Payo *et al*. 2010, Hansen *et al*. 2007, Le Roux *et al*. 1994, Mohr *et al*. 1991, Syrtsova *et al*. 2004). Polydimethylsiloxane, one of the silicone polymers, have low surface tension, hydrophobic property, non-inflammability and non-toxicity, high gas permeability (Higuchi *et al*. 2010, Zhou *et al*. 2010). These materials that were paid high attention especially in environmental analysis has been widely used commercially as materials of permeation tube to manufacture low concentration (mostly ppb to ppt level) of standard gases/ vapour mixtures and materials of solid phase micro-extraction (SPME) probe, respectively.

Static or dynamic methods are well-known way for manufacturing of standard gases. Permeation method is one of the dynamic methods by which complex mixtures can be made by permeating target compounds through polymeric tube walls and mixing them with dilution or (carrier) gas (Zondervan and Roffel 2010). If we use permeation method, we can avoid adsorption and/or condensation of gas compounds on the surface of containers which are the problems of static methods (Naganowska-Nowaka *et al*. 2005). Environmental standard gases can be prepared from liquids with

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low boiling point or condensable gases under low pressure such as generation of low concentration of water vapour standard (Neri *et al*. 2006, Huang 1998, Huang and Kacker 2003, Scace and Miller 2008). Also, using the method, standard vapour of air pollutants (Hashimoto and Tanaka 1980, Ohira and Toda 2005, Choi and Hawkins 1997) such as CO, CO_2, NO_X, SO_X, H_2S, a mixture of VOCs (Tumbiolo *et al*. 2005, Maria *et al*. 2002, Chung *et al*. 1999), halocarbons (Singh *et al*. 1977), formaldehyde (Hunter *et al*. 1999), toxins, organometallics (Larsson and Frech 2003, Gelaude *et al*. 2002) and other standards can be prepared. But, it has been well known that permeation rate can significantly be influenced by small fluctuation of temperature (0.1°C) and change with respect to time (Mitchell *et al*. 1992, Maria *et al*. 2002, Washenfelder *et al*. 2003). Also, physicochemical properties of target compounds and tubes are critical factors for gas permeation rate (Lucero 1971). Permeation rate of target compounds and flowrate of carrier gas determine concentration of mixtures, so constant concentration of standard gases can be produced by constant permeation rate and temperature. Permeation tubes made by fluoropolymers are the most widely used for manufacturing of low concentration of standard gases due to their low gas permeability. It is expected that PDMS is suitable material to manufacture high concentration of standard gases due to their 100 times higher permeation rate than that of fluoro polymers.

Probes made by PDMS has disadvantages such as low mechanical strength, weak stability in acid/base and organic solvents, and high gas permeability. On the other hand, fluoropolymers have superior chemical and thermal stability, non-adhesive property, and barrier property as mentioned before (Hansen *et al*. 2007). Therefore, it is expected that application of fluoro polymers on the PDMS surface, such as direct fluorination one of the most effective and promising method (Kharitonov 2008, Banks *et al*. 1994), would be a good way to enhance PDMS surface properties. Direct fluorination means that fluoro gas or its mixtures with inert gas (nitrogen or helium) are introduced onto the surface of polymeric materials to lead to spontaneous reaction. This method has been extensively studied and thoroughly reviewed by Kharitonov *et al*. (Kharitonov 2008, Maity *et al*. 2007, Tressaud *et al*. 2007, Kharitonov *et al*. 2005, Syrtsova *et al*. 2004, Kharitonov 2000, Kharitonov and Moskvin 1998).

Considering physicochemical properties and utilization improvement of PDMS and fluoro polymers, it is expected that mutual application would increase their availability in environmental analysis.

In case of needed high concentration of standard gases, using PDMS instead of fluoro polymer as permeation tube material would be a good way. In this research, factors (tube material, temperature, sample phase, and spatial distribution), influencing the constant permeation rate, were investigated by testing water permeation through PDMS tube under different environmental conditions. Also, novel experimental setup, which can minimize the fluctuation of permeation rate by using dual material, was proposed.

The other test in this research is direct fluorination on the surface of PDMS films under different fluorination time. Fluorination can be controlled easily and is usually rapid at room temperature without extra heat or solvents. But direct fluorination should be conducted under mild condition (low partial pressure of fluorine and room temperature) at an initial stage and more forcing condition at next stages because excessive direct fluorination can give rise to structural damage of surface polymers and irreversible deformation due to high reactivity of fluorine (Adcock *et al*. 1995, Lagow and Margrave 1979). After fluorination, changes of surface properties of PDMS films were observed by spectroscopy apparatus.

2. Experimental section

2.1 PDMS tube test

Porous polydimethylsiloxane tube (Korea Ace Scientific Co.; 4 mm inner diameter, 6 mm outer diameter; H_2 permeability at 25°C = 6587×10^{-10} cc•mm/sec•cm^2•cmHg) and relatively non-porous tetrafluoroethylene-hexafluoropropylene copolymer tube (Cole Parmer, FEP; H_2 permeability at 25°C = 1.1×10^{-10} cc•mm/sec•cm^2•cmHg) were prepared with more than 5 cm (minimum length to permeate occur) in length. Both ends of the PDMS tube were plugged with pvc balls (6 mm in diameter) as shown Fig. 1(a). More than 95% inside volume of tube was filled with distilled water and permeation rate of water was measured with temperature. To investigate spatial distribution of water influencing on the permeation rate of tube, permeation rate of water through upright and lying tubes were measured. Also, permeation rate of water through tube inserted with 0.2 g of paper wick (Kimwipes™, Yuhan-Kimberly Professional Co.) was measured to verify effect of concentration gradient of water vapour. Dual material tube made by PDMS connected with tetrafluoroethylene-hexafluoropropylene copolymer, was prepared for measuring of permeation rate of water with respect to the water phase. As shown in Fig. 1(b) and 1(c), In case of dual material tube is downward only liquid water may contact with PDMS part. In case of opposite direction, only water vapour may contact with PDMS part.

2.2 Fluorination on the PDMS films test

PDMS (purchase from Dow Corning Sylgard 184® dual-component system) base solution (18.1 g in 100 ml Hexane (HPLC grade)) and curing agent solution (1.84 g in 100 ml Hexane) were prepared. The two solutions were degassed by ultra-sonication and were mixed at a volume ratio of 1:1 in short time. 1 ml of mixed solution was located on the petri-dish and was spin coated for 5 seconds at 2000 rpm. Using a forced convection oven at 80°C, solvents on the coated films were removed and cross-linking reaction was finished. Impurities such as water vapour, oxygen and dusts on the

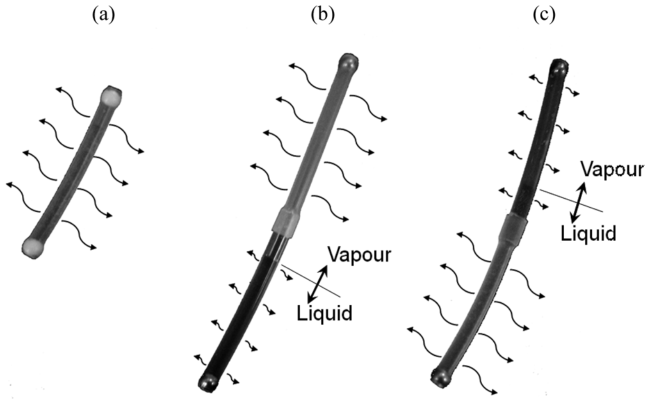


Fig. 1 Configurations of permeation tubes (a) single material tubes plugged with PVC balls. (b) dual material tube that silicone part is contacting water vapour only. (c) dual material tube that silicone part is contacting liquid water

film surface were removed by vacuum and nitrogen ([N_2]>99.9999%) purging. Diluted fluorine gas (2021 ppm in nitrogen balance) was used to fluorination and fluorination was controlled by vacuum and nitrogen purging. Temperature kept constant at 25°C. All the surface properties of PDMS were observed before and after fluorination. Using the Fourier-transform infrared spectroscopy (JASCO FTIR-4100) and scanning electron microscopy (SEM, Philips XL30S FEG), chemical species on the PDMS surface and surface morphology were observed. Also, using the drop shape analyser (KRÜSS DSA100), the contact angles of deionized water and several alcohols (purity>99%) were measured with a sessile drop method. Measured values were used to calculate the surface energy of PDMS films.

3. Results and discussion

3.1 PDMS tube test

3.1.1 The effect of temperature

Fig. 2 shows permeation rate and vapour pressure of water in the PDMS tube at different temperatures. The permeation rate and vapour pressure of water in the tube increased as the temperature increased. As we know, vapour pressure of water increases as the temperature increases. It is thought that higher vapour pressure due to higher temperature brought about increase of partial pressure difference between PDMS walls which is a driving force for the permeation. That is why permeation rate of water increased as the temperature increased. But it should be considered that other physicochemical properties of target compounds and tube which can influence on permeation rate of water through PDMS tube.

3.1.2 The effect of water phase

It has been reported in previous permeation studies that permeation rate of single material tube

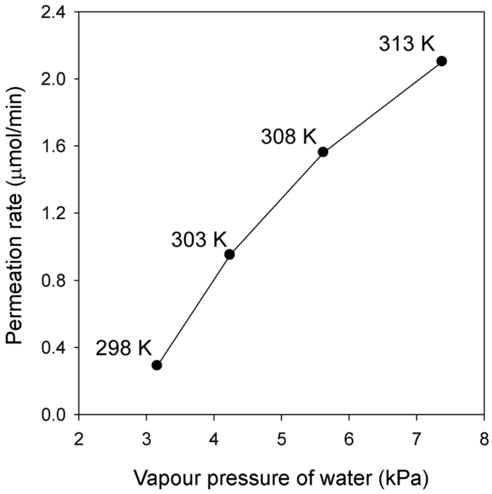


Fig. 2 The relationship between water vapour pressure and permeability through unfluorinated silicone tubes in different temperature

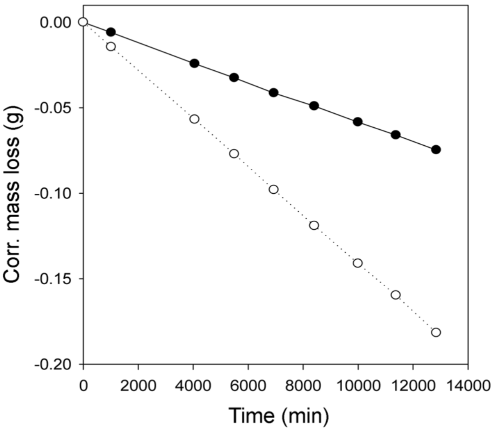


Fig. 3 Mass loss of a dual-material permeation tube due to the permeation of water vapour (●) and the permeation of liquid water (○) at 303 K

changes with time (Mitchell *et al.* 1992, Washenfelder *et al.* 2003). In this study, we hypothesized that the different permeation rate between liquid and vapour of water can affect the change of permeation rate with time. Fig. 3 shows change of permeation rate of different phase of water through dual material tube with respect to time. The average permeation rate of liquid water (0.783 mol•min^{-1}) was equal to 2.43 times as fast as that of vapour (0.322 mol•min^{-1}). Because liquid water permeation occurred under continuously water molecules collision and dissolution on PDMS wall, whereas water vapour permeation occurred under competition between refilling of water vapour due to evaporation from the interface and loss of liquid water due to permeation.

If permeation rate of water vapour through tube exceeds evaporation rate of water from the interface, headspace of water in the tube may not be saturated and partial pressure of water can not reach their maximum vapour pressure at the temperature due to loss of water from permeation. Also, unsaturated headspace volume of water may increases with respect to time. Therefore, it seems obvious that the different permeation rate between liquid and vapour of water can significantly affect the change of permeation rate of single material tube with time.

3.1.3 The effect of spatial distribution of water

During a permeation process, the water vapour from the liquid/vapour interface is diffused only along the bore of the tube, whereas water vapour is permeating through all the inner surface of the tube. Therefore, there is a concentration gradient of water vapour, in the direction to the height of the tube, between the top of the tube and interface of two phases. We hypothesized that concentration gradient of water vapour may affect permeation rate. To verify this hypothesis, permeation rates of water through upright and lying PDMS tubes were measured at 303K, 313K, as shown in Table 1.

As shown in Table 1, at 303 K, permeation rate of upright tube has decreased by 48%, and that of lying tube has decreased by 17.1%. Also, at 313K, permeation rate of upright tube has decreased by 12.2%, and that of lying tube has decreased by 5%.Through this result, it seemed obvious that spatial distribution of water inside the tube can significantly affects the total permeation rate of water. This result can be explained by the difference rate between permeation and diffusion, vaporization of water.

If permeation rate of water exceeds diffusion and vaporization rate of water, concentration of water

Table 1 Permeation rate of water (μmol/min) through unfluorinated silicone tubes in different temperature and tube orientation

Temperature	303 K			313 K		
	Early stage (1500 min)	Late stage (20000 min)	%Diff.* (%)	Early stage (1500 min)	Late stage (10000 min)	%Diff. (%)
Lying	1.137±0.044	0.971±0.045	17.1	1.989±0.027	2.094±0.014	5.0
Upright	1.162±0.025	0.785±0.015	48.0	2.020±0.123	1.801±0.087	12.2

$$*\%Diff. = \left|\frac{Q_{early}}{Q_{late}}\times 100-100\right|$$

Table 2 Permeation rate of water through unfluorinated silicone tubes in different design

	Water-only			Soaked-paper		
	Early stage (100 hours)	Late stage (500 hours)	%Diff.* (%)	Early stage (100 hours)	Late stage (350 hours)	%Diff. (%)
Permeation rate (μmol/min)	1.791±0.024	0.846±0.010	52.8	1.960±0.006	1.985±0.069	1.3

$$*\%Diff. = \left|\frac{Q_{early}}{Q_{late}}\times 100-100\right|$$

could be heterogeneous in the tube and water vapour may not be able to fully saturate the headspace. As a result, water vapour in the tube may have concentration gradient in the direction to the tube height. As time passes, the headspace volume of water increases and the total permeation rate of water decreases. Difference of permeation rate at 313K is smaller than that of at 303K which means lower concentration gradient of water vapour due to higher water vapour pressure at 313K is a good example.

Table 2 shows the change of permeation rate of water through upright tube whether paper tissue was inserted in tube or not. Difference of permeation rate between early and late stage is 1.3% at tube with paper wick and 52.8% at tube without paper wick. Permeation rate of water through the tube with inserted paper tissue is higher and more constant than that through the tube without paper tissue. This may be because concentration gradient of water vapour in the headspace was minimized by paper tissue. Paper tissue provided higher surface area to evaporate water and contact sites between soaked water and inner surface of the tube.

3.2 Fluorination on the PDMS film test

It has been reported that functional groups and/or specific atoms on the surface of polymer film could be substituted to fluorine atoms by direct fluorination (Patwardhan *et al.* 1997). In this study, direct fluorination was performed on the surface of the PDMS film under mild condition (fluorine gas 2021 ppm in nitrogen balance) with time. Fig. 4 represents FTIR analysis result on the structural change of film surfaces. Band absorbance intensities of IR spectra at 2960, 2906, 1258, 800 cm^{-1} decreased as the fluorination time increased. It has been reported that IR spectra of these region represent asymmetric and symmetric stretching (2960, 2096 cm^{-1}), symmetric deformation vibration

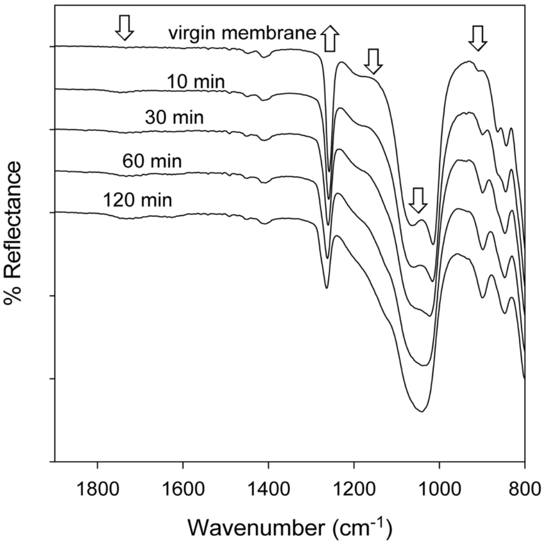
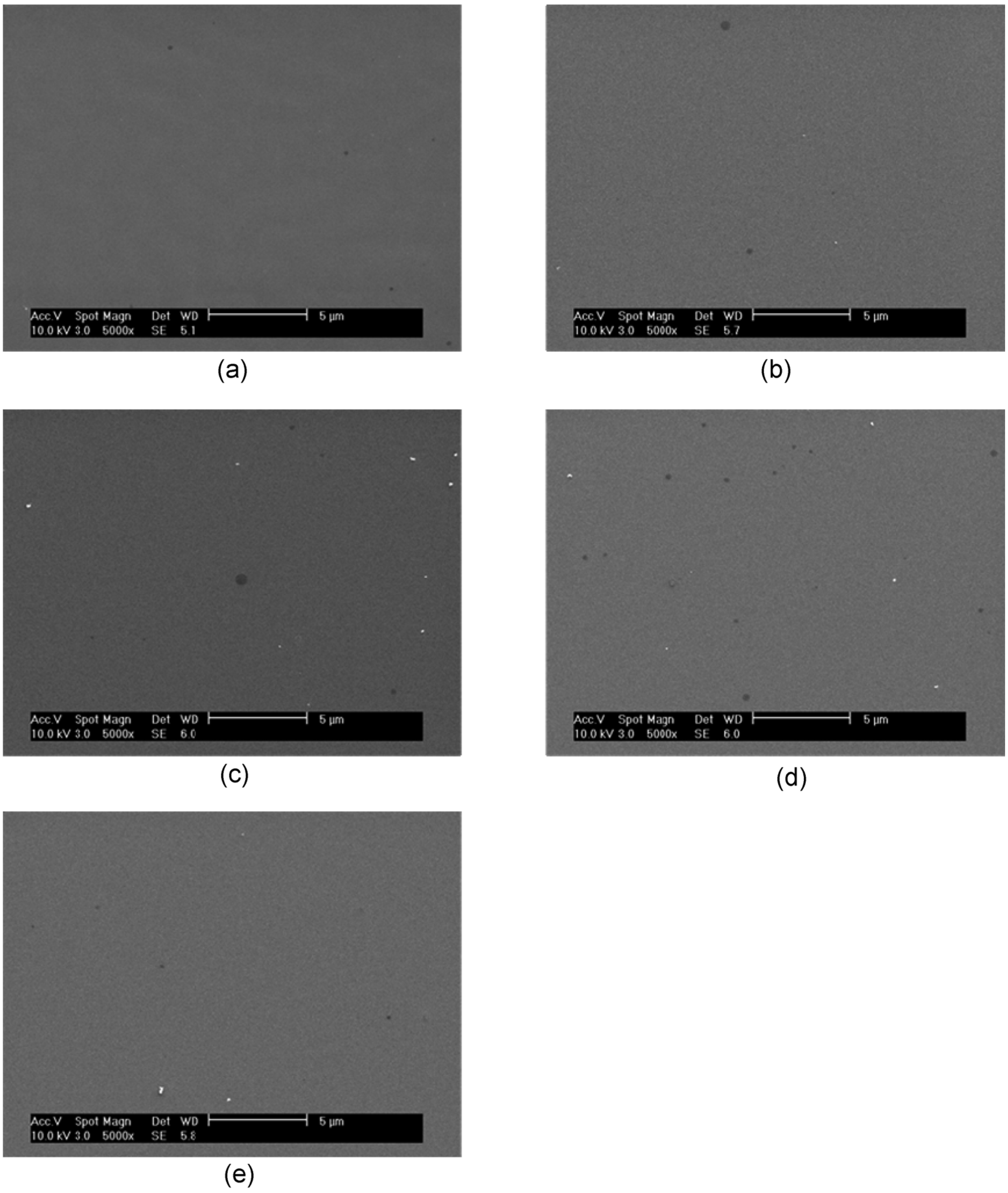


Fig. 4 FTIR spectra before and after direct fluorination of PDMS surfaces

(1258 cm$^{-1)}$ and rocking (800 cm^{-1}) of methyl groups, respectively (Smith 1960, Khoo and Liu 1998, Socrates 1980). An increase in band absorbance intensities at 1100-1150 cm^{-1} could also be attributed to formation of C-F bonds. Therefore, the changes of band absorbance intensities in these regions mean removal of methyl groups on the PDMS film surface and C-H bonds were transformed to C-F bonds by fluorine on the PDMS film surfaces. In addition, SEM images of PDMS film surfaces showed no particular change in the PDMS film topology during the fluorination. Therefore, as shown in Fig. 5, irreversible deformation (*i.e.*, within 120 min of fluorination reaction time) on the PDMS film surfaces due to excessive fluorination did not occur and we can conclude that the fluorination condition in this research to enhance surface properties of PDMS film surfaces were proper.

Table 3 shows the contact angles of water and several alcohols on the PDMS film surfaces with respect to the fluorination time. During the direct fluorination, the contact angles of water and several alcohols decreased and became 0 except water and 1-octanol after 30 minutes. The contact angles of 1-octanol on the PDMS films did not become 0 after long term-fluorination, because of its relatively high dispersive characteristic, compared to those of other alcohols in this study. The decrease of contact angles means that polarity of PDMS film surface increased due to substitution of PDMS film surfaces by fluorine.

Table 4 shows surface energy of PDMS films calculated by Owens-Wendt geometric theory during fluorination. Polar component (γs^p) and dispersion component (γs^d) of surface energy of PDMS films increased from 1.49 mN/m and 11.05 mN/m to 8.77 mN/m and 25.06 mN/m, respectively. This result came from the fluorination on the PDMS film surfaces. Therefore, it seems to be obvious that polarization of PDMS film surfaces brought about the decrease of the contact angles of water and several alcohols on the PDMS films. Generally, it is well known that the decrease of contact angles of water and the increase of surface energy on the PDMS films indicates the change of hydrophobic surfaces to hydrophilic. But, with the results in this study, it is difficult to simply conclude that the decrease of contact angles of water on the fluorinated PDMS film surfaces indicates the change of hydrophobic surfaces to hydrophilic.



(a) (b) (c) (d) (e)

Fig. 5 Scanning electron microscopy images of PDMS surfaces of (a) virgin, (b) 10 minutes, (c) 30 minutes, (d) 60 minutes and (e) 120 minutes of fluorination

4. Conclusions

Polydimethylsiloxane (PDMS) which is one of the silicon polymers, and fluoro polymers are widely used as the materials of SPME probe and permeation tube for manufacturing standard gases, respectively. However, the low gas permeability of fluoro polymers is not suitable for manufacturing

Table 3 Contact angle (°) of water and various alcohols measured by sessile drop method

Fluorination time (min)	water	methanol	ethanol	1-Propanol	2-Propanol	2-Buthanol	1-Pentanol	1-octanol
0	109.5	37.5	43.2	35.5	24.3	28.4	39.5	29.9
10	91.9	24.8	24.3	18.6	6.7	16.0	25.6	19.0
30	88.3	n.d.[1]	n.d.	n.d.	n.d.	n.d.	n.d.	10.4
60	81.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.3
120	77.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.7

1. n.d. = not detected

Table 4 Contact angle data and surface energy results calculated using Owens-Wendt geometric theory

Fluorination time (min)	Contact angle (θ)		Surface energy[1] (mN/m)		
	deionised water	Diiodomethane	Total (γ_s)	Dispersion (γ_s^d)	Polar (γ_s^p)
0	109.5	91.4	12.54	11.05	1.49
10	91.9	80.4	20.49	14.58	5.91
30	88.3	64.6	27.62	23.22	4.40
60	81.3	62.2	30.84	23.60	7.25
120	77.1	58.7	33.83	25.06	8.77

1. Calculated by Owens-Wendt geometric theory ($\gamma_s = \gamma_s^d + \gamma_s^p$)

of high concentration standard gases and weak properties of PDMS surfaces are difficulty in using PDMS as a material of SPME probe.

In this study, the characteristics of PDMS and fluoro polymers were applied to each other for advancing its drawbacks. We used PDMS instead of fluoro polymers as a material of permeation tube for manufacturing high concentration water vapour standards and performed direct fluorination on the PDMS film surfaces to apply the surface characteristics of fluoro polymers.

In PDMS tube test, the change of permeation rate of water through single-material (PDMS) tubes and dual material (PDMS connected with tetrafluoroethylene-hexafluoropropylene copolymer) tubes were investigated with respect to the temperature and spatial distribution of water, water phases (liquid, vapour). The results showed the principal influence factors on the consistency of water permeation through PDMS tube, such as temperature, different permeation rate between water phases (liquid, vapour), spatial distribution of water. These results may be useful to manufacture the high concentration standard gases using PDMS permeation tube. Also, the PDMS tube inserted with paper wick test result provided a new setup of permeation tubes to reduce the inconsistency of water permeation through single-material tubes. It can be applied to the fabrication of permeation tubes for alcohols, VOCs, semi VOCs, and specific non-polar and polar solvents used for environmental standards.

In the fluorination on the PDMS film surfaces test, spin-coated PDMS film surfaces were fluorinated by the direct fluorination and FTIR, SEM analysis on the PDMS film surfaces were conducted before and after fluorination. Also, the contact angles of water and several alcohols on the PDMS film surfaces were measured with respect to the fluorination time. SEM analysis results showed that the PDMS film surfaces were fluorinated without irreversible deformation of surfaces, and FTIR analysis result showed that the methyl groups and/or the hydrogen of methyl groups on the PDMS films were removed and substituted to fluorine by the direct fluorination. Therefore fluorination conditions used in this study were proper. The contact angles of water and several alcohols on the film surfaces decreased as the fluorination time increased. Except water and 1-octanol, the contact angles of alcohols decreased to 0 after 30 minutes of fluorination. The surface energy of PDMS films were calculated using Owens-Wendt geometric theory. It showed that the polar component of surfaces increased by 5 times more than that of virgin surfaces. The increase of polar component of surface energy brought about a better affinity to mid-polar alcohols. Therefore, the fluorinated PDMS, which was enhanced its surface properties by the fluorination, can be applied for the multiple purposes. For an example it can be applied to the development of novel passive organic sampler material such as a solid-phase micro-extraction sampler due to their higher affinity to organic compounds than to water.

Acknowledgments

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References

Adcock, J.L., Hudlicky, M.H. and Pavlath, A.E. (1995), "Chemistry of organic fluorine compounds II", *Crit. Rev. Am. Chem. Soc.*, **97**.

Banks, R.E., Smart, B.E. and Tatlow, J.C. (1994), *Organofluorine Chemistry*, Plenum Press.

Choi, M.F. and Hawkins, P. (1997), "Generation of sulfur compound vapour standards based on permeation vials in series/parallel", *Anal. Chem*., **69**, 1237-1239.

Chung, C.W., Morandi, M.T., Stock, T.H. and Afshar, M. (1999), "Evaluation of a passive sampler for volatile organic compounds at ppb concentrations, varying temperatures, and humidities with 24-h exposures. 1. Description and characterization of exposure chamber system", *Environ. Sci. Technol*., **33**, 3661-3665.

Garcia-Payo, M.C., Essalhi, M., Khayet, M., Garcia-Fernandez, L., Charfi, K. and Arafat, H. (2010), "Water desalination by membrane distillation using PVDF-HFP hollow fiber membranes", *Membrane Water Treatment*, **1**, 215-230.

Gelaude, I., Dams, R., Resano, M., Vanhaecke, F. and Moens, L. (2002), "Direct determination of methylmercury and inorganic mercury in biological materials by solid sampling-electrothermal vaporization-inductively coupled plasma-isotope dilution-mass spectrometry", *Anal. Chem*., **74**, 3833-3842.

Hansen, N.M.L., Jankova, K. and Hvilsted, S. (2007), "Fluoropolymer materials and architectures prepared by controlled radical polymerizations", *Eur. Polym. J*., **43**, 255-293.

Hashimoto, Y. and Tanaka, S. (1980), "A new method of generation of gases at parts per million levels for preparation of standard gases", *Environ. Sci. Technol*., **14**, 413-416.

Higuchi, A., Tamai, M., Tagawa, Y., Chang, Y. and Ling, Q. (2010), "Surface modification of polymeric membranes for low protein binding", *Membrane Water Treatment*, **1**, 103-120.

Huang, P.H. (1998), "Humidity standards for low level water vapor sensing and measurements", *Sens. Actuators, B*, **53**, 125-127.

Huang, P.H. and Kacker, R. (2003), "Repeatability and reproducibility standard deviations in the measurement of trace moisture generated using permeation tubes", *J. Res. Nat. Inst. Stand. Technol*., **108**, 235-240.

Hunter, M.C., Bartle, K.D., Seakins, P.W. and Lewis, A.C. (1999), "Direct measurement of atmospheric formaldehyde using gas chromatography-pulsed discharge ionisation detection", *Anal. Commun*., **36**, 101-104.

Kharitonov, A.P. (2000), "Practical applications of the direct fluorination of polymers", *J. Fluorine Chem*., **103**, 123-127

Kharitonov, A.P. (2008), "Direct fluorination of polymers–from fundamental research to industrial applications", *Prog. Org. Coat.*, **61**, 192-204.

Kharitonov, A.P. and Moskvin, Y.L. (1998), "Direct fluorination of polystyrene films", *J. Fluorine Chem.*, **91**, 87-93

Kharitonov, A.P., Taege, R., Ferrier, G., Teplyakov, V.V., Syrtsova D.A. and Koops, G.H. (2005), "Direct fluorination—useful tool to enhance commercial properties of polymer articles", *J. Fluorine Chem.*, **126**, 251-263.

Khoo, C.G.L. and Liu, J. (1998), "Temperature cycling effects in some glob top polymer materials", *Circuit World*, **24**, 11-24.

Lagow, R.J. and Margrave, J.L. (1979), "Direct fluorination: a new approach to fluorine chemistry", *Prog. Inorg. Chem.*, **26**, 162-210.

Larsson, T. and Frech, W. (2003), "Species-specific isotope dilution with permeation tubes for determination of gaseous mercury species", *Anal. Chem.*, **75**, 5584-5591.

Le Roux, J.D., Paul, D.R., Kampa, J. and Lagow, R.J. (1994), "Modification of asymmetric polysulfone membranes by mild surface fluorination. I. Transport-properties", *J. Membrane Sci.*, **94**, 121-141

Lucero, D.P. (1971), "Performance characteristics of permeation tubes", *Anal. Chem.*, **43**, 1744-1749.

Maity, J., Jacob, C., Das, C.K., Kharitonov, A.P., Singh, R.P. and Alam, S. (2007), "Fluorinated aramid fiber reinforced polypropylene composites and their characterization", *Polym. Compos.*, **28**, 462-469.

Maria, P.C., Gal, J.F., Balza, M., Pere-Trepat, E. and Tumbiolo, S. (2002), "Using thermogravimetry for weight loss monitoring of permeation tubes used for generation of trace concentration gas standards", *Anal. Chem.*, **74**, 305-307.

Mitchell, G.D., Dorko, W.D. and Johnson, P.A. (1992), "Long-term stability of sulfur dioxide permeation tube standard reference materials", *Fresenius J. Anal. Chem.*, **344**, 229-233.

Mohr, J.M., Paul, D.R., Pinnau, I. and Koros, W.J. (1991), "Surface fluorination of polysulfone asymmetric membranes and films", *J. Membrane Sci.*, **56**, 77-98

Naganowska-Nowaka, A., Konieczka, P., Przyjazny, A. and Namieœnik, J. (2005), "Development of techniques of generation of gaseous standard mixtures", *Crit. Rev. Anal. Chem.*, **35**, 31-55.

Neri, G., Bonavita, A., Rizzo, G., Micali, G., Donate, N. and Ipsale, S. (2006), "Investigation of permeation tubes for temperature-compensated gas-sensor calibrators", *IEEE Sens. J.*, **6**, 1120-1124.

Ohira, S.I. and Toda, K. (2005), "Micro gas analysis system for measurement of atmospheric hydrogen sulfide and sulfur dioxide", *Lab Chip. Miniat. Chem. Bio.*, **5**, 1374-1379.

Patwardhan, D.V., Zimmer, H. and Mark, J.E. (1997), "Synthesis of some fluorinated phenylmethylsiloxane polymers and characterization of their surface properties", *J. Inorg. Organom. Polym.*, **7**, 93-109.

Scace, G.E. and Miller, W.W. (2008), "Reducing the uncertainty of industrial trace humidity generators through NIST permeation-tube calibration", *Int. J. Thermophys.*, **29**, 1544-1554.

Singh, H.B., Salas, L., Lillian, D., Arnts, R.R. and Appleby, A. (1977), "Generation of accurate halocarbon primary standards with permeation tubes", *Environ. Sci. Technol.*, **11**, 511-513.

Smith, A.L. (1960), "Inrared spectra structure-correlation for organosilicon compounds", *Spectrochim. Acta.*, **16**, 87-105.

Socrates, G. (1980), *Infrared characteristic group frequencies*, John Wiley and Sons.

Syrtsova, D.A., Kharitonov, A.P., Teplyakov, V.V. and Koops, G.H. (2004), "Improving gas separation properties of polymeric membranes based on glassy polymers by gas phase fluorination", *Desalination*, **163**, 273-279.

Tressaud, A., Durand, E. and Labrugere, C. (2007), "Modification of surface properties of carbon-based and polymeric materials through fluorination routes:From fundamental research to industrial applications", *J. Fluorine Chem.*, **128**, 378-391.

Tumbiolo, S., Vincent, L., Gal, J.F. and Maria, P.C. (2005), "Thermo-gravimetric calibration of permeation tubes used for the preparation of gas standards for air pollution analysis", *Analyst*, **130**, 1369-1374.

Washenfelder, R.A., Roehl, C.M., McKinney, K.A., Julian, R.R. and Wennberg, P.O.(2003), "A compact, lightweight gas standards generator for permeation tubes", *Rev. Sci. Instrum.*, **74**, 3151-3154.

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