Accepted Manuscript

In-situ Monitoring on Dynamics of Solute Transport in Polymer Films

Julia S.P. Wong, Mingjun Hu, Dean Shi, Robert K.Y. Li, Janet S.S. Wong

PII: S0032-3861(14)01139-2

DOI: [10.1016/j.polymer.2014.12.039](https://doi.org/10.1016/j.polymer.2014.12.039)

Reference: JPOL 17498

To appear in: *Polymer*

Received Date: 26 August 2014

Revised Date: 12 November 2014

Accepted Date: 20 December 2014

Please cite this article as: Wong JSP, Hu M, Shi D, Li RKY, Wong JSS, In-situ Monitoring on Dynamics of Solute Transport in Polymer Films, *Polymer* (2015), doi: 10.1016/j.polymer.2014.12.039.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 In-situ Monitoring on Dynamics of Solute Transport in Polymer 2 Films

3 *Julia S. P. Wong¹, Mingjun Hu¹, Dean Shi², Robert K. Y. Li¹, Janet S. S. Wong^{3*}*

4 ¹Department of Physics and Materials Science, City University of Hong Kong, Hong
5 Kong

6 ²Ministry of Education Key Laboratory for the Green Preparation and Application of
7 Functional Materials, Faculty of Materials Science and Engineering, Hubei University,
8 Wuhan, 430062, People's Republic of China

9 ³Department of Mechanical Engineering, Imperial College London, London SW7
10 2AZ, UK

11 **KEYWORDS:** Fluorescence imaging, diffusion, polymer nanocomposites

12 AUTHOR INFORMATION

13 *Corresponding Author:

14 Janet Wong

15 Email: j.wong@imperial.ac.uk

16 Phone: +442075948991

17 Abstract

18 A new and non-invasive technique based on confocal laser scanning microscopy
19 (CLSM) that allows the visualization of penetrant diffusion *in-situ* has been
20 developed and was applied to quantify local solute dynamics in polymeric films. The
21 effectiveness of the proposed technique was demonstrated using a model penetrant,
22 rhodamine 6G (Rh-6G), and a system of polyvinyl alcohol (PVA) films with different
23 degree of cross-linking, and different content of montmorillonite (MMT) clay. The
24 penetrant's transport across PVA films were monitored by measuring the time
25 evolutions of through thickness fluorescence intensity profiles. These profiles were
26 then converted to concentration profiles, which allow local diffusion coefficients of
27 the model solute (i.e. Rh-6G) to be determined. The developed methodology was

1 applied to both single layer and bilayers films and local diffusion heterogeneity was
2 detected. Hence the technique developed can be applied to multi-layer films, and can
3 be beneficial to film developments for packaging and filtration technology.

4 **1. Introduction**

5 Understanding how gases and liquids (penetrants) permeate through membranes is
6 vital to applications such as barrier film [1, 2], separation/filtration membrane [3],
7 flexible electronics [4], and energy conversion [5, 6]. For instance, a good food
8 packaging film should prevent the sorption of moisture and/or oxygen from spoiling
9 food [7, 8]. On the other hand, efficient ions transport through membrane is required
10 for fuel cell applications [5]. The film transport characteristics, hence the selectivity
11 of the membrane in allowing/preventing the penetration of small molecules, is closely
12 related to (a) the solubility of penetrants in the membrane [9, 10], (b) the flow
13 characteristic of penetrants in the membrane, and (c) the ability of the membrane to
14 retain penetrants. For polymeric membranes, the characteristics listed above are
15 controlled by the interactions between penetrants and polymer [11], the free volume
16 of the polymer [12, 13], the average penetrant transport path (tortuosity factor) [9];
17 and the properties of the materials adjacent to the membrane. Polymeric films
18 modified with silicate nanofillers were reported to show promising barrier
19 performance [14 - 16] because the paths travelled by penetrants are lengthened to
20 bypass the fillers [15, 17 - 19]. Hence, material properties such as filler concentration
21 [4, 20], filler orientation [8, 21, 22] and matrix cross-link density [23, 24] will be
22 important in determining the overall transport of penetrants in the polymer film.

23 To date, very little work [13, 25, 26, 27] has been done to examine how through-
24 thickness penetrant concentration in polymer film changes with materials properties.

1 The ability of a polymeric film to retain penetrants is commonly evaluated by its
2 change in weight before and after it has been exposed to the penetrants [28, 29],
3 whereas the diffusion kinetics of the penetrants in the film has been examined by
4 measuring the concentration of the absorbed penetrants by extraction with solvents
5 [30]. While useful information can be gathered from these methods, very little, if any,
6 temporal and/or spatial information on the penetration or distribution of absorbed
7 species in the film can be obtained. Techniques frequently used for concentration
8 determination, such as NMR, ellipsometry and Raman spectroscopy, lack the
9 resolution needed to investigate transport processes in polymeric films. A novel
10 approach is hence needed to detect firstly if heterogeneous behaviour exists in a film
11 and more importantly to investigate the origin and the implications of such behaviour.
12 A newly developed approach, outline in this work, allows the study of penetrants
13 transport in polymeric membranes *in-situ*, with good spatial and temporal resolutions.
14 The local dynamics (diffusion) of solute in polymeric films can be determined. It will
15 improve our understanding of the physics of penetrant dynamics in polymeric film.
16 The knowledge obtained would be of great benefit in optimizing membrane design.

17 In this work, fluorescence imaging based on confocal laser scanning microscopy
18 (CLSM) was proposed for the studying of penetrant diffusion in polymer films. An
19 aqueous solution of Rhodamine 6G (Rh-6G), a widely studied fluorescent dye [25,
20 31] was used as the model penetrant. A system of polyvinyl alcohol (PVA) films was
21 prepared as the model film system. The model PVA films were modified by different
22 degree of cross-linking and different amount of montmorillonite (MMT) clay
23 incorporation. The through-thickness concentration profiles of Rh-6G in PVA films
24 were then obtained and the diffusion coefficients quantified. The sorption kinetics

1 was also examined in bilayer films composed of neat PVA and MMT filled PVA
2 films.

3 In this paper, the words, ‘membrane’ and ‘film’ are used interchangeably.

4 **2. Experimental**

5 The fabrication of the PVA films is discussed; and the quantification process of local
6 diffusion coefficient in the films using confocal laser scanning microscopy (CLSM) is
7 presented in this section.

8 **2.1 Materials**

9 Polyvinyl alcohol (PVA) films modified by different degree of cross-linking and
10 different montmorillonite (MMT) filler concentrations are used as model systems to
11 investigate the effectiveness of the CLSM technique in the monitoring of solute
12 transport dynamics.

13 The base PVA used in this study was purchased from Sigma Aldrich, and with a
14 degree of hydrolysis 99% and molecular weight, M_w , of 89,000–98,000 g mol⁻¹.
15 Sodium-montmorillonite, under the trade number of E100, with a cation exchange
16 capacity of 0.92 meq/g, was purchased from Southern Clay Products. Rhodamine-6G
17 (Rh-6G) purchased from Sigma Aldrich was used as the model penetrant in this study.
18 Rh-6G was made into a 1×10^{-6} M aqueous solution. All chemicals were used as
19 received. Ultra-pure water, with a resistivity of 18 MΩ cm (MilliQpore), was also
20 used.

21 **2.1.1 Preparation of Single Layer Film**

1 As mentioned above, a system of PVA-MMT films with: (1) various MMT
2 concentration, (2) cross-link ratio, and (3) thicknesses were prepared for this work. A
3 description for the sample preparations is given as follows. PVT-MMT films were
4 prepared by first mixing an appropriate quantity of the MMT clay with water under
5 magnetic stirring for 1 hour, followed by sonication for 30 minutes to form an
6 aqueous MMT suspension. PVA powder was then added to the aqueous MMT
7 suspension and the mixture was stirred with a magnetic stirrer at 90°C until PVA was
8 completely dissolved to make a 10 wt% polymer solution. The PVA-MMT aqueous
9 mixture was cooled to room temperature before use.

10 Cross-linking of the PVA (and PVA-MMT) films was carried by addition of a
11 mixture of the two following aqueous solutions: (1) 5 vol% methanol, 10 vol%
12 hydrochloric acid (HCl), and 2.5 vol% glutaraldehyde; and (2) 5 vol% methanol and
13 10 vol% hydrochloric acid (HCl) only, into the PVA (and PVA-MMT) aqueous
14 mixture such that the molar crosslink ratios of glutaraldehyde to PVA, i.e. the number
15 of moles of glutaraldehyde per mole of PVA repeat unit, were 0, 0.001 and 0.005.
16 Glutaraldehyde is mainly responsible for the cross-linking of the PVA chains [32-34].
17 The membrane solution was poured into petri dishes and dried at room temperature
18 for 72 hours. By varying the amount of solution in the petri dishes, films with average
19 thicknesses of 60 ± 10 μm , 100 ± 10 μm , and 180 ± 10 μm were produced. The final
20 concentrations of MMT in the PVA-MMT films were 0, 0.1, 0.5 and 1 wt%. The
21 resulting samples are designated as PVA-M-X-T, where M is the MMT
22 concentration; X is the number of moles of glutaraldehyde per mole of PVA repeat
23 unit (hence the assumed cross-link ratio); and T is the thickness of the film in μm . For
24 example, PVA-0-0.001-60 is a PVA film that has 0 wt% of MMT, crosslink ratio of
25 0.001 and 60 μm in thickness.

2.1.2 Preparation of Bi-layer Film

Two types of bi-layer film are also prepared for investigation. Each type of bi-layer sample consists of a *base layer* and a *top layer*. The membrane solutions for both base layer and top layer were prepared as described in Section 2.1.1 above. The membrane solution for the *base layer* was first poured in petri dishes and dried at room temperature for 24 hours. The membrane solution for the *top layer* was then poured on top of the *base layer* and was allowed to dry at room temperature for 48 hours. The *top layer* and the *base layer* each have a thickness of $60 \pm 5 \mu\text{m}$ and $40 \pm 5 \mu\text{m}$, respectively. Both layers have a crosslink ratio of 0.005. The resulting bi-layer films can be designated as

- PVA-0-0.005-60/PVA-0.5-0.005-40, and
- PVA-0.5-0.005-60/ PVA-0-0.005-40.

When the bilayer film was immersed in water for water absorption, both base and top layers absorbed water and were swollen. Due to different sorption properties of the two layers, the bilayer rolled up. The fact that the bilayer membrane rolls up rather than delaminates into two layers suggests good adhesion between the two layers.

2.2 Characterization of Penetrant Transport

In order to observe how Rh-6G is transported in PVA-MMT membrane, an as-cast membrane (with a diameter = 2 cm) was first immersed in water for 5 minutes to obtain a flat film. It was then placed on a glass cover slip. Excess water was removed. An O-ring was put on top of the film to fix its position as shown in **Figure 1a**. The sample was then ready to be used.

2.2.1 Visualization of Flow Behaviour of Rh-6G in the PVA film by CLSM

The transport behaviour of Rh-6G in aqueous solutions across the PVA-MMT films was investigated by obtaining the through-thickness Rh-6G concentration profiles with laser confocal imaging. Experiments were performed with a Leica SP5 confocal setup equipped with a 514 nm Argon laser. The setup composes of an inverted microscope where samples are placed on its sample stage. The laser beam is directed to the sample by a dichroic mirror and a 10× (NA = 0.4) air objective. Any fluorescence signal from the sample was collected, through the same objective, the dichroic mirror, and a bandpass emission filter (550 ± 30 nm), by a photomultiplier tube. The bandpass emission filter ensured that only emission from Rh-6G was observed. The sample stage was enclosed in an environmental chamber to warrant thermal and humidity stabilities during the experiment. All experiments were conducted at room temperature.

Figure 1. (a) A PVA film sample on glass slip with a rhodamine6G solution droplet on it; (b) Schematic showing observation of the rhodamine6G solution diffusing into the polymeric film by CLSM.

Laser confocal imaging was carried out 1 minute after a 25 μ L Rh-6G aqueous solution droplet was added onto the sample film surface (see **Figure 1a**). Excess Rh-6G solution remained on the film surface through the experiment. The examination of the through-thickness transport behaviour of Rh-6G in the PVA-MMT films requires the acquisition of multiple confocal fluorescence images, each separated by a fixed

depth, across the thickness of the film. This procedure is analogous to 3-D confocal image reconstruction and a schematic on how confocal images were obtained is shown in **Figure 1b**. Right before adding a Rh-6G solution droplet, a confocal image is first obtained at the top surface of the film, where $z = 0$, by a raster scan at 400 Hz on the x-y plane with a scan area of $1.55 \times 1.55 \text{ mm}^2$. Images were then taken through the thickness of the film (z direction) at $5 \text{ }\mu\text{m}$ intervals to obtain a sequence of images that shows how fluorescence intensity varies across the thickness of the film. It took around 55 seconds to capture a through-thickness image sequence. To investigate how the fluorescence intensity within the film changes with time, one image sequence was captured every 3 minutes (including image capture time). A time series consisted of 11 image sequences took approximately 30 minutes. Three samples were prepared for each PVA-MMT film and results presented are averaged of all three samples.

2.2.2 Extraction of Through-Thickness Intensity Profiles

Each scanned image consisted of 1024×1024 pixels. The fluorescence intensity of each pixel was assigned based on a 255 level greyscale. In each image, four areas of approximately 0.15 mm^2 , all roughly at the center of the film, were selected. Their average fluorescence intensity represents the fluorescence intensity at a particular z -position at a particular time. The intensity profile, $I(z)$, which relates average fluorescence intensity with distance away from the top of the film, z , can then be constructed. The time series of images allow the investigation of how the intensity profile, $I(z)$, changes with time.

Since measured fluorescence intensity comes from the emission of Rh-6G in the membrane, the variation of intensity among images in an image sequence provides a depth profile of Rh-6G concentration at a given time. Hence $I(z)$ can be converted to

1 the through-thickness concentration profile of Rh-6G, $c(z)$. This provides insights into
 2 the transport behavior of Rh-6G in the membrane.

3 **2.2.3 Quantification of Local Rh-6G Concentration in PVA-MMT Membrane**

4 Fluorescence intensity detected from a sample is conditional on the background
 5 fluorescence intensity owing to the setup and sample conditions. In this study, the
 6 intensity detected with a given concentration of Rh-6G, differed among samples due
 7 to the variation in the optical transparency of the PVA-MMT films. The
 8 transmissivity of light with wavelength between 550 to 600 nm, where the emission
 9 of Rh-6G is the strongest, reduces as MMT concentration of the film increased. To
 10 take this optical variation among PVA-MMT films into account, the following
 11 normalization process was applied. The **background intensity**, I_0 , is the fluorescence
 12 intensity obtained from a film before the addition of Rh-6G solution. Once the Rh-6G
 13 solution is added onto the film, I_i is defined as the **fluorescence intensity obtained at**
 14 **the solution-polymer interface**, i.e. at $z = 0$. The interface is identified as the plane
 15 with a sharp change in intensity when intensity signal is detected along the z -direction
 16 at time $t = 0$. I_0 is subtracted from I_i to obtain the **background-corrected fluorescence**
 17 **intensity**, I_{cor} . The relationships between I_{cor} and the concentration of Rh-6G solutions,
 18 c , for the 100 μm thick film with various MMT concentration (crosslink ratio = 0.005)
 19 are presented in **Figure 2a**. Within the Rh-6G concentration range of 0.5×10^{-7} M and
 20 10×10^{-7} M, the relationship between I_{cor} and c is roughly linear. The gradients, $\frac{\Delta I_{cor}}{\Delta c}$,
 21 of these lines from **Figure 2a** are plotted against I_i measured with 10^{-6} M Rh-6G
 22 solution, as shown in **Figure 2b**. Data points from samples with various MMT
 23 concentrations and film thickness all fall on one straight line (with goodness of fit, R^2
 24 = 0.96). Based on the results in **Figure 2b**, the local concentration of Rh-6G can be

1 obtained based on the background corrected intensity, I_{cor} , and the initial intensity of
 2 the sample, I_i , when the experiments were performed with 1×10^{-6} M Rh-6G solution.
 3 The relationship shown in **Figure 2b** was applied to estimate the local Rh-6G
 4 concentrations in all films.

Figure 2. (a) The relationship between background-corrected fluorescence intensity, I_{cor} and the concentration of Rh-6G solution of crosslinked ($X=0.005$) samples with various filler content. The solute droplet was 25 μ L and the sample thickness was about 100 μ m. (b) A good linear fit between the initial fluorescence intensity, I_i , and the slopes of lines in Figure 2a, $\frac{\Delta I_{cor}}{\Delta c}$.

2.2.4 Diffusion Coefficient Estimation

The methodology described in Section 2.2.3 determines how the concentration of Rh-6G changes through the thickness of a PVA-MMT film $c(z)$. Analysing how $c(z)$ evolved with time provides information on the kinetics of Rh-6G transport in the sample films. If the solute transport mechanism in PVA-MMT membranes obeys Fickian diffusion [22, 35], the diffusion coefficient, D , of Rh-6G can be calculated using Fick's second law, as shown in **Equation (1)**:

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial z} \left(\frac{\partial c}{\partial z} \right) = \frac{\partial^2 c}{\partial z^2} \quad (1)$$

where c is the concentration of Rh-6G, t is the duration after the addition of Rh-6G solute, and z is the film depth, i.e. distance from the polymer-solution interface. The term $\frac{\partial^2 c}{\partial z^2}$ for a film at any given z and t can be calculated by taking the second

1 derivative of $c(z)$. The time series of $c(z)$ will also allow us to construct $c(t)$ for
 2 each z (as the concentration c is a function of both t and z). $\frac{\partial c}{\partial t}$ for a PVA film at a
 3 given z and t is the first derivative of $c(t)$. With $\frac{\partial^2 c}{\partial z^2}$ and $\frac{\partial c}{\partial t}$ known, D at a given z and
 4 t can be calculated based on Eq. (1).

5 **3. Results and Discussion**

6 In this section, results on applying the confocal laser scanning microscopy (CLSM) to
 7 identify how the solute absorption process is related to the crosslink ratio and MMT
 8 concentration in PVA-MMT films will be presented.

9 **3.1 Effect of Crosslink Ratio in Neat PVA Films**

10 By utilizing the CLSM system, the effect of crosslink ratio on solute penetration was
 11 investigated by monitoring the time evolution of the through-thickness concentration
 12 profiles, $c(z)$ as Rh-6G penetrated the *unfilled PVA films*.

13 The normalised concentration profiles, $c(z)$ for PVA-0-0.005-100 (i.e. the un-filled
 14 100 μm thick film) are given **Figure 3a**. These profiles are normalised by the
 15 concentration of the Rh-6G solution, as such the normalised concentration at the
 16 polymer film-solution interface is taken to be unity, i.e. 1. It is obvious that $c(z)$
 17 evolves with time. The sorption of Rh-6G proceeded from the top surface (the
 18 polymer film-solution interface where $z = 0$) to the bottom surface (the polymer film-
 19 glass slide interface) of the film. $c(z)$ peaks at the polymer film-solution interface ($z =$
 20 0) at $t = 0$. Gradually, $c(z)$ for the rest of the film increases. This shows the
 21 progressive transport of Rh-6G across PVA films. Moreover, the rate of increase in
 22 Rh-6G concentration in any z decreases over time. This is because the concentration

1 gradient of Rh-6G across the film drives the Rh-6G transport. As time increases, the
2 concentration gradient decreases and hence the flux of Rh-6G reduces. It is intuitive
3 to expect the concentration of Rh-6G throughout the film will be homogeneous, hence
4 $c(z)$ being a horizontal line, if enough time is given for equilibrium to be achieved.

5 **Figure 3.** The through-thickness concentration of Rh-6G, $c(z)$, at various time for the different
6 unfilled PVA films: (a) PVA0-0-0.005-100, (b) PVA0-0-0.001-100, and (c) PVA0-0-0-100 films. The
7 solution-polymer interface is around $0 \mu\text{m}$ depth in x-axis of all figures.
8

9 Similar transport behavior is observed in films with lower cross-link ratio although
10 the diffusion of Rh-6G occurred at different rates. A comparison of concentration
11 profiles $c(z)$ for PVA-0-0.005-100, PVA-0-0.001-100 and PVA-0-0-100, as shown in
12 **Figures 3**, shows that $c(z)$ from films with higher crosslink ratio (**Figure 3a**) is
13 consistently lower than those with lower crosslink ratio (**Figure 3c**). Hence as the
14 cross-link ratio increases (from **Figure 3c** to **Figure 3a**), the rate of transport in the
15 film reduces (i.e. at any specified film depth, z , and any specified time, the
16 normalized concentration decreases with increasing cross-link ratio). As crosslinking
17 reduces the chain mobility by chain linkages [36] and creates a denser structure within
18 the films [37], less space is available for the diffusion of solute molecules. Hence, the
19 transport rate decreases.

20 3.2 Effect of MMT Concentration

21 It is well known that MMT clay in polymer matrix nanocomposites can exist as
22 particulate, intercalated, or exfoliated forms [38-42]. Our characterization of the

- 1 PVA-MMT samples suggests that the PVA-MMT composite films used in this work
- 2 consist of mostly intercalated MMT clays embedded in PVA matrix.

Figure 4. TEM images of MMT clay in membrane solution showing: (a) the overall morphology of the film; (b) exfoliated, and (c) intercalated clay layers. The thick black arrows point out clay or clay clusters in the matrix. The light grey interconnected network is the grid. These images were taken at an accelerating voltage of 200 keV. The samples were prepared by depositing a drop of the PVA membrane solution containing 0.1 wt% of MMT (PVA 0.1) and dried on 300 mesh holey carbon film TEM grid. Measurements were obtained from a Philips CM20 system.

Figure 4 shows TEM (transmission electron microscopy) images of membrane solution containing 0.1 wt% MMT dried on a grid substrate. **Figure 4a** shows the overall morphology of the sample. MMT platelets, seen as black clusters or threads, dispersed uniformly in a homogeneous polymer matrix (light grey background). Selected magnified area (**Figures 4b and 4c**) shows that most of the MMT clays have been intercalated by PVA. To supplement the TEM observations, **Figure 5** shows the WAXS (wide angle X-ray scattering) patterns of MMT clay, neat PVA and PVA-MMT films. Information on the effective intercalation of PVA chains into the MMT clay galleries in the membrane is provided by WAXS patterns in the range of $2\theta = 1 -$

1 10° (see **Figure 5**). MMT clay (MMT) exhibits a diffraction peak at $2\theta = 6.1^\circ$,
 2 corresponding to a separation between two layers of clays, i.e. d-spacing, of 1.5 nm;
 3 whereas neat PVA (PVA0) shows no peak in this range. PVA-1-0.005-180 (PVA1)
 4 shows a suppressed MMT peak shifted to $2\theta = 4.9^\circ$. This corresponds to a d-spacing
 5 of 1.8 nm, suggesting some degree of intercalation of the clay layers in the PVA
 6 matrix. The amount of shift in diffraction peak in PVA-MMT system present in
 7 **Figure 5** is consistent to those reported in literatures [38, 43, 44].

8
 9 **Figure 5.** WAXS spectra of MMT, neat PVA (PVA0), and PVA films containing 0.1, 0.5 and 1 wt%
 10 of MMT (PVA0.1, PVA0.5 and PVA1). Samples were supported on glass substrates. The Cu K α
 11 radiation ($\lambda = 1.5405 \text{ \AA}$) generated at 40 kV and 30 mA was used. Results were obtained with a
 12 scan rate of 0.01° per second, and 2θ ranging from 2 to 40° . Measurements were obtained from a
 13 Philips X'pert system.

14 The effect of MMT concentration on the transport dynamics of Rh-6G was
 15 investigated using PVA-MMT films with a fixed crosslink ratio of 0.005. Snapshot of
 16 $c(z)$ at $t = 12$ minutes and $t = 30$ minutes for the three systems, PVA-0-0.005-100,
 17 PVA-0.1-0.005-100, and PVA-1-0.005-100, i.e. with increasing MMT content from 0,
 18 to 0.1, and to 1 wt% respectively, are presented in **Figure 6a** and **6b**. The addition of
 19 MMT in PVA dramatically retards the transport of Rh-6G in the PVA films, as the
 20 $c(z)$ of films with high MMT content is below those with low MMT contents. For
 21 example, the normalised Rh-6G concentration, $c(z = 80\mu m)$ is about 0.6, 0.4 and

0.13 after 30 minutes of sorption as the MMT concentration of these 100 μm PVA-MMT films increases from 0 to 0.1, then to 1 wt%. Similar effect of MMT concentration on Rh-6G transport was also observed for crosslinked 60 μm PVA films (*not shown*). These results support the expectation that MMT restricts solute transport in PVA films.

Figure 6. Concentration profiles of Rh-6G in 100 μm thick cross-linked (X=0.005) PVA-MMT films: (a) $t = 12$ minutes; and (b) $t = 30$ minutes.

A decrease in solute intake with increasing nanoclay content in polymer films has been reported [43-45]. MMT clay can reduce water solubility in PVA films [10]. This can be due to the inclusion of nanoclay modifying the hydrophobicity of the PVA-MMT film. Indeed the water contact angles of PVA-MMT films increase with MMT concentration (see **Table 1**). This indicates that water has greater difficulty wetting, and hence penetrating the solution-PVA film interface with the addition of MMT clays. In addition, the intercalated MMT clays inside the PVA-MMT films act as physical barriers against mass transport and force solutes to take more tortuous paths during the sorption process [46]. Thus the use of MMT clay results in a reduction of water solubility and water diffusivity in PVA film. This gives rise to a decrease in the mass transfer of Rh-6G across the film. This mechanism can apply to both liquid and gas solutes [19, 47].

Table 1 The contact angle of water on PVA-MMT membranes.

	wt% MMT			
	0	0.1	0.5	1
PVA film with crosslink ratio of 0.001	57.5° ± 0.4°	61.33° ± 2.25°	69.6° ± 2.33°	75.18° ± 1.38°

3.3 Effect of Film Thickness in Neat PVA Film

Since the transport properties of a barrier film are independent of film thickness, solute molecules will take longer to diffuse through the thicker film [48] merely due to longer transport path. Hence thicker films can be more effective as barrier coatings. Boundary effect, which can be important for nanometer thick films, is neglected due to the use of sub-mm thick film in this study. The solute uptake dynamics for 60 μm , 100 μm , and 180 μm thick neat PVA films with a crosslink ratio = 0.005 was examined. Their $c(z)$ at $t = 6$ minutes and $t = 12$ minutes (only the top 50 μm of polymer films are shown to facilitate comparison) are presented in **Figure 7**. For the 60 μm films, $c(z)$ is almost constant throughout the top 30 μm of the film after 6 minute. $c(z)$ for the 100 μm and 180 μm films are closed to each other for both $t = 6$ minutes and $t = 12$ minutes and they lie below that of 60 μm film.

Figure 7. Concentration profiles of Rh-6G in crosslinked ($X=0.005$) neat PVA films having different film thicknesses, taken as (a) time = 6 minutes and (b) time = 12 minutes.

To determine if the film thickness has a genuine impact on the actual diffusion mechanism (such as the existence of a surface layer [49, 50] on the PVA films which

alters Rh-6G dynamics), normalized concentration of Rh-6G is plotted as a function of film depth normalized by square root time, $\frac{z}{\sqrt{t}}$, for the 100 μm and 180 μm films, are shown in **Figure 8**. This part of the analysis cannot be applied to the 60 μm film as its $c(z)$ plateaued in the experiment. All $c\left(\frac{z}{\sqrt{t}}\right)$ collapse into one master curve. This implies that only one diffusion coefficient is necessary to describe the transport of Rh-6G across the film [5]. D is estimated to be $2.7 \times 10^{-12} \text{ m}^2/\text{s}$ and $2.2 \times 10^{-12} \text{ m}^2/\text{s}$ for 100 and 180 μm films, respectively. The slight difference in the diffusion coefficients of these two films can be attributed to the sensitivity of the current technique.

Figure 8. The normalized concentration of Rh-6G in cross-linked neat PVA film ($X= 0.005$) is plotted against film depth normalized by square root time for (a) 100 μm and (b) 180 μm thick films. The collapse of concentration profiles into one master curve indicates a single diffusion mode.

3.4 Local Diffusion Coefficient of Rhodamine-6G Solution in PVA-MMT Films

Local diffusion coefficient can be calculated using **Equation (1)**, $c(t)$ and $c(z)$ with procedures outlined in **Section 2.2.4**. While useful information of local transport properties can be obtained, the following limitations are encountered. Firstly since the developed methodology monitors the dynamics of Rh-6G based on how concentration changes with time, the diffusion coefficient will appear close to zero if there is a lack

1 of change of Rh-6G concentration even though fast diffusion may occur. This is the
 2 case for the surface region of the film where $c(z)$ is constant and $\frac{\partial c(z)}{\partial z}$ is close to zero.
 3 Hence D close to the interface of all films, i.e. $z = 0$, and of films that were saturated
 4 with Rh6G quickly, for example thin, neat PVA film, are not shown. Similar problem
 5 will be encountered in region where $c(z)$ is very low. Secondly if the diffusion rate is
 6 similar to or faster than the rate image is captured, the local diffusion coefficient
 7 cannot be determined accurately and large error is expected. Thirdly, the estimation of
 8 D with **Equation (1)** requires the use of $\frac{\partial^2 c}{\partial z^2}$ as such D will be indeterminable at z
 9 where $c(z)$ shows a point of inflexion, i.e. $\frac{\partial^2 c}{\partial z^2} = 0$. Hence D obtained at z where $\frac{\partial^2 c}{\partial z^2}$
 10 is closed to zero are neglected. Fourthly, the results have considerable scatter due to
 11 the procedures of taking second derivatives of discrete data, which amplifies the
 12 experimental error. With these limitations in mind, local diffusion coefficients have
 13 been determined for all films used in this study.

14 The relationships between the film depth, z , and local diffusion coefficient of Rh-6G
 15 in PVA-1-0.005-100 (i.e. 100 μm PVA-MMT films (crosslink ratio = 0.005) with 1
 16 wt% MMT) is shown in **Figure 9a**. It can be seen that the local diffusion coefficient
 17 is fairly constant across the film irrespective of time. This observation applies to all
 18 films examined in this work. The effect of MMT concentration on local diffusion
 19 coefficients of PVA-MMT films is presented in **Figure 9b**. An addition of MMT
 20 slows down the diffusion of Rh-6G in PVA films. The average diffusion coefficient
 21 decreases with increasing MMT concentration with 0% MMT, 0.1 wt% MMT and 1
 22 wt% MMT resulting in average $D = 2.7 \times 10^{-12} \text{ m}^2/\text{s}$, $1.3 \times 10^{-12} \text{ m}^2/\text{s}$ and $0.4 \times 10^{-12} \text{ m}^2/\text{s}$
 23 respectively. Note the diffusion coefficient of Rh-6G in water is about $2 \times 10^{-10} \text{ m}^2/\text{s}$
 24 [51]. Hence Rh-6G diffused 2 orders of magnitude slower in PVA-MMT films than in

1 bulk water. This is attributed to the modification of water solubility in PVA films in
 2 the presence of MMT. The addition of fillers also hinders the diffusion of solute in the
 3 polymer matrix [39]. This was confirmed by evaluating the water solubility of PVA
 4 films used in this study by measuring gravimetrically the 24-hour water uptake of
 5 these films.

Figure 9. Change of local diffusion coefficients of Rh-6G with the film depth of 100 μm crosslinked PVA (X=0.005) film with various MMT concentration. (a) The change of local diffusion coefficient with time for PVA1-0.005-100 μm film. (b) The time average of local diffusion coefficient is plotted against film depth for 0 wt%, 0.1 wt% and 1 wt% MMT reinforced PVA films.

The water uptake, w , based on at least three measurements per film is defined in

Equation (2) as

$$w = \frac{(W_{wet} - W_{dry})}{W_{dry}} \quad (2)$$

where W_{dry} and W_{wet} are the weight of the film before and after water absorption respectively. By assuming volume additivity, the volume fraction of water, ϕ_w in the film can then be calculated if ρ_p and ρ_w , being density of the dry polymer film and that of water respectively, are known. ϕ_w is related to the water sorption coefficient

K_w as shown in **Equation (3)** [52]

$$K_w = \frac{\phi_w M_w}{c_w V_w} \quad (3)$$

where M_w , c_w and V_w are the molar mass, molar volume and concentration of water (1 for pure water) respectively. The addition of Rh-6G in the water may affect these (2 values. Due to the low concentration of Rh-6G used, this effect is neglected. Hence (3 $K_w \approx \phi_w$. The calculated values are listed in Table 2. (4

Table 2 The effect of MMT incorporation on water sorption of PVA films. (5

	PVA-0-0.005-100	PVA-0.1-0.005-100	PVA-1-0.005-100
ρ_p (g/m ³)	1423	1523	1590
ϕ_w, K_w	0.64	0.63	0.56
D of Rh-6G (m ² /s)	2.7×10^{-12}	1.3×10^{-12}	0.4×10^{-12}

The increase in MMT content decreases the amount of water uptake although the (6 effect is quite moderate compared to its effect on the diffusion of Rh-6G of the PVA (7 film. An increase in MMT content from 0 to 0.1, to then 1 wt% results in 12.5% drop (8 in water uptake, while D drop by almost an order of magnitude. This highlights that (9 the incorporation of MMT in PVA films may influence the diffusion process and the (10 equilibrium concentration differently. (11

The reduction in D of Rh-6G in PVA-MMT films as MMT content increases, while (12 can be contributed to the creation of a more tortuous diffusion path, it can also be due (13 to a change in free volume in the PVA films as MMT is added into them. In a (14 hydrated polymer film, the free volume v_f can be related to the water content in the (15 film [53]. The diffusion coefficient of Rh-6G (a monovalent salt), can then be related (16 to the average free volume of the PVA-MMT films as shown in **Equation (4)** [53]. (17

$$D = a \exp \left[-\frac{Yv^*}{v_f} \right] = a \exp \left[-\frac{Yv^*}{bK_w} \right] \quad (4)$$

where a , Y , and b are adjustable constants, and v^* is the minimum free volume element necessary to allow Rh-6G to diffuse in the PVA films. **Figure 10** shows how diffusion coefficient of Rh-6G changes with $1/K_w$. Their relationship resembles that represented by **Equation (4)**, suggesting that the change in free volume due to the addition of MMT may play a role controlling Rh-6G diffusion in PVA films.

Figure 10. An inverse relationship is observed between diffusion coefficient of Rh-6G and the water sorption coefficient of the PVA-MMT films.

3.4 Flow behaviour of Rh-6G in the Bilayer film

Bilayer films fabricated with procedures described in **Section 2.1.2** was used to investigate if the developed technique is capable of determining the sorption dynamics of multilayer films and identifying local changes in diffusion behaviour due to the existence of a boundary within the film. A 2×10^{-5} M Rh-6G aqueous solution was used in this part of the study. **Figure 11** presented how normalised intensity profiles obtained from bilayer films evolve with time. The sorption of the Rh-6G proceeded from the top surface ($z = 0$), passed through the interface between the top and bottom layers and eventually Rh-6G reached the bottom. At around $z = 60 \mu\text{m}$, where the polymer interface was, both films exist abrupt changes in $I(z)$, although such change is more dramatic for the bilayer which the 0.5 wt% MMT-PVA (PVA-0.5-0.005-40) was the bottom layer (**Figure 11a**). As shown in **Figure 11a**, the

intensity of the top neat PVA layer ($z = 0 \mu\text{m}$ to $60 \mu\text{m}$), increases at a faster rate than that happens in the bottom MMT-filled PVA layer ($z = 62 \mu\text{m}$ - $115 \mu\text{m}$). It demonstrates that Rh-6G solute diffuses quickly in the neat PVA layer and then is blocked by the MMT-filled PVA layer. In **Figure 11b**, the top layer is composed of MMT-filled PVA (PVA-0.5-0.005-60) whose solute sorption is less efficient. The effect of the interface at $z = 60$ in **Figure 11b** is less obvious as the top MMT filled PVA layer, which only allows slow diffusion of Rh6G within it, is limiting the sorption kinetic of the whole bilayer film. Hence despite the bottom layer, being neat PVA, allows Rh-6G to diffuse more quickly than the MMT filled layer, the sorption was governed by the solute transports on the top layer.

Figure 11. Normalised intensity profiles of Rh-6G in bilayer films: (a) Top: neat PVA (PVA0) film and bottom: 0.5 wt% MMT-PVA film (b) Top: 0.5 wt% MMT-PVA film and bottom: neat PVA film. The dash lines (for guide only) indicate the interface between the top and bottom films.

4. Conclusions

A technique based on the confocal laser scanning microscopy (CLSM) has been presented to be a versatile tool for the monitoring of solute (Rh-6G) diffusion through polymer (PVA) films. The usefulness of the technique has been demonstrated by PVA model samples modified by different degree of crosslinking and MMT clay addition. Based on the CLSM measurement, the diffusion coefficient of the solute through the films can be calculated, which are in agreement with data from the open literature.

1 Furthermore, the CLSM technique can also be used to observe the interface of bi-
2 layer films.

3 In this investigation, MMT filled polymer films are used as the “model” systems,
4 which can find potential applications in packaging films. The technique also has
5 potential for usage in the the rapidly developing technologies in layer-by-layer (L-b-
6 L) films [54] and biomembranes [55]. The *in-situ* diffusion measurement technique
7 can be a useful tool to characterise the multi-layer structures in these film/membrane
8 systems. Definitely, future research will be meaningful in this direction.

9 **Author Contributions**

10 The manuscript was written through contributions of all authors. All authors have
11 given approval to the final version of the manuscript.

12 **Acknowledgments**

13 This work is supported by the Research Grants Council of the Hong Kong Special
14 Administrative Region, China (Project No. CityU 118313), and EPSRC Grants
15 (EP/J015385/1 and EP/L023202/1). The authors are also indebted to Dr. Y. W. Lam
16 (City University of Hong Kong) for providing the spectrometers and confocal laser
17 scanning microscope facilities for solute transport measurement.

18 **References**

- 19 1. Siracusa, V., Blanco I., Romani S., Tylewicz U., Rocculi P., Rosa M. D., Poly (lactic acid) -
20 Modified Films for Food Packaging Application : Physical , Mechanical , and Barrier Behavior.
21 *Journal of Applied Polymer Science* 125, E390–E401 (2012).
- 22 2. Baukh, V., Huinink, H. P., Adan, O. C. G., Erich, S. J. F. & Van der Ven, L. G. J. Predicting
23 water transport in multilayer coatings. *Polymer* 53, 3304–3312 (2012).

- 1 3. Hiltner, a., Liu, R. Y. F., Hu, Y. S. & Baer, E. Oxygen transport as a solid-state structure
2 probe for polymeric materials: A review. *Journal of Polymer Science Part B: Polymer Physics*
3 43, 1047–1063 (2005).
- 4 4. Huang, H.-D. Ren P.-G., Chen J., Zhang W.-Q., Ji X., Li Z.-M., High barrier graphene oxide
5 nanosheet/poly(vinyl alcohol) nanocomposite films. *Journal of Membrane Science* 409-410,
6 156–163 (2012).
- 7 5. Eastman, S. A. Kim S., Page K.A., Rowe B.W., Kang S., Soles C. L., Effect of Confinement on
8 Structure, Water Solubility, and Water Transport in Nafion Thin Films. *Macromolecules* 45,
9 7920–7930 (2012).
- 10 6. Qin, Y., Du, Q., Yin, Y., Jiao, K. & Li, X. Numerical investigation of water dynamics in a novel
11 proton exchange membrane fuel cell flow channel. *Journal of Power Sources* 222, 150–160
12 (2013).
- 13 7. Hasegawa, T., Matsui, T. & Matsumoto, K. Comparative Study of Additives on Visualized
14 Dynamic Sorption Behavior of Perylene in Cellulose Acetate Film by Confocal Laser Scanning
15 Microscope Technique. *Journal of Applied Polymer Science* 116, 1710–1717 (2010).
- 16 8. Leelaphiwat, B. P. Chonhenchob V., Singh S.P., Kruenate J., Wichai U., Ong K.C.,
17 Transport Coefficients of Eucalyptol through Various Polymeric Films. *Packaging technology*
18 *and science* 25, 161–172 (2012).
- 19 9. Shishatskii, A. M., Yampol'skii, Y. P. & Peinemann, K.-V. Effects of film thickness on density
20 and gas permeation parameters of glassy polymers. *Journal of Membrane Science* 112, 275–
21 285 (1996).
- 22 10. Kim, J.-Y., Kim, C. & Chang, I.-S. Effect of the Addition of Organoclay on the Solubility of
23 Polyvinyl Alcohol Gels Used in the Immobilization of Microorganisms for Wastewater
24 Treatment. *Environmental Engineering Science* 29, 14–18 (2012).
- 25 11. Minelli, M., Campagnoli, S., De Angelis, M. G., Doghieri, F. & Sarti, G. C. Predictive Model
26 for the Solubility of Fluid Mixtures in Glassy Polymers. *Macromolecules* 44, 4852–4862
27 (2011).
- 28 12. Wong, S.-S., Altinkaya, S. A. & Mallapragada, S. K. Drying of semicrystalline polymers:
29 mathematical modeling and experimental characterization of poly(vinyl alcohol) films.
30 *Polymer* 45, 5151–5161 (2004).
- 31 13. Ulrich, K., Centeno, S. a., Arslanoglu, J. & Del Federico, E. Absorption and diffusion
32 measurements of water in acrylic paint films by single-sided NMR. *Progress in Organic*
33 *Coatings* 71, 283–289 (2011).
- 34 14. Krook, M., Morgan, G. & Hedenqvist, M. S. Barrier and mechanical properties of injection
35 molded montmorillonite/polyesteramide nanocomposites. *Polymer Engineering & Science*
36 45, 135–141 (2005).
- 37 15. Horst, F., Tuckart, W., Blanco, L. Del, Failla, M. D. & Quinzani, L. M. Effect of Clay
38 Concentration on the Wear Behavior and Permeability of Polypropylene / Clay
39 Nanocomposites. *Journal of Applied Polymer Science* 125, E496–E502 (2012).

- 1 16. Kato, M., Okamoto, H., Hasegawa, N., Tsukigase, A. & Usuki, A. Preparation and
2 properties of polyethylene-clay hybrids. *Polymer Engineering & Science* 43, 1312–1316
3 (2003).
- 4 17. Min, U., Kim, J. C. & Chang, J. H. Transparent Polyimide Nanocomposite Films : Thermo-
5 Optical Properties , Morphology , and Gas Permeab ... *Polymer Engineering & Science* 51,
6 2143–2150 (2011).
- 7 18. Watkins, A. W., Southard, S. L. & Anseth, K. S. Characterizing multilaminated hydrogels
8 with spatially varying network structure and solute loading using confocal laser scanning
9 microscopy. *Acta Biomaterialia* 3, 439–448 (2007).
- 10 19. Priolo, M. a, Holder, K. M., Gamboa, D. & Grunlan, J. C. Influence of clay concentration
11 on the gas barrier of clay-polymer nanobrick wall thin film assemblies. *Langmuir* 27, 12106–
12 12114 (2011).
- 13 20. Estrada, M. R. On the Swelling of Polychloroprene-MMT Nanocomposite Films. *Journal of*
14 *Applied Polymer Science* 125, 2986–2992 (2012).
- 15 21. Sun, L., Boo, W.-J., Clearfield, A., Sue, H.-J. & Pham, H. Q. Barrier properties of model
16 epoxy nanocomposites. *Journal of Membrane Science* 318, 129–136 (2008).
- 17 22. Maksimov, R. D., Lagzdins, A., Lilichenko, N. & Plumé, E. Mechanical properties and
18 water vapor permeability of starch/montmorillonite nanocomposites. *Polymer Engineering*
19 *& Science* 49, 2421–2429 (2009).
- 20 23. Balaguer, M. P., Cerisuelo, J. P., Gavara, R. & Hernandez-Muñoz, P. Mass transport
21 properties of gliadin films: Effect of cross-linking degree, relative humidity, and temperature.
22 *Journal of Membrane Science* 428, 380–392 (2013).
- 23 24. Ca, V., Ruiz, J. & Manteco, A. Synthesis and properties of hydrogels from poly (vinyl
24 alcohol) and ethylenediaminetetraacetic dianhydride. *Polymer* 42, 6347–6354 (2001).
- 25 25. Pantelic, N. & Seliskar, C. J. Dynamics of Rhodamine 6G Sorption into a Porous Tri-block
26 Copolymer Thin Film. *Journal of Physical Chemistry C* 111, 18595–18604 (2007).
- 27 26. Koichiro H., Hisao M., K. T. Sorption kinetics of methanol in thin PMMA films studied by
28 optical reflectivity. *Soft Matter* 7, 10319–10326 (2011).
- 29 27. Jeck, S., Scharfer, P., Schabel, W. & Kind, M. Water sorption in semicrystalline poly(vinyl
30 alcohol) membranes: In situ characterisation of solvent-induced structural rearrangements.
31 *Journal of Membrane Science* 389, 162–172 (2012).
- 32 28. Ju, H., Sagle, A. C., Freeman, B. D., Mardel, J. I. & Hill, A. J. Characterization of sodium
33 chloride and water transport in crosslinked poly(ethylene oxide) hydrogels. *Journal of*
34 *Membrane Science* 358, 131–141 (2010).
- 35 29. Samanta, T. & Mukherjee, M. Swelling Dynamics of Ultrathin Films of Strong
36 Polyelectrolytes. *Macromolecules* 44, 3935–3941 (2011).

- 1 30. Cheknane, B., Zermane, F., Baudu, M., Bouras, O. & Basly, J. P. Sorption of basic dyes
2 onto granulated pillared clays: thermodynamic and kinetic studies. *Journal of colloid and*
3 *interface science* 381, 158–63 (2012).
- 4 31. Barranco, A. & Groening, P. Fluorescent plasma nanocomposite thin films containing
5 nonaggregated rhodamine 6G laser dye molecules. *Langmuir* 22, 6719–22 (2006).
- 6 32. Li, R. H., Barbari, T. A. Performance of poly(vinyl alcohol) thin-gel composite
7 ultrafiltration membranes. *Journal of Membrane Science* **105**, 71-78 (1995).
- 8 33. Martens, P., Anseth, K.S., Characterization of hydrogels formed from acrylate modified
9 poly(vinyl alcohol) macromers. *Polymer* **41**, 7715–7722 (2000)
- 10 34. Anjali Devi D., Smith B., Sridhar S., Aminabhavi. T. M., Pervaporation separation of
11 dimethylformamide/water mixtures through poly(vinyl alcohol)/poly(acrylic acid) blend
12 membranes. *Separation and Purification Technology* **51**, 104–111 (2006)
- 13 35. Paranhos, C. M., Soares, B. G., Oliveira, R. N. & Pessan, L. a. Poly(vinyl alcohol)/Clay-
14 Based Nanocomposite Hydrogels: Swelling Behavior and Characterization. *Macromolecular*
15 *Materials and Engineering* 292, 620–626 (2007).
- 16 36. Yarimkaya, S. & Basan, H. Swelling Behavior of Poly(2-hydroxyethyl Methacrylate-co-
17 acrylic Acid-co-ammonium Acrylate) Hydrogels. *Journal of Macromolecular Science, Part A:*
18 *Pure and Applied Chemistry* 44, 939–946 (2007).
- 19 37. Yi, C., Wang, Z., Li, M., Wang, J. & Wang, S. Facilitated transport of CO₂ through
20 polyvinylamine/polyethylene glycol blend membranes. *Desalination* 193, 90–96 (2006).
- 21 38. Qian, Z., Zhou, H., Xu, X. & Ding, Y. Effect of the grafted silane on the dispersion and
22 orientation of clay in polyethylene nanocomposites. *Polymer composites* 30, 1234–1242
23 (2009).
- 24 39. Maria, H. J. *et al.* Transport of organic solvents through natural rubber/nitrile
25 rubber/organically modified montmorillonite nanocomposites. *Journal of Materials Science*
26 48, 5373–5386 (2013).
- 27 40. Paranhos, Caio M., Soares, Bluma G., Oliveira Renata N., Pessan, Luiz A., Poly(vinyl
28 alcohol)/Clay-Based Nanocomposite Hydrogels: Swelling Behavior and Characterization.
29 *Macromolecular Materials Engineering* **292**, 620–626 (2007)
- 30 41. Strawhecker K. E., Manias E., Structure and Properties of Poly(vinyl alcohol)/Na+
31 Montmorillonite Nanocomposites. *Chemistry of Materials* **12**, 2943-2949 (2000).
- 32 42. Doppers, L. M., Breen, C., Sammon C., Diffusion of water and acetone into Poly(vinyl
33 alcohol) nanocomposites using ATR-FTIR . *Vibrational Spectroscopy* **35**, 27-32 (2004).
- 34 43. Kokabi M., S. M. and Z. M. H. PVA–clay nanocomposite hydrogels for wound dressing.
35 *PVA–clay nanocomposite hydrogels for wound dressing* 43, 773–781 (2007).

- 1 44. Paranhos, C. M., Soares, B. G., Oliveira, R. N. & Pessan, L. a. Poly(vinyl alcohol)/Clay-
2 Based Nanocomposite Hydrogels: Swelling Behavior and Characterization. *Macromolecular*
3 *Materials and Engineering* 292, 620–626 (2007).
- 4 45. Sirousazar M., M. Kokabi, Z. M. H. and A. R. B. Polyvinyl Alcohol-Na-Montmorillonite
5 Nanocomposite Hydrogels Prepared by Freezing thawing Method Structural, Mechanical,
6 Thermal, and Swelling Properties. *Journal of Macromolecular Science, Part B: Physics* 51,
7 1335–1350 (2012).
- 8 46. Bharadwaj, R. K. Modeling the Barrier Properties of Polymer-Layered Silicate
9 Nanocomposites. *Macromolecules* 34, 9189–9192 (2001).
- 10 47. Dunkerley, E. & Schmidt, D. Effects of Composition, Orientation and Temperature on the
11 O₂ Permeability of Model Polymer/Clay Nanocomposites. *Macromolecules* 43, 10536–
12 10544 (2010).
- 13 48. Rachna S., Jaya B., Anil, K. B. Studies on Transport of Vapor and Solute Molecules
14 through Polyvinyl Alcohol-Based Clay Containing Nanocomposites. *Polymer Composites* 32,
15 537–545 (2011).
- 16 49. Wang, Z., Wang, Z. Y., Ma, J., Bock, W. J. & Ma, D. Effect of film thickness, blending and
17 undercoating on optical detection of nitroaromatics using fluorescent polymer films.
18 *Polymer* 51, 842–847 (2010).
- 19 50. Tanaka, K., Hashimoto, K., Kajiyama, T. & Takahara, A. Visualization of Active Surface
20 Molecular Motion in Polystyrene Film by Scanning Viscoelasticity Microscopy. *Langmuir* 19,
21 6573–6575 (2003).
- 22 51. Gendron, P.-O., Avaltroni, F. & Wilkinson, K. J. Diffusion coefficients of several
23 rhodamine derivatives as determined by pulsed field gradient-nuclear magnetic resonance
24 and fluorescence correlation spectroscopy. *Journal of fluorescence* 18, 1093–101 (2008).
- 25 52. Geise, G.M., Freeman, B.D., & Paul, D.R. Sodium chloride diffusion in sulfonated
26 polymers for membrane applications. *Journal of Membrane Science* 427, 186-96 (2013).
- 27 53. Yasuda, H., Lamaze, C.E., & Ikenberry L.D. *Permeability of solutes through hydrated*
28 *polymer membranes Part I: Diffusion of sodium chloride*, Die Makromol. Chem 118, 19-35
29 (1968).
- 30 54. Ariga, K., Yamauchi., Rydzek, G., Ji, Q., Yonamine, Y., Wu, K.C.-W., & Hill, J.P. Layer-by-
31 layer Nanoarchitectonics: Invention, Innovation, and Evolution. *Chemistry Letters* 43, 36-68
32 (2013).
- 33 55. Mashaghi, A., Mashaghi, S., Reviakine, I., Heeren, R.M.A., Sandoghdar, V. & Bonn, M.
34 Label-free characterization of biomembranes: from structure to dynamics. *Chemical Society*
35 *Reviews* 43, 887-900 (2014).

HIGHLIGHT:

- Novel *in-situ* method is developed to probe local dynamics of solutes in membrane
- Crosslink ratio and filler content affect the sorption performance of polymer films
- The diffusion of solute in polymeric bi-layer membrane is characterized