



In-situ monitoring on dynamics of solute transport in polymer films



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ABSTRACT

A new and non-invasive technique based on confocal laser scanning microscopy (CLSM) that allows the visualization of penetrant diffusion *in-situ* has been developed and was applied to quantify local solute dynamics in polymeric films. The effectiveness of the proposed technique was demonstrated using a model penetrant, rhodamine-6G (Rh-6G), and a system of polyvinyl alcohol (PVA) films with different degree of cross-linking, and different content of montmorillonite (MMT) clay. The penetrant's transport across PVA films were monitored by measuring the time evolutions of through thickness fluorescence intensity profiles. These profiles were then converted to concentration profiles, which allow local diffusion coefficients of the model solute (i.e. Rh-6G) to be determined. The developed methodology was applied to both single layer and bilayers films and local diffusion heterogeneity was detected. Hence the technique developed can be applied to multi-layer films, and can be beneficial to film developments for packaging and filtration technology.

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1. Introduction

Understanding how gases and liquids (penetrants) permeate through membranes is vital to applications such as barrier film [1,2], separation/filtration membrane [3], flexible electronics [4], and energy conversion [5,6]. For instance, a good food packaging film should prevent the sorption of moisture and/or oxygen from spoiling food [7,8]. On the other hand, efficient ions transport through membrane is required for fuel cell applications [5]. The film transport characteristics, hence the selectivity of the membrane in allowing/preventing the penetration of small molecules, is closely related to (a) the solubility of penetrants in the membrane [9,10], (b) the flow characteristic of penetrants in the membrane, and (c) the ability of the membrane to retain penetrants. For polymeric membranes, the characteristics listed above are controlled by the interactions between penetrants and polymer [11], the free volume of the polymer [12,13], the average penetrant transport path (tortuosity factor) [9]; and the properties of the materials adjacent to the membrane. Polymeric films modified with silicate nanofillers were reported to show promising barrier

performance [14–16] because the paths travelled by penetrants are lengthened to bypass the fillers [15,17–19]. Hence, material properties such as filler concentration [4,20], filler orientation [8,21,22] and matrix cross-link density [23,24] will be important in determining the overall transport of penetrants in the polymer film.

To date, very little work [13,25–27] has been done to examine how through-thickness penetrant concentration in polymer film changes with materials properties. The ability of a polymeric film to retain penetrants is commonly evaluated by its change in weight before and after it has been exposed to the penetrants [28,29], whereas the diffusion kinetics of the penetrants in the film has been examined by measuring the concentration of the absorbed penetrants by extraction with solvents [30]. While useful information can be gathered from these methods, very little, if any, temporal and/or spatial information on the penetration or distribution of absorbed species in the film can be obtained. Techniques frequently used for concentration determination, such as NMR, ellipsometry and Raman spectroscopy, lack the resolution needed to investigate transport processes in polymeric films. A novel approach is hence needed to detect firstly if heterogeneous behaviour exists in a film and more importantly to investigate the origin and the implications of such behaviour. A newly developed approach, outline in this work, allows the study of penetrants transport in polymeric membranes *in-situ*, with good spatial and

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temporal resolutions. The local dynamics (diffusion) of solute in polymeric films can be determined. It will improve our understanding of the physics of penetrant dynamics in polymeric film. The knowledge obtained would be of great benefit in optimizing membrane design.

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

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

2. Experimental

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

2.1. Materials

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

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

2.1.1. Preparation of single layer film

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

Crosslinking of the PVA (and PVA-MMT) films was carried by addition of a mixture of the two following aqueous solutions: (1) 5 vol% methanol, 10 vol% hydrochloric acid (HCl), and 2.5 vol% glutaraldehyde; and (2) 5 vol% methanol and 10 vol% hydrochloric acid (HCl) only, into the PVA (and PVA-MMT) aqueous mixture such that the molar crosslink ratios of glutaraldehyde to PVA, i.e. the number of moles of glutaraldehyde per mole of PVA repeat unit, were 0, 0.001 and 0.005. Glutaraldehyde is mainly responsible for

the crosslinking of the PVA chains [32–34]. The membrane solution was poured into petri dishes and dried at room temperature for 72 h. By varying the amount of solution in the petri dishes, films with average thicknesses of 60 ± 10 μm, 100 ± 10 μm, and 180 ± 10 μm were produced. The final concentrations of MMT in the PVA-MMT films were 0, 0.1, 0.5 and 1 wt%. The resulting samples are designated as PVA-M-X-T, where M is the MMT concentration; X is the number of moles of glutaraldehyde per mole of PVA repeat unit (hence the assumed crosslink ratio); and T is the thickness of the film in μm. For example, PVA-0-0.001-60 is a PVA film that has 0 wt% of MMT, crosslink ratio of 0.001 and 60 μm in thickness.

2.1.2. Preparation of bilayer film

Two types of bilayer film are also prepared for investigation. Each type of bilayer 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 h. 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 h. The **top layer** and the **base layer** each have a thickness of 60 ± 5 μm and 40 ± 5 μm, respectively. Both layers have a crosslink ratio of 0.005. The resulting bilayer 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 min 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 Fig. 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.

Laser confocal imaging was carried out 1 min after a 25 μL Rh-6G aqueous solution droplet was added onto the sample film surface (see Fig. 1a). Excess Rh-6G solution remained on the film surface through the experiment. The examination of the through-thickness

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