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# Oxygen Diffusion into Polymer-Clay Composite Films as a Function of Clay Content and Temperature

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**Summary:** A simple fluorescence technique is proposed for the measurement of the diffusion coefficient of oxygen into polystyrene-clay composite films as a function of clay content and temperature. The composite films were prepared from a mixture of surfactant-free pyrene-labeled polystyrene latexes and modified Na-montmorillonite clay of various compositions at room temperature. Diffusion measurements were performed with films at room temperature for seven different clay contents (0, 5, 10, 20, 30, 50 and 60 wt.%). The diffusion coefficients of oxygen increased from $7.4 \times 10^{-10}$ to $26.9 \times 10^{-10}$ $cm^2s^{-1}$ with increasing clay content. On the other hand, diffusion measurements were performed over a temperature range of 25–70 °C for 0, 5 and 20 wt.% clay content films. The calculated diffusion activation energies decreased from 2.44 to 0.44 kcal/mol with increasing clay content. No clay content and temperature effects were observed on quenching rate constant and mutual diffusion coefficient values. The results showed that the diffusion coefficients are strongly dependent on both the temperature and clay content in the film.

**Keywords:** clay; composite; diffusion; fluorescence; polystyrene latex

## Introduction

In recent years, polymer/clay (P/C) nanocomposites have become increasingly important because they combine the structural, physical and chemical properties of both clays and polymers.[1,2] The efficiency of clay modifies many properties of the polymer, such as absorbance, ion exchange abilities, and thermal and solvent resistance. They give improved mechanical properties, gas barrier properties and decreased flammability compared with simple polymers.[3] The improved composites are widely used in areas such as construction, electronics, consumer products, and transportation.[4]

The enhancement of barrier properties in composites depends on several factors, such as the amount, length and width of filler particles, as well as their orientation and dispersion. Lu et al. examined the influence of 10 nm diameter silica particles on oxygen diffusion in PDMS polymer films.[5] A decrease was observed in oxygen diffusion coefficients, *D*, with increasing silica contents of PDMS. This reduction in *D* was attributed to the tortuous path of diffusing gas molecules and reduced molecular mobility of polymer chains caused by the filler particles. Recently, Lu and Mai developed a simple renormalization group model to assess the influence of geometric factors of layered silicate fillers on the gas barrier properties of polymer–clay nanocomposites.[6] Both studies showed that the aspect ratio of exfoliated silicate plates has a critical role in controlling the microstructure of polymer–clay nanocomposites and their gas barrier performance. In some of our earlier studies, we examined the effect of annealing[7]and packing[8] on the oxygen diffusion coefficient, *D*, in

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poly(methyl methacrylate) by using steady state (SSF) and photon transmission (PT) techniques. In these studies, we found that while the *D* values increased by increasing the film thickness (packing),[8] no temperature effect[7] was observed on diffusion coefficient, *D*.

In this study, we studied oxygen diffusion into PS/clay composite films depending on the MNaLB clay content and temperature by using the fluorescence quenching method. The approach was to monitor oxygen quenching of a fluorophore (pyrene), which was believed to be homogeneously dispersed within the films, accurately described by the linear Stern-Volmer equation[10] as a function of time. In determination of *D* values, the time-dependent emission intensity measured during the experiment corresponded to the average oxygen concentration throughout the film. By fitting the resulting intensity-time profile to an appropriate diffusion model for the film configuration, an accurate measure of the diffusion coefficients for the composite film was obtained.

## Experimental Part

### MNaLB Clay

The Na-activated bentonite (NaLB) was obtained from natural bentonite, which was collected from the bentonite deposits in Lalapaşa-Edirne, Thrace, Turkey (courtesy of Bensan Corp.) of 35% water content by treating the clay with 4 wt.% (w/w) $NaHCO_3$ solution. NaLB was dispersed in distilled water at room temperature by stirring for 24 h (6 wt.% NaLB stock dispersion). Meanwhile, the natural pH value of NaLB was found as 10.7. The cationic surfactant benzyldimethyltetradecyl ammonium chloride (BDTDACl) was dissolved in water at 20 mmol/l concentration. 5 ml of the BDTDACl stock solution, 6.25 ml of a 6 wt.% NaLB stock dispersion and 1.25 ml of distilled water were mixed and the final dispersion was shaken in order to obtain 3 wt.% NaLB and 8 mmol/l BDTDACl (modified clay). This dispersion was shaken overnight and an adsorption time of 24 h was adopted for the surfactant. The modified Na-montmorillonite clay (MNaLB) dispersion obtained was diluted to contain 0.0141g/ml MNaLB. The particle size distributions (PSD) of the bentonite was determined by sedimentation. The particle size was in the range 50–0.4 μm; the average particle size of NaLB was 10 μm. After the clay modification, the measured PSD of MNaLB was in the range of 10–0.4 μm.

### PS Latex

Pyrene (P)-labelled polystyrene (PS) particles were produced via the emulsifier-free radical polymerization process. The polymerization was carried out in a 200-ml thermostated round-bottomed four-necked flask, equipped with a glass anchor stirrer, reflux condenser and nitrogen inlet. Styrene monomer (commercial) was introduced in the reactor containing boiled and deionised water and the fluorescent monomer pyren-1-ylmethyl methacrylate (PolyFluor$^{TM}$394) was first dissolved in a small amount of styrene. The potassium persulfate (KPS) initiator was dissolved in water and added when the polymerization temperature was equilibrated at 70 °C. The stirring rate was 300 rpm. The recipe for the prepared latex is as follows: 100 ml water, 4 g of styrene, 0.1 g of KPS (dissolved in 2 ml water) and 0.0129 g of fluorescent monomer (dissolved in 1 g styrene). The polymerization was conducted during 18 h under nitrogen atmosphere. The particles obtained are spherical and fairly monodisperse, all having very similar mean diameters (320 nm).

### Film Preparation

PS/MNaLB composite films were prepared by the casting method. Distilled water was used to disperse the used materials. Seven different films with 0, 5, 10, 20, 30, 50 and 60 wt% MNaLB content were prepared from the dispersion of PS latex/MNaLB clay by using the relation:

$$W_{\mathrm{MNaLB}}\,(\mathrm{wt.\%}) = ((W_{\mathrm{MNaLB}})/(W_{\mathrm{PS}} + W_{\mathrm{MNaLB}})) \times 100 \qquad (1)$$

where $W_{\mathrm{MNaLB}}$ and $W_{\mathrm{PS}}$ are the weights of MNaLB clay and PS latex, respectively. By placing the same number of drops on glass plates with the size $0.8 \times 2.5\,\mathrm{cm}^2$ and allowing water to evaporate, dry films were obtained. The thickness of the films was determined from the mass and the density of samples; it ranged from 10 to 16 μm. Then the film samples were annealed at 200 °C, above the $T_g$ of PS (105 °C) for 10 min to complete the film formation process of PS particles. In fluorescence measurements of oxygen diffusion, films were placed in a round quartz tube filled with nitrogen, in a Perkin Elmer Model LS-50 fluorescence spectrophotometer. Slit widths were kept at 8 nm. P was excited at 345 nm wavelength and in all experiments the intensity at the emission maximum (395 nm) was used for the P intensity ($I$) measurements. $I$ was monitored against time for each clay content of the composite films after the quartz tube was opened to air for $O_2$ diffusion experiments by using the time-drive mode of spectrophotometer.

## Theoretical Considerations

### Fluorescence Quenching by Oxygen

When samples containing fluorescent probes are exposed to air or their solutions saturated with oxygen, the fluorescence intensities of the samples decrease and the rates of fluorescence decay increase. These phenomena are due to oxygen quenching of the probe's excited state. The mechanism of quenching involves a sequence of spin-allowed internal conversion processes, which takes place within a weak encounter complex of probe and oxygen. The product is either a singlet ground state or an excited triplet species.[9] Data generated from oxygen quenching studies on small molecules in homogeneous solution are usually analyzed using the Stern-Volmer relation, provided that the oxygen concentration $[O_2]$ is not too high.[10]

$$\frac{I_0}{I} = 1 + k_q \tau_0\,[O_2] \tag{2}$$

In this equation, $I$ and $I_0$ are the fluorescence intensities in the presence and absence of oxygen, respectively, $k_q$ is the bimolecular quenching rate constant and $\tau_0$ is the fluorescence lifetime in the absence of $O_2$. This equation requires that the decay of fluorescence be single-exponential and, moreover, that quenching interactions occur with a unique rate constant $k_q$. From the slope of a plot of $I_0/I$ versus $[O_2]$, $k_q$ can be determined provided that $\tau_0$ is known. Diffusion coefficients related to the quenching events can be calculated from the time-independent Smoluchowski-Einstein[10] equation,

$$k_q = \frac{4\pi \mathrm{N_A}(D_P + D_q)\mathrm{pR}}{1000} \tag{3}$$

where $D_P$ and $D_q$ are diffusion coefficients of the excited probe and quencher, respectively, $p$ is the quenching probability per collision, $R$ is the sum of the collision radii ($R_P + R_q$), and $\mathrm{N_A}$ is Avagadro's number. Equation (2) and (3) can also be applied to the case of quenching of polymer-bound excited states in glass as long as the fluorescence decay is exponential and $k_q$ is single-valued. A simplifying factor in the interpretation of $k_q$ is the general assumption that $D_P \ll D_q$ when the probe is covalently attached to a polymer.

### Diffusion in Plane Sheet

When Fick's second law of diffusion in plane is solved by assuming a constant diffusion coefficient, the following equation is obtained for concentration changes in time[11]

$$\frac{C}{C_0} = \frac{x}{d} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\cos n\pi}{n}\sin\frac{n\pi x}{d}\,\exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right) \tag{4}$$

where $d$ is the thickness of the slab, $D$ is the diffusion coefficient of the diffusant, and $C_0$ and $C$ are the concentration of the diffusant at time zero and $t$, respectively; $x$ corresponds to the distance at which $C$ is measured. We can replace the concentration terms directly with the amount of diffusant by using Equation 5;

$$M = \int_{v} C \mathrm{d}V \tag{5}$$

when Equation 5 is considered for a plane volume element and substituted into Equation 5, the following solution is obtained:[11]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \exp\left(\frac{D(2n+1)^2\pi^2 t}{d^2}\right) \tag{6}$$

where $M_\mathrm{t}$ and $M_\infty$ are the amounts of diffusant entering the plane at time $t$ and infinity, respectively.

## Results and Discussion

Figure 1 shows the intensity change with time for both MNaLB content (Figure 1a) and temperature (Figure 1b), respectively. The pyrene emission intensity ($I_\mathrm{P}$) decreases with time due to the diffusion of oxygen into the film and reaches a plateau when the films are saturated. It has to be noted that the quenching rate for high clay contents and temperature is higher indicating rapid diffusion of oxygen into the film.

In order to interpret the above findings, Equation 2 was expanded in a series for low quenching efficiency, i.e. $k_\mathrm{q}\ \tau_0[\mathrm{O}_2] \ll 1$ producing the following useful result

$$I \approx I_0(1 - k_\mathrm{q}\tau_0[\mathrm{O}_2]) \tag{7}$$

During $O_2$ diffusion into the latex films, P molecules are quenched in the volume which is occupied by $O_2$ at time $t$. Then P intensity at time $t$ can be represented as

$$I_t = \frac{\int I \mathrm{d}v}{\int \mathrm{d}v} = I_0 - \frac{k_\mathrm{q}\tau_0 I_0}{\mathrm{V}}\int [\mathrm{O}_2]\mathrm{d}v \tag{8}$$

where d$v$ and $V$ are the differential and total volume of composite film presented in Figure 2.

Performing the integration the following relation is obtained

$$I_t = I_0\left(1 - k_\mathrm{q}\frac{\tau_0}{\mathrm{V}}\mathrm{O}_2(t)\right) \tag{9}$$

where $\mathrm{O}_2(t) = \int [\mathrm{O}_2]\mathrm{d}v$ is the amount of oxygen diffused into the latex film at time $t$. Here $\mathrm{O}_2(t)$ corresponds to $M_\mathrm{t}$ in Equation 6. Combining Equation 6 for $n = 0$ for oxygen with Equation 9, the following useful relation is obtained to interpret the diffusion curves in Figure 2

$$\frac{I_t}{I_0} = \mathrm{A} + \frac{8C}{\pi^2}\exp\left(-\frac{D\pi^2 t}{d^2}\right) \tag{10}$$

where $d$ is the film thickness and $D$ is the oxygen diffusion coefficient, $C = \frac{k_\mathrm{q}\tau_0\mathrm{O}_2(\infty)}{\mathrm{V}}$ and $\mathrm{A} = 1 - \mathrm{C}$.

By fitting the resulting intensities versus the time profile in Figure 1 to Equation 8, the oxygen diffusion ($D$) coefficients were determined. The dependence of $D$ on the

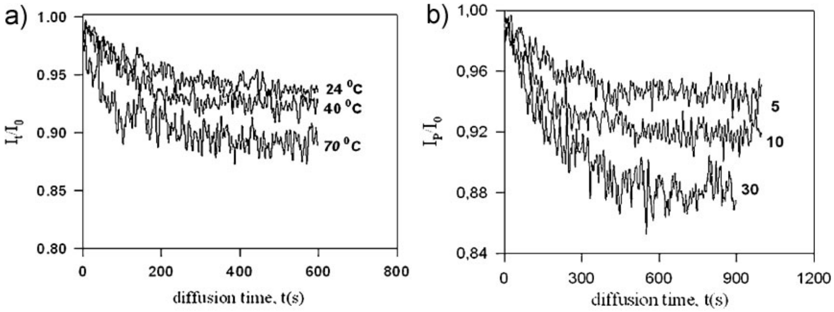

***Figure 1.***
The time dependence of pyrene (P), fluorescence intensity, *I*, in oxygen diffusion into the **(a)** film containing 5 wt.% MNaLB at various temperatures and **(b)** composite films with different clay contents. Numbers on curves indicate temperatures (°C) and clay contents (%) in the film.

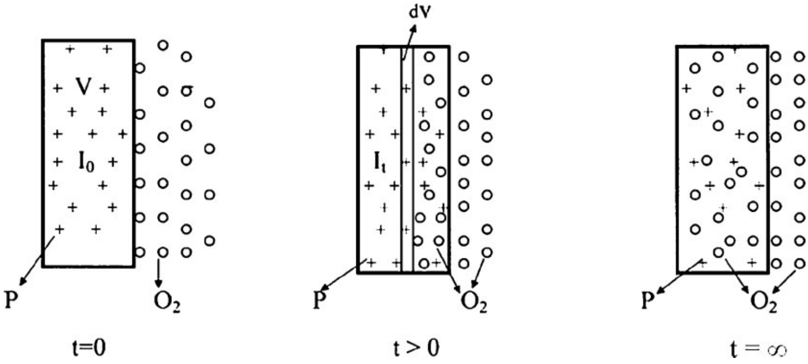

***Figure 2.***
Oxygen diffusion into a latex film.

MNaLB clay content and temperatures are given in Figure 3a and b, respectively. It is seen that diffusion of oxygen was accelerated by increasing both clay fraction and temperature. The increase in $D$ with increasing clay content may be attributed to the presence of a large fraction of microvoids inside the higher MNaLB content films.

Oxygen can diffuse very rapidly to the bulk of the composite films through these voids.

### Diffusion Activation Energies

The transport of gases through the membranes can be described as a thermally activated process that obeys the Arrhenius behavior. The temperature dependence of coefficient $D$ can be written as follows:

$$D = D_0 \exp\left(\frac{-\Delta E_D}{k_B T}\right) \tag{11}$$

Here $k_B$ is the Boltzmann constant, $D_0$ is pre-exponantial factor, $\Delta E_D$ is the activation energy associated with the oxygen diffusion. The activation energy was determined from the logarithmic plots of the $D$ coefficient against the reciprocal of the absolute temperature in Figure 3a. Ln$D$ is plotted vs 1000/$T$ for different clay contents in Figure 4. The values of activation energy associated with oxygen diffusion ($\Delta E_D$) for different clay contents were calculated from the slope of these plots by fitting the data in Figure 4 to Equation 11 by a

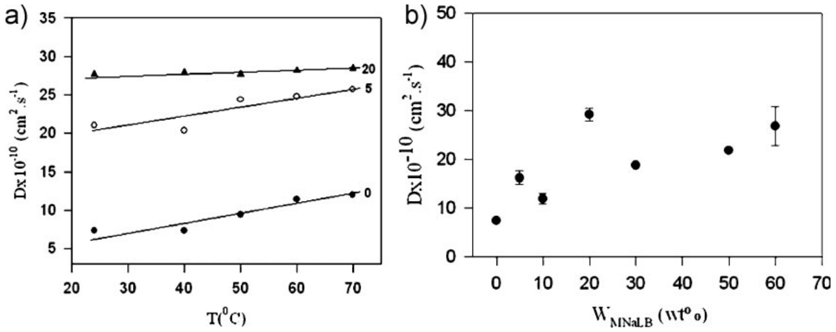

***Figure 3.***
Plot of the diffusion coefficients, $D$ (a) versus temperatures, $T$ (°C) for the 0, 5 and 20 wt.% MNaLB content films and (b) versus WMNaLB (wt.%).

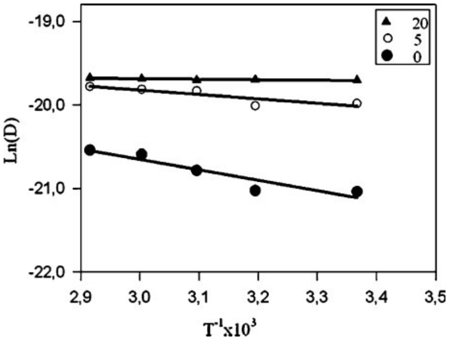

***Figure 4.***
Plot of the logarithmic form of Equation 8 for the data in Figure 3 a. $\Delta E_D$ values are obtained from the slopes of the straight lines for each MNaLB content in the film, respectively.

least-square fit. $\Delta E_D$ values were 10.2, 4.3 and 0.5 $kcal \cdot mol^{-1}$ for films containing 0, 5 and 20 wt.% MNaLB, respectively. These results show that $\Delta E_D$ decreases with increasing clay content, which confirms our above assumptions. In other words, the energy requirement for the oxygen diffusing in the porous medium is much less than in rigid environment.

## Conclusion

This work has shown that it is possible to measure the diffusion coefficient of oxygen into composite films quite accurately by using a simple SSF technique. The oxygen diffusion coefficients ($D$) and related activation energies in PS-MNaLB composite films were determined and compared. The results showed that diffusion of oxygen was accelerated by increasing in clay content and temperature. The high diffusion rate of oxygen in the composite is attributed to the formation of voids (pores) in the film which facilitates oxygen diffusion. A decrease in the activation energy associated with the oxygen diffusion process ($\Delta E_D$) is observed with increasing clay fraction.

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