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Fluorescence quenching method for monitoring oxygen diffusion into PS/CNT composite films

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ABSTRACT

Oxygen permeabilities of nanocomposite films consisting of multi wall carbon nanotubes (MWNT) and polystyrene (PS) were determined to investigate the oxygen diffusion depending on MWNT and temperature. A method which is based on quenching of an excited phosphorescent by oxygen was applied for the measurements. The composite films were prepared from mixtures of (MWNT) and surfactant-free pyrene (P)-labeled (PS) latexes of various compositions at room temperature. These films were then annealed at 170 °C which is well above the glass transition (T_g) temperature of polystyrene, for 10 min. Diffusion experiments were performed for eight films with different MWNT content (0, 1.5, 3, 5, 10, 15, 25 and 40 wt%) to evaluate the effect of MWNT content on oxygen diffusion. Diffusion coefficients were found to increase from 1.1×10^{-12} to 41×10^{-12} $cm^2\ s^{-1}$ with increasing MWNT content. On the other hand, to examine the effect of temperature on oxygen diffusion, diffusion measurements were performed over a temperature range of 24–70 °C for three different MWNT contents (3, 15, and 40 wt%) within the films. The results indicated that the values of the diffusion coefficient D are strongly dependent on both temperature and MWNT content in the film. It was also observed that the diffusion coefficients obey Arrhenius behavior, from which diffusion energies were determined, which increased with increase of MWNT content and temperature.

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1. Introduction

In the last few years, the most desirable property of polymer films is their resistance to the gas diffusion. Because single component polymer films have poor mechanical and gas barrier properties, there has been growing interest in producing new materials by filling polymers with inorganic natural (minerals) and/or synthetic (carbon black and silica) compounds [1–5]. They give improved mechanical properties, gas barrier properties, and decreased flammability relative to the pure polymers [6]. In 2000, the potential for CNTs as gas sensors was first reported based on an increase in the conductivity by several orders of magnitude upon exposure of CNTs to oxygen [7]. Oxygen is the one of the most important reactants to be considered in the diffusion phenomenon. Several spectroscopic techniques that utilize oxygen quenching to determine the rate of oxygen diffusion through polymer films have been reported. Cox [8] and Dunn [9], and MacCallum and Rudkin [10] measured oxygen diffusion coefficients by fluorescence quenching in planar sheets of poly(dimethyl siloxane) [8], filled poly(dimethyl siloxane) samples [9], and polystyrene [10]. They monitored oxygen quenching of a fluorophore as a function of time by assuming that fluorophores dispersed homogeneously within the film. The mathematical determination of D varied, but a single underlying assumption in all cases was that the time-dependent emission intensity was measured during the experiment. In some cases, the intensity versus time curve was converted to a concentration versus time curve using the Stern–Volmer relationship [8,9]. Lu et al. [11–13] have used time-scan experiments to measure the decay of luminescence intensity as oxygen diffuses into polymer films under constant illumination and the growth of intensity as oxygen diffuses out of the film. They interpreted their data with the aid of theoretical expressions based on Stern–Volmer quenching kinetics with Fick's laws of diffusion

In the present work we used a method for determining diffusion coefficients of oxygen in CNT/PS composites based on luminescence quenching. The luminescence of some fluorophores quench in the presence of oxygen. Initially, pyrene (P)-labeled polystyrene and multi-wall carbon nanotube composite film is equilibrated at a particular oxygen concentration and then after displacement of nitrogen atmosphere over the sample by oxygen, the film begins to expose to lower oxygen concentration. For pyrene, the intensity of quenching is proportional to the concentration of

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oxygen. The average oxygen concentration change in the sample was monitored by studying the average intensity change of the pyrene using a spectrofluorometer. We assume the quenching is accurately described by a linear Stern–Volmer equation [14] and that the optical density is low enough that the sample is uniformly excited. By fitting the resultant intensity versus time profile to an appropriate diffusion model for the film configuration, a measure of the diffusion coefficients for the composite film were obtained.

2. Experimental

2.1. PS Latex

Pyrene labeled PS particles was produced via surfactant free emulsion polymerization process. The polymerization was performed batch-wisely using a thermostated reactor equipped with a condenser, thermocouple, mechanical stirring paddle and nitrogen inlet. The agitation rate was 400 rpm and the polymerization temperature was controlled at 70 °C. Water (100 ml) and styrene (5 g) were first mixed in polymer ization reactor where the temperature was kept constant (at 70 °C). Potassium peroxodisulfate (KPS) initiator (0.1 g) dissolved in small amount of water (2 ml) was then introduced in order to induce styrene polymerization. The polymerization was conducted during 18 h. The polymer has a high glass transition temperature (T_g = 105 °C). The latex dispersion has an average particle size of 400 nm. Fig. 1 shows SEM image of PS latex produced for this study.

2.2. MWNT carbon nanotube

Commercially available MWNTs (Cheap Tubes Inc., VT, USA,) were used as supplied in black powder form without further purification. The MWNT are 10–30 μm long, average inner diameter 5–10 nm, outer diameter 20–30 nm, the density is approximately 2.1 g/cm^3 and purity higher than 95 wt%. A stock solution of MWNTs was prepared following the manifacturers regulations: nanotubes were dispersed in deionized (DI) water with the aid of Polyvinyl Pyrolidone (PVP) in the proportions of 10 parts MWNTs; 1–2 parts PVP; 2.000 parts DI water by bath sonication for 3 h. PVP is a good stabilizing agent for dispersions of carbon nanotubes, enabling preparation of polystyrene composites from dispersions of MWNT in polystyrene solution. Fig. 2 shows the TEM image of MWNTs used in this study (www.cheaptubesinc.com).

2.3. Preparation of PS/MWNT composite films

Eight different mixtures were prepared with 0, 1.5, 3, 5, 10, 15, 25, and 40 wt% MWNT. Each mixture was stirred for 1 h followed by sonication for 30 min at room temperature. By placing the same number of drops on a glass plates with similar surface areas (0.8 cm × 2.5 cm) and allowing the water to evaporate at 60 °C in the oven, dry films were obtained. After drying, samples were separately annealed above T_g of PS for 10 min at temperature 170 °C. After annealing step, films were removed from the oven and cooled down to room temperature. The thickness of the films was determined from the weight and the density of samples and ranges from 2 to 5 μm. Scanning electron microscope (SEM) images were taken by using LEO Supra VP35 FESEM

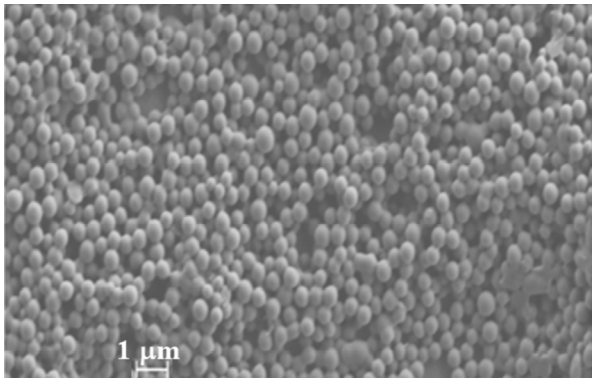


Fig. 1. SEM picture of pure PS latex.

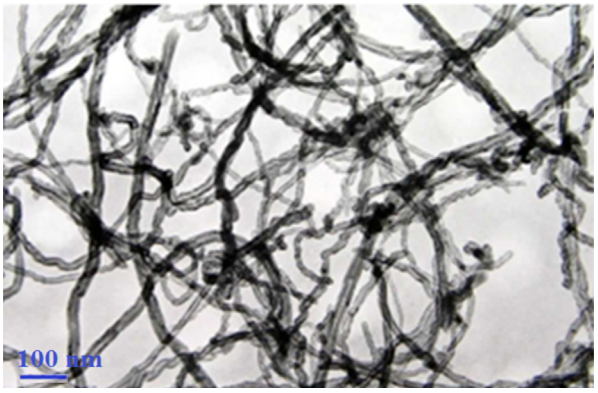


Fig. 2. TEM picture of MWNT.

2.4. Therotical considerations

2.4.1. Fluorescence quenching by oxygen

Data generated from oxygen quenching studies on small molecules in homogeneous solution are usually analyzed using the Stern–Volmer relation (Eq. (1)), provided that the oxygen concentration [O_2] is not too high [14].

$$\frac{I_0}{I} = 1 + k_q \tau_0 [O_2] \quad (1)$$

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 τ_0 is the fluorescence lifetime in the absence of O_2.

Diffusion coefficients related to the quenching events can be calculated from the time-independent Smoluchowski–Einstein [14] equation,

$$k_q = pk_o = \frac{4\pi N_A (D_P + D_q) pR}{1000} \quad (2)$$

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 N_A is Avagadro's number. Eqs. (1) and (2) 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-value. Simplifying for interpretation of k_q is the assumption that $D_P \ll D_q$ when the fluorescence probe is covalently attached to a polymer.

2.4.2. Diffusion in plane sheet

Fick's second law of diffusion was used to model diffusion phenomena in plane sheet. The following equation is obtained by assuming a constant diffusion coefficient, for concentration changes in time [15]

$$\frac{C}{C_0} = \frac{x}{d} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos\ n\pi}{n} \sin \frac{n\pi x}{d} \exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right) \quad (3)$$

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

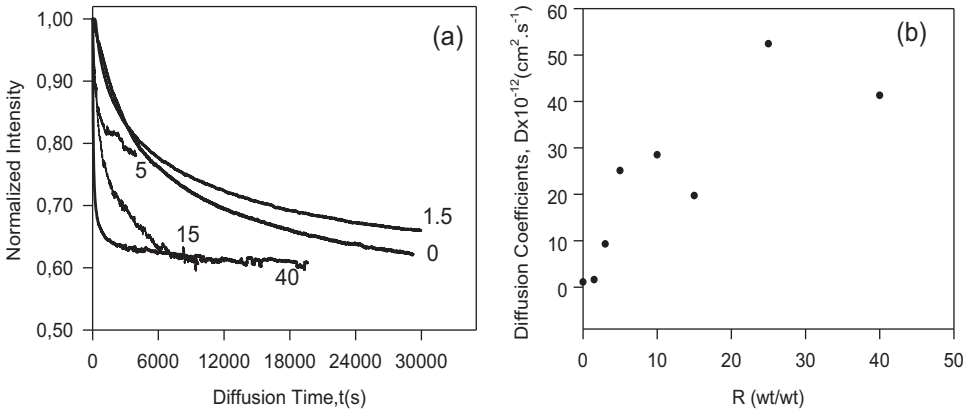


Fig. 3. (a) The time behavior of pyrene, P, fluorescence intensity, *I*, during oxygen diffusion into the composite films with different MWNT content. Numbers on each curve indicates the MWNT content (%) in the film. (b) Plot of the diffusion coefficients, *D* versus W_{MWNT} (wt%).

time zero and *t*, respectively. *x* corresponds to the position at which *C* is measured. We can replace the concentration terms directly with the amount of diffusant, *M* by using the following relation:

$$M = \int_v C dV \tag{4}$$

when Eq. (4) is considered for a volume element in the plane sheet and substituted in Eq. (3), the following solution is obtained [15]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{D(2n+1)^2\pi^2 t}{d^2}\right) \tag{5}$$

where M_t and M_∞ represent the amounts of diffusant (oxygen) entering the plane sheet at time *t* and infinity, respectively.

3. Results and discussion

In Fig. 3(a), normalized pyrene intensity, I_p curves are presented against diffusion time for films having different MWNT content exposed to oxygen. It is seen that as oxygen diffused through the planar film, the emission intensity of the pyrene decreased according to Eq. (1) for each MWNT content film and was saturated once oxygen equilibrated in the film. Here, it has to be noted that in Fig. 3(a) the quenching rate for low MWNT content film is lower than for high MWNT content film predicting the more rapid quenching of excited pyrenes by O_2 molecules diffused into the high MWNT content composite films.

All curves behave almost in the same fashion, as oxygen diffused through and equilibrated in the film. It is also seen that the diffusion curves reach their equilibrium value at shorter times for higher MWNT content films.

In order to interpret the above findings, Eq. (1) can be used by expanding in a series for low quenching efficiency, i.e. $k_q\tau_0[O_2] \ll 1$ which then produces the following useful result:

$$I \approx I_0(1 - k_q\tau_0[O_2]) \tag{6}$$

During O_2 diffusion into the latex films, P molecules are quenched in the volume which is occupied by O_2 molecules at time, *t*. Then *P* intensity at time *t* can be represented by the volume integration of Eq. (6) as

$$I_t = \frac{\int I dv}{\int dv} = I_0 - \frac{k_q\tau_0 I_0}{V}\int dv[O_2] \tag{7}$$

where *dv* and *V* are the differential and total volume of composite film. Performing the integration the following relation is obtained

$$I_t = I_0\left(1 - k_q\frac{\tau_0}{V}O_2(t)\right) \tag{8}$$

where $O_2(t) = \int dv[O_2]$ is the amount of oxygen molecules diffuse into the film at time *t*. If it is assumed that $O_2(t)$ corresponds to M_t then Eq. (5) can be combined for oxygen with Eq. (8) and the following useful relation is obtained which can be used to interpret the diffusion curves in Fig. 3(a)

$$\frac{I_p}{I_0} = A + \frac{8C}{\pi^2}\exp\left(-\frac{D\pi^2 t}{d^2}\right) \tag{9}$$

where *d* is now present as the film thickness, *D* is the oxygen diffusion coefficient, $C = k_q\tau_o O_2(\infty)/V$ and $A = 1 - C$. Here $O_2(\infty)$ is the amount of oxygen molecules diffused into the film at time infinity. As a result, we combined the linear Stern–Volmer equation with the diffusion model to extract the diffusion coefficients from the experimental data. The logarithmic form of Eq. (9) can be written as follows:

$$Ln\left(\frac{Ip}{I_0} - A\right) = Ln\left(\frac{8C}{\pi^2}\right) - \frac{D\pi^2}{d^2}t \tag{10}$$

This model is fitted with the experimental data using a linear least-squares fitting method to extract both k_q and diffusion coefficient (*D*) values.

In Fig. 3(b) the increase in *D* values with increasing carbon nanotube content may be attributed to the presence of a large fraction of micro voids inside the higher MWNT content films. Oxygen can diffuse very rapidly to the inside of the composite films through these voids.

Normalized pyrene intensity, I_p, curves are presented in Fig. 4 as a function of time for the 40 wt% MWNT content film exposed

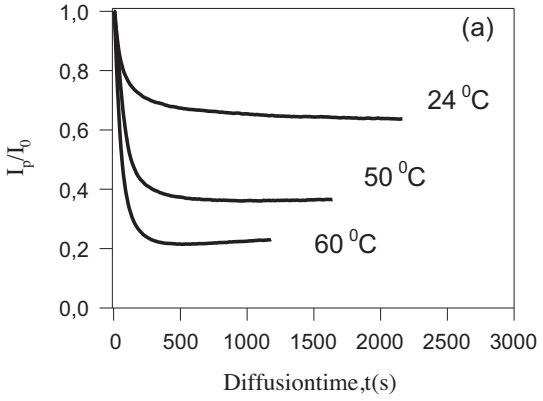


Fig. 4. The time behavior of the pyrene, P, fluorescence intensity, *I*, during oxygen diffusion into the 40 wt% MWNT content film at various temperatures. Numbers on each curve indicate the temperature.

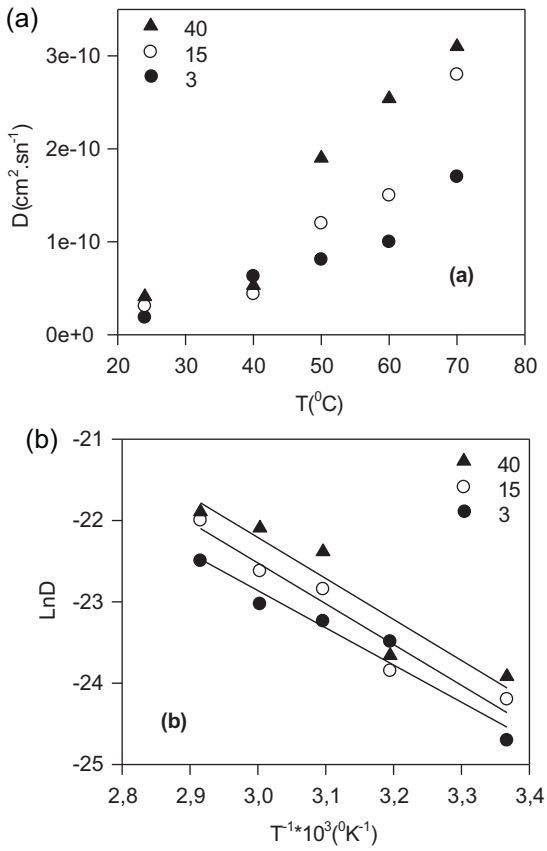


Fig. 5. (a) Plot of the diffusion coefficients, D versus temperatures, T for the 3, 15 and 40 wt% MWNT content films. (b) Ln(D) versus 1000/T for the different MWNT fraction content films, respectively. (ΔE_D) values are obtained from the slopes of the straight lines for each MWNT content film.

to oxygen at three different temperatures. It is seen that as oxygen diffused through the planar film, the emission intensity of the pyrene decreased according to Eq. (1) for each temperature. The rate of decrease in intensity is higher at higher temperatures predicting the more rapid quenching of excited pyrene molecules by O_2 molecules diffused into the films. It is worthy to note that in Fig. 5(a) as expected the D increases with increase in temperature for all composite films. Increase in temperature naturally increases the Brownian motion of oxygen molecules given them more chance to meet the P molecules in the composite film.

In Fig. 6 also confirm these results. Before annealing, no deformation in PS particles is observed and PS particles keep their original spherical shapes for both samples. After annealing treatment at 170 °C, SEM images show that completes particle coalescence has been achieved. It can be clearly seen that the composite film consists of a network of bundles of CNT, especially in the 40 wt% MWNT content film, and indicates significant porosity. As shown in Fig. 6, carbon nanotubes are not well distributed in the polymer matrix and voids between the carbon nano-particles and polymer matrix appeared allowing oxygen molecules to move rapidly. Therefore, O_2 molecules can easily pass through these voids. Thus, the permeability of O_2 gas is increased, yielding high diffusion coefficients. As a result, more rapid diffusion of oxygen [14] into the higher MWNT content films occurs due to the presence of a large number of micro voids in these films.

These results are consistent with previous studies [16–19]. Generally, enhancement in the gas permeability of polymers by putting inorganic fillers into the organic polymer resulted from the disturbed polymer chain packing by the nano fillers [16]. Therefore, the well dispersed state of carbon nanotubes and their good adherence effectively increases gas permeability as the result of effective insertions between the polymer chains of the matrix. It was reported that addition of 2 wt% of modified carbon nanotubes loading to the polyethersulfone resulted in about 19.97% increases in the permeability of CO_2, while the permeability of CH_4 increased up to 33.79%. However, for small gas molecules, such as CO_2, the permeability increased slightly with the addition of carbon nanotubes in the polyethersulfone (PES) host matrix. The main pathways of gas transport through the mixed matrix membranes are through the dense layer of the PES matrix, highly selective carbon nanotubes and non-selective gaps or voids between the matrix and sieve particles. It was observed that the main factor affecting the increase of CH_4 permeability with the addition of carbon nanotubes into the polymer host resulted from the extremely rapid diffusion of gas molecules adsorbed inside the carbon nanotubes. SEM data also showed that the carbon nanotubes are well dispersed in the polymer matrix and serve as channels to transport gas molecules [17–19]. It is known that the addition of filler into polymer films above a critical percentage creates voids [17,18] in the polymer matrix. Ponomarev and Gouterman [17] have reported that the addition of high amounts of titanium oxide (TiO_2) in pressure sensitive (PSP) paints cause the presence of a large fraction of micro voids inside the films. As a result, air can diffuse very rapidly to the inside of the coating through these voids.

When the pyrene diffusion in the latex film is omitted and $p = 1$ is taken then Eq. (2) becomes as

$$k_q = \frac{4\pi N_A D_m \boldsymbol{R}}{1000} \tag{11}$$

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. For quenchers as small as molecular oxygen, this assumption is reasonable. Here D_m is called as mutual diffusion coefficient which can now be assumed to be the self-diffusion coefficient of O_2 in the composite film. Since k_q is known and if R is taken as the radius of pyrene [19] then the averaged D_m values are found and

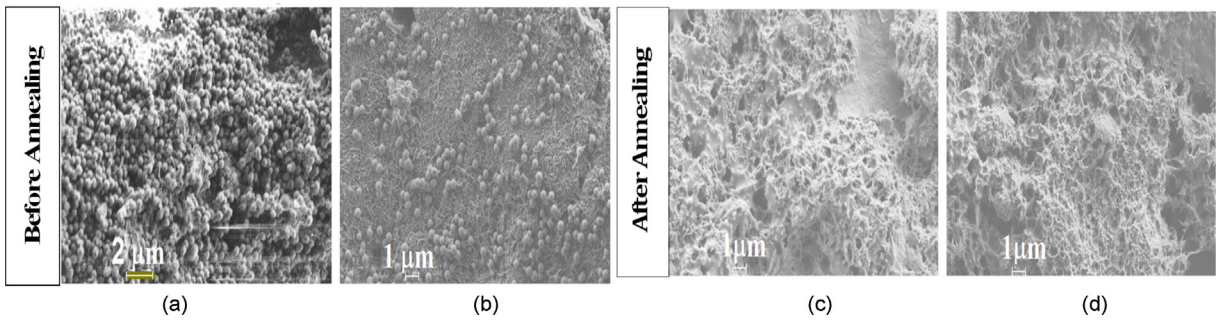


Fig. 6. SEM pictures of composite films prepared with 15 and 40 wt% MWNT content before annealing (a and b) and after annealing at 170 °C (c and d), respectively.

Table 1
Experimentally obtained mutual diffusion (D_m) coefficients at various temperatures.

$D_m \times 10^{-5}$ (cm^2 s^{-1})			
T(°C)	3	15	40
24	1.4 ± 0.05	1.1 ± 0.01	1.7 ± 0.10
40	2.2 ± 0.007	0.3 ± 0.008	3.8 ± 0.19
50	0.7 ± 0.02	0.4 ± 0.008	2.5 ± 0.02
60	0.2 ± 0.01	0.3 ± 0.005	2.2 ± 0.01
70	2.9 ± 0.007	0.5 ± 0.014	0.5 ± 0.02

Table 2
Activation energies of O_2 diffusion depending on MWNT content (see Eq. (12)).

MWNT (wt%)	3	15	40
ΔE_D (kJ mol^{-1})	68	76	100

listed in Table 1 for the composite films having different MWNT content.

It is seen in Table 1 that D_m is independent of MWNT content in composite films i.e. once O_2 penetrates into the film then it moves in short range independent of the material structure. D_m value obtained in the present study (10^{-5} cm^2 s^{-1}) is one order larger than that previously obtained (10^{-6} cm^2 s^{-1}) by using the same technique [19–21]. This shows that the voids in composite films helps the rapid quenching of excited pyrene molecules and reduce their response time.

4. Diffusion energies

The diffusion of small molecules through membranes can be described as a thermally activated process that obeys Arrhenius behavior. The temperature dependence of the diffusion coefficient, D, can be written as follows:

$$D = D_0 \exp\left(\frac{-\Delta E_D}{k_B T}\right) \quad (12)$$

here k_B is the Boltzmann constant, D_0 is pre-exponantial factor, ΔE_D is the activation energy as 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 Fig. 5(b), Ln(D) was plotted versus 1000/T for the different MWNT fraction, respectively. The value of the activation energy associated with oxygen diffusion (ΔE_D) for different MWNT fractions was calculated from the slope of these plots by fitting the data in Fig. 3(b) to the Eq. (12) by a least square fit. The results are given in Table 2, where ΔE_D increases with increasing MWNT content. The energy need for oxygen diffusion in the high MWNT medium is much higher than in a low MWNT environment. Most probably, the motion of O_2 molecules is screened by the large number of MWNT barriers during their journey in the high MWNT content medium, in where O_2 needs higher energy to overcome this difficulty.

5. Conclusions

We have present a simple, fast, and practical route to measure the diffusion of oxygen into PS/MWNT composite films at elevated temperatures for different MWNT contents using a combination of fluorescence quenching method and Fickian transport [22–24]. The oxygen diffusion coefficients (D) and related activation energies (ΔE_D) in these composite films were determined and compared. The results showed that diffusion of oxygen was accelerated by both increase in MWNT fraction 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. The increase in the energy associated with the oxygen diffusion process (ΔE_D) is observed with increase in MWNT fraction. In conclusion, this work has shown that simple seady state fluorescence (SSF) technique can be used to measure the diffusion coefficient of oxygen molecules into composite films quite accurately.

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