Analyzing the Diffusion Process for Polymer Solution Using FTIR-ATR Technique: Special Considerations

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Abstract—Diffusion of small molecules through the polymers has significant importance in different scientific and engineering fields such as medicine, textile industry, membrane separations, packaging in food industry, extraction of solvents and of contaminants, and etc. This paper reports the use of Fourier transform infrared-attenuated total reflectance (FTIR-ATR) and partial least squares (PLS) analysis to study the compositional change of polymer solution exposed to the certain atmosphere. Diffusion coefficient of tetrahydrofuran (THF) in solution of polystyrene was obtained by means of analyzing the spectral data collected by FTIR-ATR instrument. Desorption by which the solvent evaporates from boundary of polymer solution, with respect to the time, showed that three regions of compositional change appeared: plateau, steep slope, and gentle slope regions. Providing the desorption data from the second region which is the essential part of mass transfer, the value of diffusion coefficient of THF was obtained 5.8×10^{-6} cm^2/sec. Finally, affecting factors and limitations of FTIR-ATR technique on reliability of spectral data are discussed.

Key words: Diffusion, polymer solution, FTIR-ATR, polystyrene, Tetrahydrofuran.

I. INTRODUCTION

POLYMER solutions are important for a variety of purposes, especially, for manufacturing fibers and membranes. Generally, solidification of polymer in shape of interest takes place by solvent evaporation from and/or nonsolvent diffusion into the polymer solution. During the process, polymer solution is undergoes a change in the concentration of components. Great varieties of methods are available for analyzing the diffusion coefficient of the penetrant into the polymer solutions and films. For non-condensable gases such as carbon dioxide, nitrogen, and methane, pressure decay techniques [1] and membrane permeation [2] are often employed. While for condensable gases or vapors, gravimetric techniques are more useful [3-5]. Dielectric relaxation spectroscopy [6], quartz crystal microgravimetry [7], fluorescence [8], dynamic light scattering [9], Raman spectroscopy [10,11] and NMR spectroscopy[12,13] are other methods to measure the diffusion coefficient. Each of these experimental techniques has demonstrated the ability to obtain diffusion coefficients in polymers. Some disadvantages of these techniques include difficulties in operation, a lack of

detailed information regarding to the diffusion process (molecular-level phenomena), indirect methods of detection, and the inability to monitor the diffusion process continuously, are reasons for pursuing new techniques without the aforementioned limitations [14,15]. Fourier transform infrared-attenuated total reflection (FTIR-ATR) is a promising tool for determination of the diffusion coefficient of small molecules in polymer solutions and makes it possible to investigate the mass transfer during diffusion process.

IR-ATR technique has been used about 40 years for analyzing the diffusion in polymers. Since early studies in 1975 by Lavrent'ev and coworkers as mentioned in reference [14], till now many experiences were released on diffusion of different systems. A well-reported review on history of the subject can be found in reference [14]. Unfortunately, poor adhesion between the polymer and the ATR element and also the lack of speed and accuracy of measurement due to technical restrictions limited the precision of the technique during that time. In the mid-1980s, by introducing the FTIR spectrometers, the speed and resolution of measurement increased dramatically, enabling an in-situ technique with higher precision. Many issues can be listed in which the FTIR-ATR technique were employed to analyze the diffusion process of the systems; among them are removing the calcium carbonate from latex films [16], diffusion of water and its effect on swelling and drying in the latex films[17], diffusion of decanol in hydrogenated polybutadiene and monitoring the changes in chemistry of both solute and polymer [18], probing the state of water in proton exchange membranes [19-21], sorption and releasing drug from controlled delivery systems of therapeutic agents [22-25], and many other existing reports available in literatures. Many of these studies have compared results from FTIR–ATR spectroscopy to one or more of other techniques, demonstrating excellent agreement between the techniques.

Diffusion is movement of penetrant from one part of a system to another and it is mainly a result of random molecular motions [26]. Understanding the diffusion of small molecules in polymeric materials is important to a number of applications such as membrane separations [27], barrier materials [28-30], drug delivery [22-25], fuel cells [31,32] and chemical sensors [33]. In textile industry diffusion is important in many processes. The rate of solvent outflow and nonsolvent inflow in fiber and membrane formation, time of dying and amount of dye uptake in dyeing process, the rate of water absorption and

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conditioning time in protective clothes are some examples of importance of diffusion coefficient in textile and polymer fields.

Investigating molecular interactions and their roles in the diffusion process is another ability of FTIR-ATR technique in which it has been taken attention in the literatures [14, 34-38]. Elabd and Barbari [38] investigated the effects of solute–solute interactions with their study on methyl ethyl ketone (MEK)/butanol mixtures in polyisobutylene (PIB). By deconvoluting the carbonyl and hydroxyl regions of the spectra as a function of time, diffusion coefficients and hydrogen-bonding interactions were quantitatively measured. Free MEK, self-associated butanol, and MEK–butanol complex were identified from the spectra. Diffusion coefficient of the butanol cluster was less than the MEK–butanol complex and it was less than free MEK. To elucidate the differences between interacting and non-interacting systems, the MEK/butanol/PIB results were compared to those for MEK/acetonitrile mixture.

Regarding to the above demonstration on ability of FTIR-ATR technique for analyzing the diffusion process of polymer/penetrant mixture, we were motivated to give some special considerations on measuring and quantifying the spectral data collected from FTIR-ATR for polystyrene/tetrahydrofuran (PS/THF) solution during the solvent evaporation. In this paper, the principles behind FTIR-ATR are discussed. We focus on describing the technique and an ATR-diffusion model based upon Fick's second law is described in detail for PS/THF mixture. In addition, the methods of quantification of spectra are reviewed.

II. THEORY AND EXPERIMENTS

Diffusion of small molecule in polymer film is described by Fick's second law, presented by Eq. (1) [39],

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial C}{\partial x} \right], \tag{1}$$

where C is the concentration, x the distance and $\partial C/\partial x$ the gradient of the concentration along the x axis, D a constant that is called diffusion coefficient, and $\partial C/\partial t$ is concentration change of penetrant with respect to the time, t.

Diffusion of small molecules depends on the physical properties of the polymer network and the interactions between the polymer segments and the small molecules. According to the rate of diffusion of penetrant with respect to the relaxation rate for polymer matrices, the process of diffusion is classified into two categories: Fickian and non-Fickian diffusions. According to the Fick's second law, the basic equation of mass uptake by polymer film can be given by Eq. (2) [26].

$$\frac{M_t}{M_\infty} = kt^n, \tag{2}$$

where, the exponent n is called the type of diffusion mechanism, and k is constant which depends on diffusion coefficient and thickness of film.

Fickian diffusion (Case I) is often observed in polymer system when the temperature is well above the glass transition temperature of the polymer (T_g). Therefore, it is expected that M_t/M_∞ (M_∞ is the amount of penetrant absorbed at equilibrium) is proportional to the square-root of time i.e. $n = 0.5$. Other mechanisms has been established for diffusion phenomenon and categorized based on the exponent n, as follow [40];

$$n > 1 \qquad \text{Supercase II}$$
$$n = 1 \qquad \text{Case II}$$
$$1 > n > 1/2 \qquad \text{Anomalous}$$
$$1/2 > n \qquad \text{Pseudo-Fickian}$$

The Case II diffusion is the second most important mechanism of diffusion for the polymer. This is a process of moving boundaries and a linear sorption kinetics, which is opposed to Fickian. A sharp penetration front is observed by which it advances with a constant rate. More detailed features of the process, such as the induction period and front acceleration in the latter stage, have been documented in the literatures [41].

An exponent between 1 and 0.5 signifies anomalous diffusion. Case II and Anomalous diffusion are usually observed for polymer whose glass transition temperature is higher than the experimental temperature. The main difference between these two diffusion modes concerns the solvent diffusion rate [15,26].

Infrared spectroscopy is a widely used technique that has been an important tool for investigating diffusion process. FTIR-ATR spectroscopy has proven to be very accurate and reliable because it is an in-situ technique that can provide reliable short-time data often missed in other techniques [14,31,38,42-44]. In comparison with other techniques such as NMR spectroscopy, FTIR-ATR technique is also simple to use and relatively inexpensive. FTIR–ATR spectroscopy is a technique that sets itself apart from other techniques with its ability to provide molecular-level contrast between penetrant(s) and the polymer to understand the chemical interactions that occur on a molecular level and how they affect the overall transport rates in a polymer. It can also investigate and measure diffusion of multi-component system. Therefore, in recent years, this technique has been increasingly employed to investigate mass transfer and diffusion process.

The polystyrene solution (15 wt.%) was prepared by dissolving PS in THF as solvent under gentle stirring at room temperature until a clear polymer solution was obtained. Tetrahydrofuran from Merck, Germany and polystyrene of commercial grade (Solarene G144) with melt flow index of 8.5 (200 °C, 5 kg) from Dongbu Hannong Chemical Co. were purchased and used as received. Polymer solution was cast directly on the surface of a multiple reflection ATR crystal (ZnSe, refractive index 2.4 and incident angle 45°). The thickness of polymer solution was equal to 740 micrometer. The recording of the spectrum was simultaneously started and spectra were recorded with an one second interval after

casting the solution on the ATR crystal. FTIR-ATR spectrum was measured by using a Nexus 670 (Nicolet) spectrometer in kinetic mode.

III. MEASUREMENT OF DIFFUSION WITH ATR ACCESSORY

A. Principles of FTIR-ATR

According to the principle of ATR technique [45], when light propagates through a dense medium (an ATR Crystal) and is reflected at the interface with a rarer medium (a polymer film), attenuated total internal reflection (ATR) occurs. The rare medium absorbs light at this interface and attenuates the light. The schematic of ATR crystal is shown in Figure 1.

The angle of incident light must be greater than the critical angle (θ_c) to occur total internal reflection:

$$\theta_c = \sin^{-1}\left(\frac{n_1}{n_2}\right). \tag{3}$$

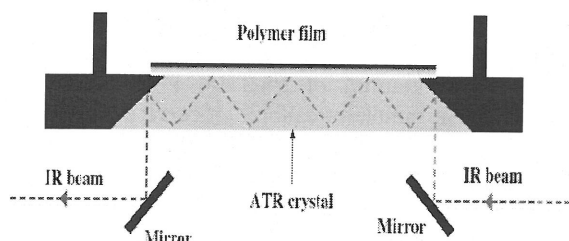n_1 and n_2 represent the refractive indices of the rare and dense medium, respectively.

Fig. 1. The schematic of ATR crystal.

An electromagnetic field that penetrates into the rarer medium forms an evanescent wave which its strength, E, decays exponentially with distance from the surface, x, as given by Eq. (4). The distance, which is on the order of micrometers, makes ATR generally insensitive to sample thickness, allowing for dynamic measurement in a layer with certain thickness. Figure 2 shows the interface of ATR crystal with an evanescent wave.

$$\frac{E}{E_0} = \exp(\gamma x), \tag{4}$$

where E_0 is the electric field strength at the interface, E/E_0 is the loss in the electric field strength, and γ is evanescent wave decay coefficient which is the reciprocal of penetration depth. In terms of refractive indices, the angle of incidence (θ) and the wavelength of light (λ), the penetration depth of the IR beam in sample can be calculated by Eq. (5).

$$dp = \frac{\lambda}{2\pi\left(n_1^2 \sin^2 \theta - n_2^2\right)^{0.5}}. \tag{5}$$

In order to obtain quantitative information from ATR spectroscopy, the basic relationship between the absorption of electromagnetic waves and the quantity of the absorbing material should be obtained. Basically, the well-known Beer-Lambert law gives this relationship as presented by Eq. (6).

$$dI = -\varepsilon CIdx, \tag{6}$$

where I is the light intensity at position x, ε is the molar extinction coefficient and C is the concentration of absorbing group. In FTIR-ATR with assumption that only weak absorption occurs, one can combine the evanescent field strength equation with the Beer-Lambert law and write:

$$\frac{I}{I_0} = e^{-A} \approx (1-A), \tag{7}$$

where I_0 is the intensity of the incident light and A is the measured absorption. Substitute Eq. (7) into the differential form of the Beer-Lambert law and integration given by:
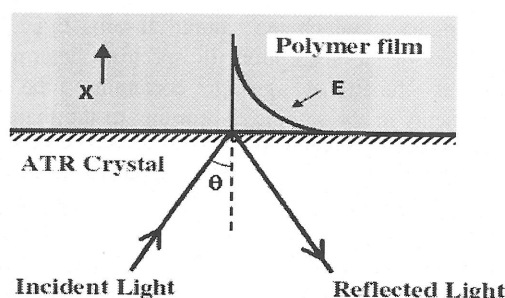
$$A = \int_0^L \frac{\varepsilon CI}{I_0}. \tag{8}$$

Fig. 2. Interface of ATR crystal and polymer film.

In the ATR configuration, the limits of integration are 0 to L, reflecting the diffusion of the penetrant through the thickness of the film, from one side. Having the intensity $I = E^2$, the Eq. (8) can be rewritten to yield an expression for multiple reflections, N, as:

$$A = \int_0^L N\varepsilon^* CE_0^2 \exp(-2\gamma z)dx, \tag{9}$$

where $\varepsilon^* = \varepsilon/I_0$. Eq. (9) directly relates changes in concentration to those in the absorbance spectrum, during the experiment.

B. Collection of spectra

As shown in Figure 1, a special arrangement of ATR accessories is employed to measure the spectrum at a certain time during the process. In our study, a certain volume of PS/THF solution was cast directly on the surface of the flat crystal (ZnSe, a 45°ATR prism) equipped with a bottomless liquid cell. The interfacial area of polymer solution that was equal to 1.35 cm^2 was controlled by a frame, made of nonabsorbent material. Using nitrogen gas, atmosphere of polymer solution was purged by 100 ml/min flow rate and the recording of the spectrum was started simultaneously. FTIR-ATR spectrums were recorded by a Nexus 670 spectrometer in real time mode, allowing a measurement of a spectrum with an one second interval. The spectrum was measured at a wavenumber resolution of 4 cm^{-1} as single scan for a spectral range from 4000 to 750 cm^{-1}. All the measurements were made at temperature 25 °C.

Figure 3 shows spectra collected from PS/THF solution

under evaporation process. Evaporating the THF from top-surface of solution causes to form a concentration gradient under diffusion control. After a certain period of time, the change in concentration is started at the bottom-surface of solution which is a typical layer of ATR analyzing. As seen in Figure 3, the characteristic peak of THF in region between 2800 cm^{-1} and 2900 cm^{-1} decreased as results of decreasing the concentration of THF into the bottom layer of polymer solution, in contact with ATR prism. Reverse behavior is observed for characteristic peak of PS in region between 2900 cm^{-1} and 2950 cm^{-1}.

IV. QUANTIFICATION OF FTIR-ATR SPECTRA

A. Calibration

FTIR spectrometer measured the interaction of light with experimental samples. It records the frequency (or wavelength) at which the sample absorbs light and the intensities of the absorption. IR spectrum determines the chemical functional group containing the whole components of the sample. According to the theory, each functional group absorbs characteristic frequencies of infrared radiation uniquely in which the intensity of absorption is related to the concentration of the functional group in the sample. Making relationship between intensity of characteristic frequency and concentration of component, it can be possible to determine an unknown quantity of functional group using a certain quantitative techniques.
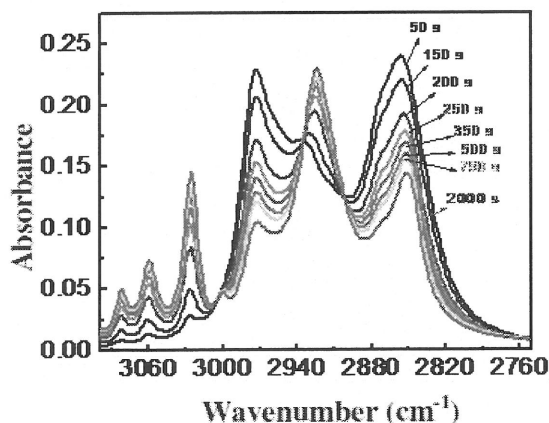

Fig. 3. Sequence of time-evolved spectra from polystyrene solution during desorption of tetrahydrofuran.

The simplest quantitative technique is based on Beer-Lambert law. Beer's law relates peak intensity to sample concentration, and this relationship is linear as shown in Eq. (10).

$$A = abC , \qquad (10)$$

where A is absorbance measured at a given frequency, a is absorptivity of the component at the measured frequency and determined based on certain calibration models, b and C are path length and concentration of the component, respectively.

Generally, when component peaks overlap significantly, simple Beer's law does not result correctly. There are many

other quantitative techniques which can be used to generate a calibration model. Multivariate calibration model such as classical least squares (CLS), stepwise multiple linear regression (SMLR), partial least squares (PLS), and principal component regression (PCR) produce a model that is more sophisticated than a simple Beer's law. PLS and PCR calibration techniques are statistical approach to quantitative analysis that make it possible to deconvolute and calibrate the component peaks or regions that overlap severely.

In principle, in the ATR experiments the absorptivity is not constant and is related to the penetration depth of evanescent wave and refractive index of media, consequently, it changes with the absorption band wavelength and variation of composition. Since deviation of the system from Beer's law can lead to significant errors in the predicted concentration of component, a multiple absorptivity value or multivariate calibration model should be considered [19].

Before starting to quantify the collected spectra, as shown in Figure 3, one needs to choose a proper calibration model. Probing the multivariate calibration models, as earlier mentioned, a good fitting was obtained using PLS model for the standards samples (samples with certain concentration) of PS/THF. Figure 4 shows a representative sample of calibration curve. From Figure 4, it becomes clear that using PLS calibration model, one is able to predict the concentration of THF in unknown samples.

Choosing the PLS calibration model not only is a result of successful procedure of fitting in this study but is a vision of Bohatier and coworkers [46] for quantifying the water absorption kinetics and the mass transfer in a polymer solution. They employed the PLS calibration model to analyze the spectra collected using the near-infrared (NIR) spectrometer. Besides, there exists a successful case of using the PCR calibration model to determine the concentration of components in the diffusion layers during the immersion precipitation process by Karimi and Kish [47].

B. Calculation of concentration

It is possible to measure the dynamic change of components by measuring the spectra of sample at real time. Using a calibration model, each spectrum collecting at the certain time was introduced to the TQ Analyst developed by Nicolet Inst. Co., and then the concentration of THF and PS were obtained.

Figure 5 shows the variation of concentration of THF regarding to the spectra collected by FTIR-ATR instrument. Three regions are observed; first region showing no change in concentration with respect to the time is extended from zero time up to the beginning of concentration change. Changing in concentration is continuing up to a steep change in slope of the curve, here, is the end of the second region of mass transfer. The third region also shows a variation in concentration similar to that which is observed in the second region but with a gentle slope.
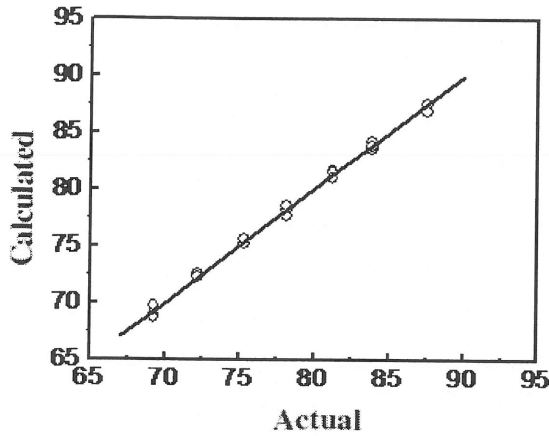
Fig. 4. Calibration curve for calculate concentration of THF in tetrahydrofuran/polystyrene systems. Open symbols are experimental data and solid line is calculated calibration.

C. Analysis of diffusion coefficient

The substitution of the Fickian concentration profile into the Eq. (9) and integration give the following expression:

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1 - \exp(-2\gamma L)]}$$
$$\times \sum_{n=0}^{\infty}\left[\frac{\exp(g)(f\exp(-2\gamma L) + (-1)^n(2\gamma)}{(2n+1)(4\gamma^2 + f^2)}\right], \quad (11)$$

where $g = \dfrac{-D(2n+1)^2\pi^2 t}{4L^2}$ and $f = \dfrac{(2n+1)\pi}{4L}$. A_∞ is the absorbance at equilibrium. Eq. (11) is analogous to the mass uptake in gravimetric technique [14].

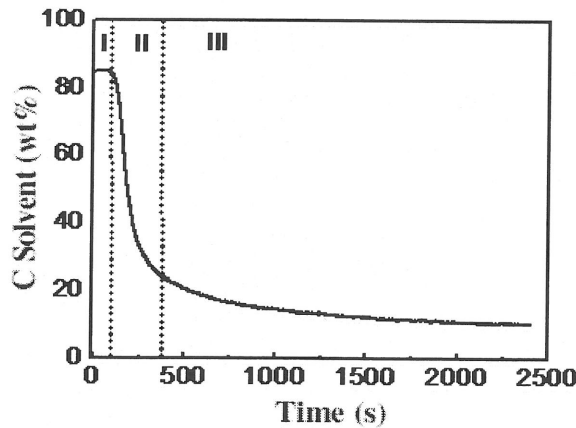Fig. 5. The variation of concentration of THF in PS/THF solution during solvent evaporation close to ATR crystal.

If $dp \le 0.1L$ Eq. (11) can be approximated by Eq. (12) [14].

$$\frac{A_t}{A_\infty} = 1 - \frac{4}{\pi}\times\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right]. \quad (12)$$

By eliminating all terms in the series of Eq. (12) beyond the first, it can be simplified:

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1 - \exp(-2\gamma L)]}$$
$$\times\left[\frac{\exp\left(\dfrac{-D\pi^2 t}{4L^2}\right)\left(\dfrac{\pi}{2L}\exp(-2\gamma L) + (2\gamma)\right)}{\left(\dfrac{\pi^2}{4L^2} + 4\gamma^2\right)}\right], \quad (13)$$

where $\gamma = 1/dp$ and depends on the experimental conditions.

In Eq. (13), it is assumed that the value of γ is constant. This is not entirely correct because it depends on the polymer refractive index, which can vary as the concentration of penetrant increases. Eq. (13) could be simplified if following condition could be found in the experiment [37]:

$$4\gamma^2 \gg \frac{\pi^2}{4l^2} \quad \text{and} \quad 1 \gg \exp(-2\gamma l)$$

therefore,

$$\ln\left(1 - \frac{A_t}{A_\infty}\right) = \ln\left(\frac{4}{\pi}\right) - \frac{D\pi^2}{4l^2}t. \quad (14)$$

With Eq. (14), the logarithm of the absorbance data is plotted as a function of time, and then the diffusion coefficient, D, is given by the slope of a linear least square regression.

Sometimes, one prefers to calculate the diffusion coefficient by means of concentration rather than absorbance data as a function of time. As discussed in part III (A), concentration is related to absorbance through the differential Beer-Lambert law and incorporates the evanescent wave of the ATR infrared light. The solution to the partial differential equation in Eq. (1) is given by:

$$\frac{C(x,t)}{C_\infty} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right]$$
$$\times\cos\left[\frac{(2n+1)\pi x}{2L}\right], \quad (15)$$

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2},$$
$$C(x = \pm L, t) = C_\infty,$$
$$C(x, t \le 0) = 0.$$

$C(x,t)$ is the THF concentration at any spatial coordinate x and time interval t and C_∞ is the saturated penetrant concentration.

Applying the values of concentration obtained from the ATR spectra (Figure 5) and defining the initial and boundary conditions (as presented below the Eq. 15) for the ATR configuration with a PS solution of thickness, $2L = 740\mu m$, diffusion coefficient of THF was calculated using Eq. (15) and resulted an average value of 5.8×10^{-6} cm^2/sec for the second region of the process (see Figure 5).

TABLE I
CHARACTERISTIC FEATURES OF COMMON CRYSTAL MATERIALS

Material	ATR spectral range (cm^{-1})	Refractive index	Uses
Germanium (Ge)	5500-675	4	Good for most samples. Strong absorbing samples, such as dark polymers
Silicon (Si)	8900-1500 & 360-120	3.4	Resistant to basic solution
AMTIR (As, Ge, Se glass)	11000-725	2.5	Very resistant to acidic solutions
ZnSe	15000-650	2.4	General use
Diamond	25000-100	2.4	Good for most samples. Extremely caustic or hard samples

V. FACTORS AFFECTING ATR ANALYSIS

A. Optical contact

One of the important factors is related to the optical contact necessary for reliable data; in other words, the adhesion of the polymer film to the ATR needs to be strong. Before an experiment, care must be taken to ensure adhesion is excellent and that penetrant sorption does not affect on the contact between the polymer film and ATR crystal. Glassy polymers can become brittle on drying and can easily lift off the crystal surface so this problem is more important. Some methods are used to ensure that there is a good contact such as casting of films upon the ATR crystal and a physical clamping device.

B. Type of optically dense ATR prism

The material madding the ATR prism is variety; they are chosen for experimental measurement based on two characteristics, refractive index and interfacial tension. Some usual crystals and their characteristic features are listed in Table I. Zinc Selenide (ZnSe) is the most commonly used crystal and preferred for all routine applications. Usage of this crystal is limited to strong acids and alkalis. Complex agents (ammonia and EDTA) will erode its surface because of the formation of complexes with the zinc.

Interfacial tension between ATR prism and the components of the solutions may change the composition of solution in contact with prism. Under this situation, before doing the main measurement, one should check the concentration polarization at the interface by probing the variation of intensity of characteristic peak with respect to the time.

Refractive index of ATR prism affects depth of penetration of infrared beam into the sample which is an important factor controlling the concentration of penetration at a certain depth.

C. Refractive index

Another problem that can occur during the diffusion process is concentration dependence of refractive index for the solution attached on the ATR prism. In the systems involving a big variation in concentration, a different mathematical approach will be required to account for changes in the refractive index and depth of penetration during the diffusion process.

D. Angle of incidence IR beam

Another variable is angle of incidence, it should be at least as great as the critical angle. Critical angle is largely determined by the material properties of the polymer and the crystal. By increasing the refractive index of the ATR crystal, the critical angle will decrease.

VI. LIMITATION OF FTIR-ATR SPECTROSCOPY

A. Local analyzing

It should be noted that the absorbance intensity that is measured by FTIR-ATR spectroscopy depends on the concentration of functional group exiting at the interface of polymer solution/ATR crystal. It means that the measurement is a local determination and does not give information about the layers far from interface, while some techniques such as gravimetry measure the weight of whole polymer film, thereby corresponding to a global determination. However, local ATR analyzing, sometimes, can be aimed especially for stratification process.

B. Wavelength dependence of penetration depth

The penetration depth varies with the wavelength of the incident beam (Eq. (5)). Photons with higher wavenumbers penetrate the sample less than photons with lower wavenumbers and penetration depth decreases at higher wavenumbers. This effect should be corrected by applying the ATR correction to the raw spectrum. Most FTIR software packages incorporate an ATR correction algorithm. The penetration depth will decrease by increasing the refractive index of the ATR crystal. High index crystal is needed when analyzing high index materials [32].

C. Bands overlapping

Differentiating components that produce overlapping bands in spectral data make limitation to employ some ideal mathematical approach for quantifying the spectra. Bands overlapping potentially lead to erroneous results. Straightforward solution for this restriction is deconvolution of overlapping bands. Several quantitative techniques are introduced in which they are able to calibrate and quantify the spectral data using component peaks or region that overlap significantly (see part IV(A)). However, at high concentration systems, the number of adjustable parameters necessary for peak fitting increase and can cause difficulties in data analysis and then could result in unreliable data.

VII. CONCLUSION

Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy was successfully employed to analyze the diffusion phenomenon of

polystyrene/tetrahydrofuran (PS/THF) by means of Fick's second law. Spectral data collected by instrument were quantified using partial least square technique, after calibration with standard solutions. Three different trends were observed in changing the THF concentration with respect to the time; plateau, steep slope, and gentle slope were the trends of changing. The second region was chosen to calculate the diffusion coefficient of THF which was 5.6×10^{-6} cm^2/sec. According to the experiences, optical contact, refractive index, type of ATR prism, and angle of incident IR beam are important factors that influence the reliability of spectral data. Even with some limitations of FTIR-ATR technique such as local analyzing, wavelength dependence of penetration depth, and band overlapping, it becomes a suitable technique to study diffusion of small molecules in polymer films and solutions in situ.

REFERENCES

[1]   D. Liu and D. L. Tomasko, "Carbon dioxide sorption and dilation of poly (lactide-co-glycolide)", *J. Supercrit. Fluids*, vol. 39, no. 3, pp. 416-425, 2007.

[2]   B. A. H. Smith and M. V. Sefton, "Permeability of a heparin–polyvinyl alcohol hydrogel to thrombin and antithrombin III", *J. Biomed. Mater. Res.*, vol. 22, no. 8, pp. 673-685, 1988.

[3]   D. S. G. Hu and K. J. N. Chou, "Kinetics of water swelling and development of porous structure in ionic poly (acrylonitrile-acrylamide-acrylic acid) hydrogels", *Polymer*, vol. 37, no. 6, pp. 1019-1025, 1996.

[4]   M. Karimi, W. Albrecht, M. Heuchel, M. H. Kish, J. Frahn, Th. Weigel, D. Hofmann, H. Modaress and A. Lendlein, "Determination of water/polymer interaction parameter for membrane-forming systems by sorption measurement and a fitting technique", *J. Membrane Sci.*, vol. 265, no. 1-2, pp. 1-12, 2005.

[5]   P. Chandra and W. J. Koros, "Sorption and transport of methanol in poly(ethylene terephthalate)", *Polymer*, vol. 50, no. 1-2, pp. 236-244, 2009.

[6]   H. Zhang and J. Mijovic, "Using Two-Dimensional Dielectric Relaxation Spectroscopy To Study the Effect of Water on the Dynamics of Epoxy–Amine Network", *Macromolecules*, vol. 37, no. 16, pp. 5844-5846, 2004.

[7]   B. D. Vogt, C. L. Soles, H. J. Lee, E. K. Lin and W. L. Wu, "Moisture Absorption and Absorption Kinetics in Polyelectrolyte Films: Influence of Film Thickness", *Langmuir*, vol. 20, no. 4, pp. 1453-1458, 2004.

[8]   M. B. Wisnudel and J. M. Torkelson, "Small-Molecule Probe Diffusion in Polymer Solutions: Studies by Taylor Dispersion and Phosphorescence Quenching", *Macromolecules*, vol. 29, no. 19, pp. 6193-6207, 1996.

[9]   A. C. Van Asten, W. T. Kok, R. Tilssen, and H. Roppe, "Characterization of thermal diffusion of polystyrene in binary mixtures of THF/dioxane and THF/cyclohexane", *J. Polym. Sci. Pol. Phys.*, vol. 34, no. 2, pp. 283-295, 1996.

[10] H. J. Kim, A. E. Fouda and K. Jonasson, "In situ study on kinetic behavior during asymmetric membrane formation via phase inversion process using Raman spectroscopy", *J. Appl. Polym. Sci.*, vol. 75, no. 1, pp.135-141, 2000.

[11] F. J. Tsai and J. M. Torkelson, "The roles of phase separation mechanism and coarsening in the formation of poly (methyl methacrylate) asymmetric membranes", *Macromolecules*, vol.23, no. 3, pp. 775-784, 1990.

[12] M. Horstmann, M. Urbani and W. S. Veeman, "Self-Diffusion of water in block copoly (ether–ester) polymers: An NMR study", *Macromolecules*, vol. 36, no. 18, pp. 6797-6806, 2003.

[13] R. A. Grinsted and J. L. Koenig, "Study of multicomponent diffusion into polycarbonate rods using NMR imaging", *Macromolecules*, vol. 25, no. 4, pp. 1229-1234,1992.

[14] Y. A. Elabd, M. G. Baschetti and T. A. Barbari, "Time-resolved Fourier transform infrared/attenuated total reflection spectroscopy

for the measurement of molecular diffusion in polymers", *J. Polym. Sci. Pol. Phys.*, vol. 41, no. 22, pp. 2794-2807, 2003.

[15] M. Karimi, "Diffusion in Polymer Solids and Solutions" ,in *Mass Transfer in Chemical Engineering Processes*, J. Markos Ed, Rijeka, Croatia: InTech, 2011, pp. 17-40.

[16] J. R. Xu and C. M. Balik, "Measurement of diffusivities of small molecules in polymers using FT-IR-ATR", *Appl. Spectrosc.*, vol. 42, no. 8, pp. 1538-1543, 1988.

[17] J. R. Xu and C. M. Balik, "Infrared attenuated total reflectance study of latex paint films exposed to aqueous sulfur dioxide", *J. Appl. Polym. Sci.*, vol. 38, no. 1, pp. 173-183, 1989.

[18] N. E. Schlotter and P. Y. Furlan, "Small molecule diffusion in polyolefins monitored using the infrared evanescent field", *Vib. Spectrosc.*, vol. 3, no. 2,pp. 147-153, 1992.

[19] M. C. Ferrari, J. Catalano, M. G. Baschetti, M. G. De Angelis and G. C. Sarti, "FTIR-ATR study of water distribution in a short-side-chain PFSI membrane", *Macromolecules*, vol. 45, no. 4, pp. 1901-1912, 2012.

[20] S. U. Hong, T. A. Barbari and J. M. Sloan, "Multicomponent diffusion of methyl ethyl ketone and toluene in polyisobutylene from vapor sorption FTIR-ATR spectroscopy", *J. Polym. Sci. Pol. Phys.*, vol. 36, no. 2, pp. 337-344, 1998.

[21] W. Wang, Y. Jin and Z. Su, "Spectroscopic study on water diffusion in poly(ester urethane) block copolymer matrix", *J. Phys. Chem. B.*, vol. 113, no., 48, pp. 15742-15746, 2009.

[22] K. C. Farinas, L. Doh, S. Venkataraman and R. O. Potts, "Characterization of solute diffusion in a polymer using ATR-FTIR spectroscopy and bulk transport techniques", *Macromolecules*, vol. 27, no. 18, pp. 5220-5222, 1994.

[23] A. S. Cantor, "Drug and excipient diffusion and solubility in acrylate adhesives measured by infrared-attenuated total reflectance (IR-ATR) spectroscopy", *J. Control. Release*, vol. 61, no. 1, pp. 219-231, 1999.

[24] B. D. Hanh, R. H. H. Neubert and S. Wartewig, "Investigation of drug release from suspension using FTIR-ATR technique: part I. Determination of effective diffusion coefficient of drugs", *Int. J. Pharm.*, vol. 204, no. 1-2, pp. 145-150, 2000.

[25] B. D. Hanh;, R. H. H. Neubert and S. Wartewig, "Investigation of drug release from suspension using FTIR-ATR technique: part II. Determination of dissolution coefficient of drugs", *Int. J. Pharm.*, vol. 204, no. 1-2, pp. 151-158, 2000.

[26] L. Massaro and X. X. P. Zhu, "Physical models of diffusion for polymer solutions, gels and solids", *Prog. Polym. Sci.*, vol. 24, no. 5, 731-775, 1999.

[27] S. P. Nunes and K. V. Peinemann, *Membrane Technology in the Chemical Industry*. New York: Wiley, 2001.

[28] S. Banerjee, R. P. Semwal and S. Agarwal, "Measurement of diffusivities of sulfur mustard (SM) and its analog oxygen mustard (OM) in cured butyl, nitrile and natural rubber sheets by weight gain and FT-IR-ATR methods", *J. Appl. Polym. Sci.*, vol. 57, no. 12, pp. 1483-1490, 1995.

[29] R. P. Semwal, S. Banerjee, L. R. Chauhan, A. Bhattacharya, N. B. S. N. Rao, "Study of diffusion and sorption of bis-(2-chloroethyl) sulfide (SM) and bis-(2-chloroethyl)ether (OM) through polypropylene (PP) and biaxial-oriented polypropylene (bopp) films by the FTIR–ATR spectroscopic method", *J. Appl. Polym. Sci.*, vol. 60, no. 1, pp. 29-35, 1996.

[30] Y. S. Tung, R. Mu and D. O. Henderson, "Diffusion kinetics of TNT in nitrile rubber via FTIR-ATR spectroscopy", *Appl. Spectrosc.*, vol. 51, no. 2, pp. 171-177, 1997.

[31] D. T. Hallinan and Y. A. Elabd, "Diffusion of water in Nafion using time-resolved FTIR-ATR Spectroscopy", *J. Phys. Chem. B.*, vol.113, no. 13, pp. 4257-4266, 2009.

[32] D. T. Hallinan, M. G. De Angelis, M. G. Baschetti, G. C. Sarti and Y. A. Elabd, "Non-Fickian diffusion of water in Nafion", *Macromolecules*, vol. 43, no. 43, 4667-4678, 2010.

[33] R. Gobel, R.W. Seitz, S.A. Tomellini, R. Krska and R. Kellner, "Infrared attenuated total reflection spectroscopic investigations of the diffusion behavior of chlorinated hydrocarbons into polymer membranes", *Vib. Spectrosc.*, vol. 8, no., 2, pp. 141-149, 1995.

[34] M. R. Pereira and J. Yarwood, "ATR-FTIR spectroscopic studies of the structure and permeability of sulfonatedpoly (ether sulfone) membranes. Part 1.—Interfacial water–polymer interactions", *J. Chem. Soc. Faraday Trans.*, vol., 92, no., 15, pp. 2731-2735, 1996.

[35] S. Hajatdoost, C. Sammon and J. Yarwood, "FTIR-ATR studies of diffusion and perturbation of water in polyelectrolyte thin films. Part 4. Diffusion, perturbation and swelling processes for ionic solutions

in SPEES/PES membranes", *Polymer*, vol. 43, no. 6, pp. 1821-1827, 2002.

[36] C. Deng, C. Sammon and J. Yarwood, "Sorption and perturbation of water at polyelectrolyte interfaces. Paper 5-effects of water isotopic dilution", *Polymer*, vol. 44, no. 7, pp. 2057-2065, 2003.

[37] G. T. Fieldson and T. A. Barbari, "Spectroscopy to Characterize Penetrant Diffusion in Polymers", *Polymer*, vol. 34, No. 6, pp. 1146-1153, 1993.

[38] Y. A. Elabd and T. A. Barbari, "Multicomponent diffusion of hydrogen-bonding solutes in a polymer", *AIChE J.*, vol. 48, no. 8, pp. 1610-1620, 2002.

[39] J. Crank and G. S. Park, *Diffusion in Polymers*. London: Academic Press, 1968.

[40] L. H. Sperling, *Introduction to Physical Polymer Science*, 4th ed., New York: Wiley, 2006.

[41] A. H. Windle, "Case II Sorption", in *Polymer Permeability*, J. Comyn, Ed., Northern Ireland: Elsevier Applied Science, 1985, 75-118.

[42] Y. A. Elabd and T. A. Barbari, "Separating solvation from molecular diffusion in polymers", *AIChE J.*, vol. 47, no. 6, pp. 1255-1262, 2001.

[43] J. Guo and T. A. Barbari, "Unified dual mode description of small molecule sorption and desorption kinetics in a glassy polymer", *Macromolecules*, vol. 42, no. 15, pp. 5700-5708, 2009.

[44] J. Guo and T. A. Barbari, "A Dual mode, local equilibrium relaxation model for small molecule diffusion in a glassy polymer", *Macromolecules*, vol. 41, no. 1, pp. 238-245, 2008.

[45] M. W. Urban, *Attenuated Total Reflectance Spectroscopy of Polymers: Theory and Practice*, Washington DC: American Chemical Society, 1996.

[46] C. P. Bohatier, W. Werapun, D. Bouyer, W. Chinpa and A. Deratani, "Near-infrared spectroscopy for the quantitative determination of mass transfer and water absorption kinetics by a polymer solution", *J. Polym. Sci. Pol. Phys.*, vol. 48, no. 18, pp. 1960-1965, 2010.

[47] M. Karimi, M. H. Kish, "Poly (methyl methacrylate) Membrane: Dynamic Measurement of Concentrations During Water-Induced Phase Separation", *Macromol. Sym.*, vol. 279, no. 1, 210-220, 2009.