

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

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SYNOPSIS

The diffusion of sulfur mustard (SM) and oxygen mustard (OM) in polypropylene (PP) and biaxial-oriented PP (BOPP) was measured using Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy, which allows one to study the diffusion of liquid through thin polymer films *in situ*. The temperature-dependent diffusion coefficients of OM and SM for PP and BOPP are also reported; these are in good agreement with the values obtained by the weight gain method. The activation energy of diffusion is determined by both methods. The polymer-penetrant interaction parameter (K) and transport number (n) are calculated for the system PP/OM and BOPP/OM by weight gain method. The “ n ” values indicate a Fickian mode of diffusion. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric materials are widely used in industry and defence for food packaging,¹ protective clothings,^{2,3} gloves,⁴ etc. Some commercially available polymer films used for the above applications are highly vulnerable to many toxic chemicals. Although there is ample literature on the permeability/diffusion of industrial chemicals through polymeric membranes/films,⁵⁻⁸ there are very few investigations toward the permeability of toxic chemical/warfare agents through such films.

Sulfur mustard (SM), chemically known as bis-(2-chloroethyl)sulfide is a well-known vesicant, which damages the body cells seriously even on short time exposure. Moreover, it is alleged to have been used in the Iran-Iraq conflict. Therefore, SM and its analog bis-(2-chloroethyl)ether (oxygen mustard [OM]) were chosen as candidate agents for investigation of their permeability/diffusion through different polymeric materials.^{9,10}

The diffusion of liquids through polymers depends on the nature of the polymer, temperature, concentration of the penetrant molecules, and their shape and size.¹¹ The diffusion is expected to follow Fick's laws where the polymer matrix is unaffected by the penetrant.¹² The most widely used method for the determination of the diffusion coefficient is the weight gain method.^{10,13} This method consists of the study of liquid sorption through polymer samples under isothermal-isobaric conditions. In the case of samples of thickness L , under the boundary conditions $0 < x < L$ and $0 < C < C_{\text{equil}}$, Fick's second law is solved as follows:

$$M_t/M_\infty = 4/L(Dt/-)^{1/2} \quad (1)$$

where M_t = amount of the sorbate/desorbate at the moment of time t and M_∞ = equilibrium amount of the sorbate. The diffusion is claimed to be Fickian when the plot of M_t/M_∞ vs. $t^{1/2}$ is an L -shaped curve with its rectilinear parts in the region of $M_t/M_\infty < 0.6$, and the diffusion coefficient (D) can be calculated from the slope of the linear part.¹⁴

Attenuated total reflectance (ATR) is a useful measurement device for surface characterization of

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penetrant diffusion through polymers.^{9,10,15,16} The FTIR-ATR method has been employed successfully for the characterization of the polymer-penetrant interaction at the molecular level and also for *in situ* determination of the diffusion coefficient^{10,15-19} of small molecules. It also provides simultaneous measurements of diffusion coefficients of a mixture of different IR active species, having well-defined IR peaks. Any change on the polymer surface due to polymer-penetrant interaction can also be observed. The authors have already developed a method for studying the diffusion of SM through polymer-based paint films.⁹

The present investigation deals with the study of permeability/diffusion of sulfur mustard (SM) and its chemical analog oxygen mustard (OM) through polypropylene (PP) and biaxial-oriented PP (BOPP) at different temperatures by the FTIR-ATR method to evaluate their suitability as protective materials against chemical warfare agents.

EXPERIMENTAL

Materials

Commercial films of PP (0.0075 cm) and BOPP (0.0040 cm) were obtained from the Defense Food Research Laboratory, Mysore (M/S COSMO Ltd., Delhi, India). OM (E. Merck, Germany) was distilled prior to use. SM was synthesized by a known method²⁰ and GC purity was found to be 99.9%.

The thickness of the polymer films was measured at different points with an accuracy of ± 0.001 cm using a micrometer screw gauge. The polymer film surface was cleaned with acetone and kept under vacuum for 24 h. The mechanical properties of the films were measured by a universal testing machine (Testometric, Goodbrand GBX Micro 350, 5KN, U.K.).

Procedure

Spot Disc (SD) Test (Breakthrough Time, BTT Test)

The permeation resistance of PP and BOPP toward SM were evaluated at 25°C by the known SD test method.^{10,21}

Weight Gain Experiment

Dried polymer films, 2×4 cm², were immersed in a capped test tube containing OM. The test tube was placed in a thermostatically controlled water bath.

The samples were taken out periodically and weighed after removing the excess liquid from the surface. The experiments were performed at three different temperatures (25, 35, and 45°C), with a variation of $\pm 2^\circ\text{C}$. A Mettler analytical balance having a sensitivity of 10^{-6} g was used for this experiment.

FTIR-ATR Measurements

A Perkin-Elmer 1720X FTIR-ATR spectrometer equipped with DTGS detector and a flat plate ATR sampling accessory was used to record the IR spectra. A KRS-5 crystal of size $50 \times 20 \times 2$ mm with an angle of incidence of 45° was used. All ATR spectra were recorded at 4 cm^{-1} resolution and 10 scans were accumulated in 0.7 min for each sample. Computer subtraction between the polymer and KRS-5 and the polymer and penetrant were performed with the use of the band at 700 cm^{-1} for SM (C—Cl stretching) and 1124 cm^{-1} for OM (C—O—C stretching). For the FTIR-ATR experiment, the films were cut into pieces and a $1 \times 5\text{ cm}^2$ area was exposed with $20\ \mu\text{L}$ of the diffusants. The exposed side of the films were covered with tin foil and sealed. A sealed specimen was placed inside the ATR accessory as the unexposed side face of the KRS-5 crystal. The penetration of SM and OM through PP and BOPP were monitored at different intervals of time for the three different temperatures. The FTIR-ATR spectra for polymer (spectra for PP/BOPP), OM, and SM are presented in Figure 1. FTIR-ATR experiments were also carried out at 25, 35, and 45°C ($\pm 2^\circ\text{C}$).

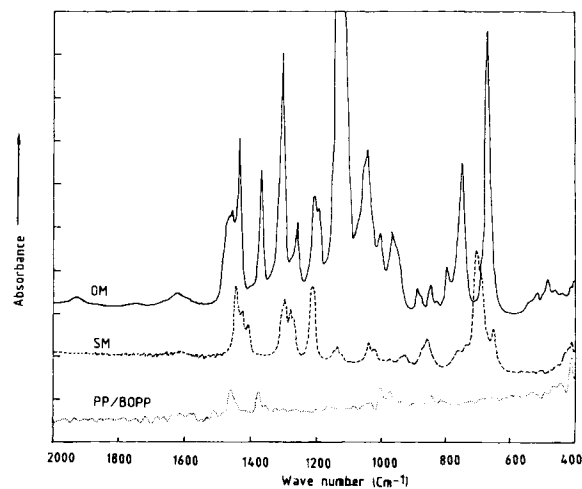


Figure 1 FTIR-ATR spectra of polymer (PP/BOPP), OM, and SM.

RESULTS AND DISCUSSION

From the results presented in Table I, it is clear that BOPP provides the maximum protection toward SM. In the case of PP, the low breakthrough time/retardation time (θ) can be explained due to its low crystallinity as compared to BOPP. The literature shows the effects on sorption and transport of the penetrant caused by factors such as orientation and crystallinity of the polymer matrix.^{22,23} The very high tensile strength (TS) of BOPP (TS, 2130 kg/cm²; % elongation, 40) compared to PP (TS, 340 kg/cm²; % elongation, 715) is indicative of its high order of orientation/crystallinity. The crystallinity of the PP and BOPP samples were evaluated by DSC and it was found that the crystallinity of BOPP is about double that of PP.

The diffusion coefficients of OM through PP and BOPP films were calculated from the plot of M_t/M_∞ vs. $t^{1/2}$ using eq. (1) (Figs. 2 and 3). The values are presented in Table II. The temperature-dependent diffusion coefficients of OM for PP and BOPP are also determined to calculate the activation energy of diffusion from the plot of $\log D$ vs. $1/T$. Higher values of activation energy of diffusion of OM in BOPP (Table II) indicate the low diffusion coefficient of OM.

The weight gain parameters are also fitted in the following empirical equation to confirm whether or

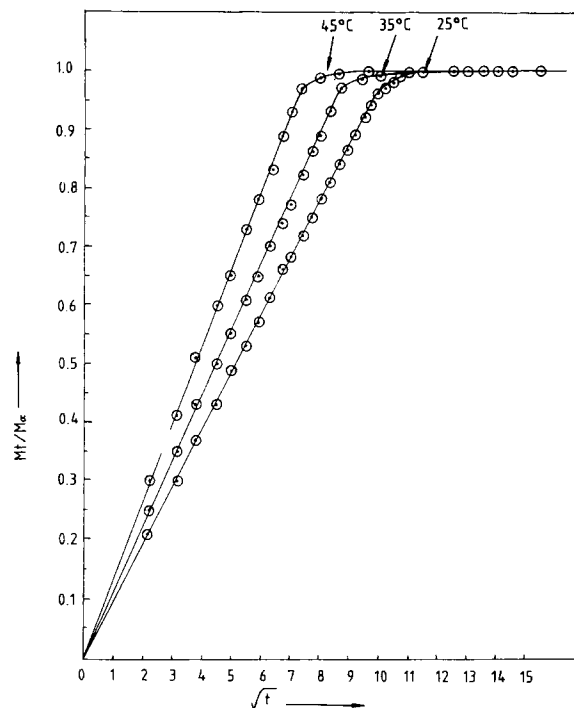


Figure 2 Plot of M_t/M_∞ vs. $t^{1/2}$ for the PP/OM system.

not the sorption mechanism follows the Fickian mode²⁴:

$$M_t/M_\infty = Kt^n \quad (2)$$

Table I Diffusion Coefficient and Activation Energy Data of OM and SM for PP and BOPP by FTIR-ATR Method

Temp (°C)	FTIR-ATR								E_d (kJ/mol)	BTT ^a (min) at 25°C
	PP (0.0075 cm)				BOPP (0.0040 cm)					
	θ (min)		$D \times 10^9$ cm ² /s		θ (min)		$D \times 10^{10}$ cm ² /s			
25	PP/OM	PP/SM	PP/OM	PP/SM	BOPP/OM	BOPP/SM	BOPP/OM	BOPP/SM	25.07 (PP/OM)	155 (PP/SM)
35	64	95	2.54	1.64	102	132	4.36	3.36	30.52 (PP/SM)	220 (BOPP/SM)
									28.43 (BOPP/OM)	
45	45	65	3.47	2.40	75	92	5.92	4.89	31.88 (BOPP/SM)	

^a BTT stands for breakthrough time, Ref. 21.

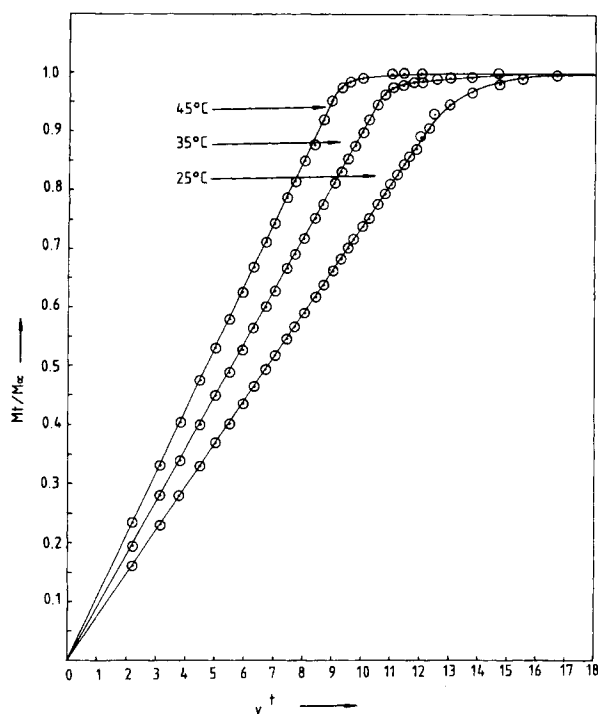


Figure 3 Plot of M_t/M_∞ vs. $t^{1/2}$ for the BOPP/OM system.

where M_t and M_∞ are same as defined earlier and K is a constant characteristic of polymer-solvent system. The value of n indicates whether the transport mechanism is Fickian or not and is known as the transport number.^{10,24} The n and K values at three different temperature ranges were calculated from the plot of $\ln M_t/M_\infty$ vs. $\ln t$ and the values are presented in Table II. The calculated n values indicate that the diffusion of OM through PP and BOPP in the temperature range 25–45°C follows the Fickian mode of transport. The lower K values for BOPP as compared to PP indicate less diffusant-polymer interaction. Therefore, it is expected that BOPP should provide a lower value of the diffusion

coefficient for OM. The result reveals the same trend.

A highly sensitive FTIR-ATR method was employed successfully to calculate the diffusion coefficients and activation energies of diffusion of OM and SM (chemical warfare agent) through PP and BOPP. The exposed polymer films were kept inside the ATR sampling accessory and the surface concentration of the penetrant was monitored periodically for different intervals of time to calculate the correct retardation time (time required for penetration of the penetrant through the polymer films, θ) in the temperature range 25–45°C. For the OM and SM permeation study, the IR absorbance band at 1124 cm^{-1} (C—O—C stretching frequency) and 700 cm^{-1} (C—Cl stretching frequency), respectively, were chosen for monitoring at different intervals of time. The increments of the concentration of OM and SM in the permeation side at 25°C are shown in Figure 4. The diffusion coefficients of OM and SM at 25, 35, and 45°C through PP and BOPP were calculated from the plot absorbance vs. time (Figs. 5 and 6) using the following permeation equation^{1,10}:

$$D = L^2/6\theta \quad (3)$$

where L is the thickness of the polymer films used in the investigation. The diffusion coefficient results for OM by FTIR-ATR and weight gain methods are in good agreement. A little higher values of the diffusion coefficients of OM and SM by the FTIR-ATR method may be due to the penetration of IR radiation in the polymer films. The detection of the diffusant starts before its permeation and provides low retardation times (θ).⁹ The diffusion coefficient values (Table I) of SM are lower than the values of OM, which may be due to the presence of comparatively bulky “S” atom in SM. The structures of OM and SM are given below:

Table II Analysis of Sorption Results of Polymer-Oxygen Mustard (OM) System by Weight Gain Method

Temp (°C)	PP (0.0075 cm)/OM			BOPP (0.0040 cm)/OM			E_d (kJ/mol)
	$D \times 10^9$ cm ² /s	n	K (g/g min ⁿ)	$D \times 10^{10}$ cm ² /s	n	K (g/g min ⁿ)	
25	1.76	0.500	0.094	2.86	0.500	0.073	25.91 (PP/OM)
35	2.39	0.489	0.113	4.24	0.505	0.084	
45	3.22	0.490	0.140	5.88	0.500	0.103	28.59 (BOPP/OM)

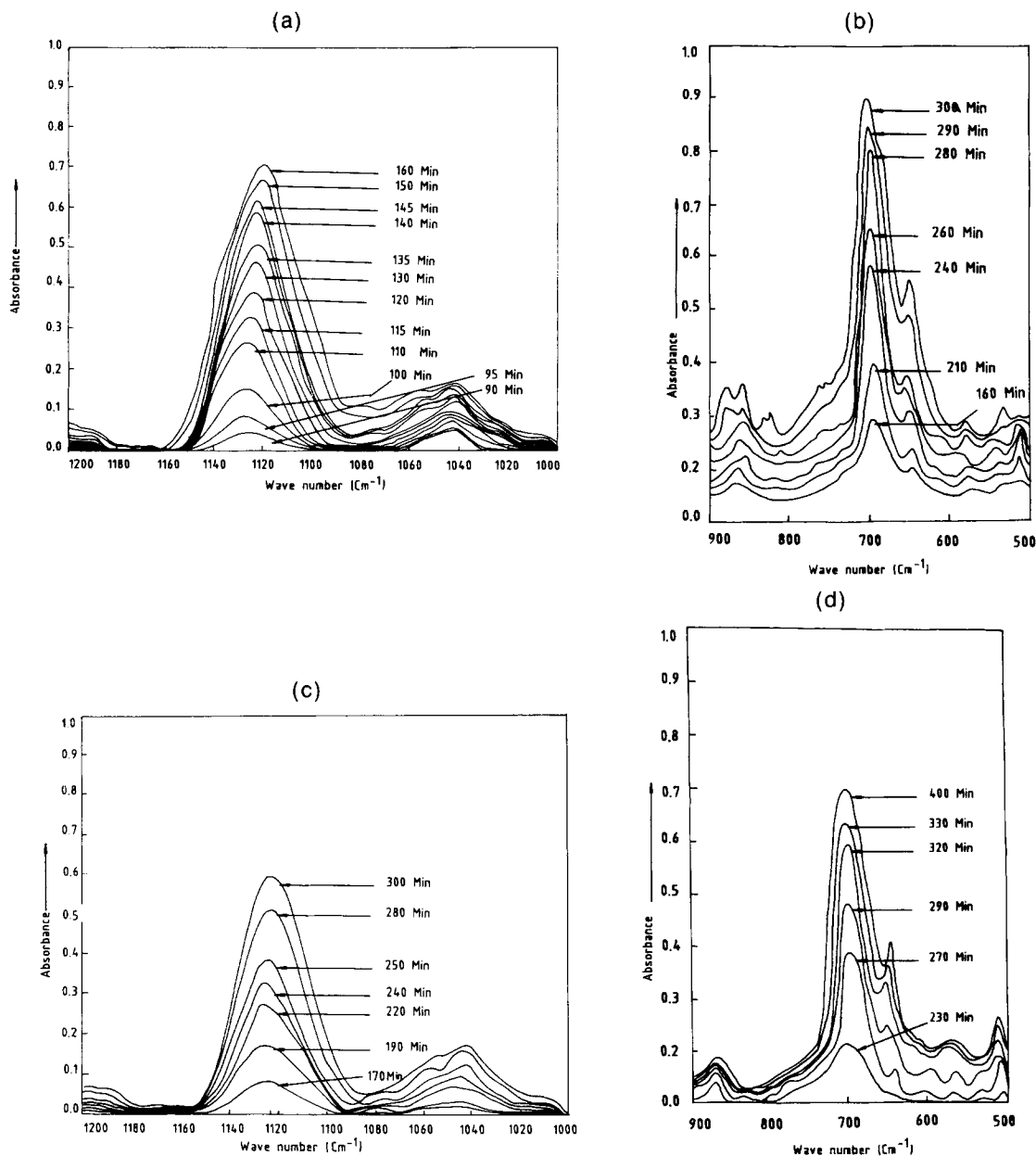
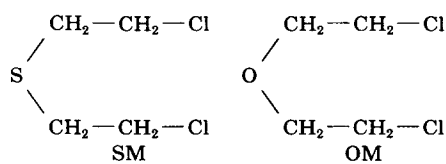


Figure 4 FTIR-ATR spectra of the (a) OM/PP system, (b) SM/PP system, (c) OM/BOPP system, and (d) SM/BOPP system.



The diffusion coefficient values, in general, increase with increase of temperature, indicating more diffusant-polymer interaction. Although it is not possible to calculate K values from the present FTIR-ATR investigations, it can be assumed that SM is

also behaving similarly like OM as studied by the weight gain method. The activation energies of the diffusion of OM and SM are calculated from the plots of $\text{Log } D$ vs. $1/T$ (temperature in K) as shown in Figure 7. The results show that the activation energy of diffusion (E_d) increases with decrease of diffusion coefficient. The low value of the diffusion coefficient and higher value of the activation energy for OM and SM for BOPP in comparison with PP is attributed to higher orientation and, hence, crystallinity in BOPP.^{22,23} The calculated activation en-

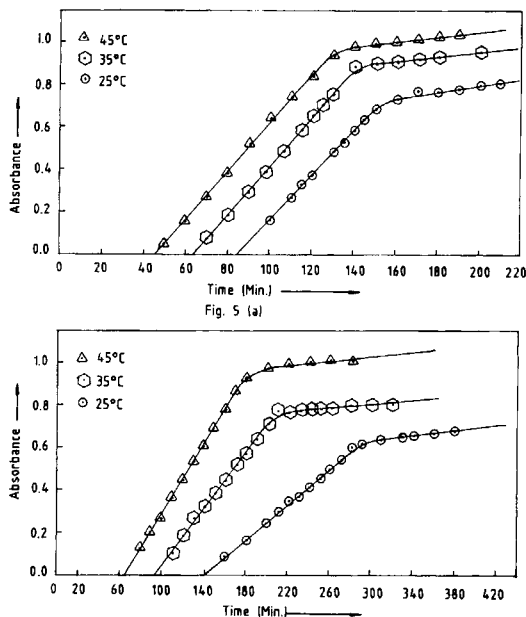


Figure 5 (a) Plot of absorbance vs. time for the OM/PP system at different intervals of time; (b) plot of absorbance vs. time for the SM/PP system at different intervals of time.

ergy values of OM for PP and BOPP are comparable by both methods.

The FTIR-ATR spectra of the polymer films before and after exposure were compared and the

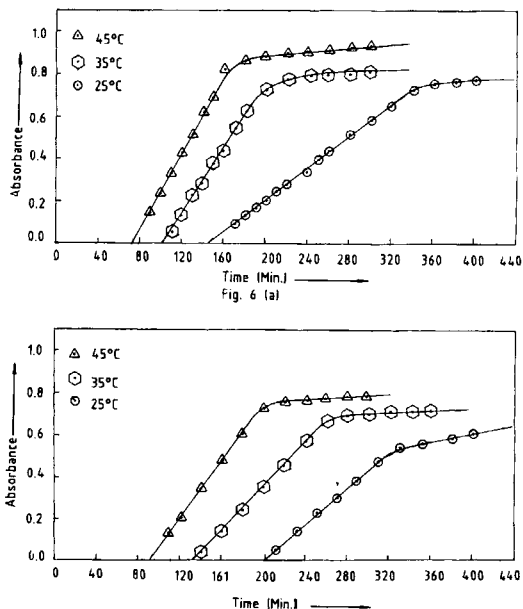


Figure 6 (a) Plot of absorbance vs. time for the OM/BOPP system at different intervals of time; (b) plot of absorbance vs. time for the SM/BOPP system at different intervals of time.

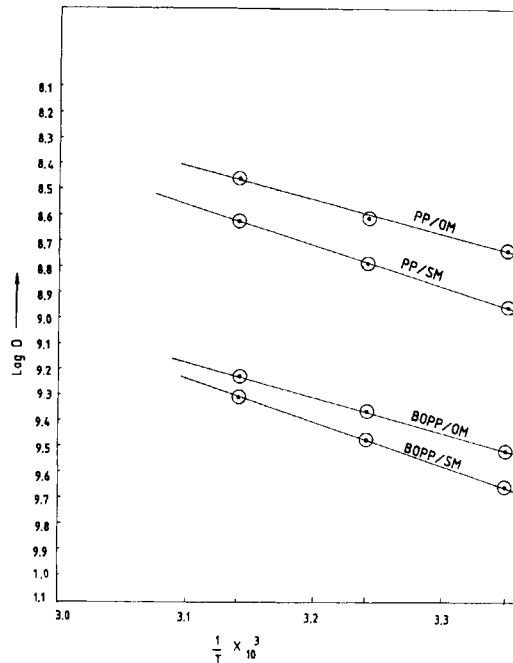


Figure 7 Plot of Log D vs. $1/T \times 10^3$ (T is absolute temperature).

spectra were matching completely, which implies that there is no chemical interaction between the polymer and the penetrant.¹⁰

CONCLUSION

From the above investigation, it can be concluded that BOPP is a better material for protection against chemical warfare agents and can be used as packaging material for defence applications. This study also shows that FTIR-ATR is a very convenient method for *in situ* study of the diffusion of toxic chemicals.

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