

Relaxation Characteristics of Poly(vinylidene fluoride) and Ethylene-chlorotrifluoroethylene in the Transient Uptake of Aromatic Solvents

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Abstract—Poly(vinylidene fluoride) (PVDF) and ethylene-chlorotrifluoroethylene (ECTFE) exhibited non-Fickian diffusion behaviors in the transient uptake of aromatic solvents. The diffusional exponents at the final stage of uptake exhibited asymptotic values ranging from 0.9-1.0 for the sigmoidal sorption of PVDF and 1.2-2.0 for the drastic accelerating sorption of ECTFE. The asymptotic diffusional exponent decreased with rising temperature. PVDF film exhibited a linear increase in both machine and transverse directions with fractional uptake, whereas ECTFE film increased linearly in the transverse direction and exponentially in the machine direction. A rate-type viscoelastic [Camera-Roda and Sarti, 1990] model was applied to reproduce the anomalous sorption of fluoropolymer-solvent systems. The fitted Deborah numbers ranged from 0.2-0.3 for PVDF, and 2-5 for ECTFE. The diffusivity ratio, D_{eq}/D_0 , of PVDF-solvent system was fitted as tenth order of magnitude lower than that of ECTFE-solvent system. The fraction of initial surface concentration, S_0 , was fitted in the range of 0.6-0.8 for both ECTFE and PVDF. It is plausible to assume that diffusion coupled with comparable structural relaxation has the asymptotic diffusional exponents that are strongly dependent on accelerating curvature, and total sorption is contributed by relaxation-induced viscoelastic volume change along with concentration-driven Fickian diffusion.

Key words: Poly(vinylidene Fluoride), Ethylene-Chlorotrifluoroethylene, Transient Sorption, Relaxation Kinetics

INTRODUCTION

The diffusional behavior of many solvents in glassy or semicrystalline polymers cannot be adequately described by a concentration-dependent form of Fick's law with constant boundary conditions, especially when mass transfer is coupled with structural relaxation [Crank and Park, 1968; Frish, 1980; Carbonell and Sarti, 1990; Ramesh and Duda, 2000]. The structural relaxation is usually referred to as swelling, microcavity formation, breakage of (interchain) physical bonds, and phase transition during solvent uptake [Williams et al., 1955; Alklonis, 1979; Rogers, 1985; Bae et al., 1994; Lee and Knaebel, 1997]. Various relaxation spectrums were practically observed in polymer-solvent systems due to the plasticization degree of the imbibed solvent. The mathematical models for transient sorption intrinsically include the relaxation-induced sorption in polymeric materials [Long and Richman, 1960; Berens and Hopfenberg, 1978; Neogi, 1983; Durning, 1985; Camera-Roda and Sarti, 1986, 1990; Doghieri et al., 1993].

Three basic classes of non-Fickian behaviors can be distinguished depending on the relative contribution of diffusion and relaxation kinetics [Crank, 1975].

1. Case I (which appears as Fickian diffusion): the rate of diffusion is much less than that of relaxation process.
2. Case II (moving front): diffusion is very rapid compared with relaxation at the moving boundary.
3. Case III (non-Fickian or anomalous diffusion): diffusion and

relaxation rates are comparable.

For very slow structural change, the diffusion exhibits seemingly Fickian behavior which is referred to as Case I. The relaxation coefficient is usually negligible during transient sorption. Case II sorption deals with the phenomenon where the morphological changes appear to be abrupt, and the relaxation coefficient is usually assumed to be constant over the average concentration [Alfrey, 1965]. For comparable rates of structural relaxation to diffusion, the diffusion behavior is usually referred to as Case III. The relaxation coefficient usually exhibited a linear or an exponential dependence on solvent concentration.

Characterization of the diffusion process can be also classified by the use of transport kinetics.

$$F = M_t/M_{eq} = kt^n \quad (1)$$

where M_t is the sorbed mass of solvent at time t , M_{eq} is the sorbed mass at equilibrium state, k is a constant incorporating characteristics of polymer-solvent system, and n is the diffusional exponent, which is indicative of the transport mechanism. A value of the exponent $n=0.5$ in planar geometry implies Fickian diffusion, and a value of $n=1$ implies Case II diffusion, whereas anomalous (Case III) transport is implied for values of $0.5 < n < 1$ [Astarita and Nicolais, 1983].

Rate-type viscoelastic models were suggested to accommodate the significant non-Fickian diffusion such as sigmoidal, Case II, drastic accelerating sorption. The Camera-Roda and Sarti model [1986, 1990] intrinsically allowed the Fickian diffusion with an effective diffusivity changing in time to accommodate a broader spectrum of relaxational kinetics. Doghieri et al. model [1993] originated

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from Camera-Roda and Sarti [1986] model based on thermodynamically-derived relaxation time. Kalospiros et al. [1991, 1993] model was simply endowed with two adjustable parameters based on Maxwell-type viscoelastic equation. Among them, the CMRT [Camera-Roda and Sarti, 1990] model was used to reproduce anomalous sorption data that was observed in fluoropolymer-solvent systems.

$$\frac{\partial \phi}{\partial t} = -\frac{\partial J}{\partial x}, J = J_f + J_r;$$

$$J_f = -D_f \nabla \phi, J_r = -D_r \nabla \phi - \tau \frac{\partial J_r}{\partial t} \quad (2)$$

The diffusive mass flux was expressed as the sum of Fickian flux and relaxational flux: J_f =Fickian term, and J_r =relaxation term; ϕ is the volume fraction of the penetrant in the matrix. The τ and D stand for the values of relaxation time and diffusivity that were assumed to be exponentially dependent on the solvent concentration, as established by simplified versions of the free volume [Fujita, 1961].

The CMRT model lumped the relaxation properties into the non-Fickian diffusive flux term, J_r , to reduce the complexity due to coupling of stress, concentration, and chemical interactions. Even though model equations were able to reproduce all the Fickian and non-Fickian behaviors, they still had unresolved problems of how to correlate the relaxation parameters with molecular interactions and rearrangement. In practice, relaxation terms of concentration-dependent processes are another semi-empirical expression of the time-dependent process.

The following sections present transient sorption data for aromatic solvents in several fluoropolymers (such as PFA, PVDF, and ECTFE). A rate-type viscoelastic model was applied to the anomalous sorption behaviors observed in PVDF and ECTFE in terms of relaxation characteristics in conjunction with diffusion behavior.

EXPERIMENTAL

Several fluoropolymers (such as PFA, PVDF, ECTFE) were tested: Perfluoro-alkoxy copolymer (PFA) is the melt processable copolymer containing a fluorocarbon backbone with randomly distributed perfluorinated ether side chain. Ethylene-chlorotrifluoroethylene copolymer (ECTFE) is an essentially alternating copolymer of ethylene and chlorotrifluoroethylene. Poly(vinylidene fluoride) copolymer (PVDF) is the addition polymer of 1,1-difluoroethene that is readily polymerized as a partially crystalline polymer. The commercially available forms of PVDF and ECTFE were uniaxially oriented in the machine direction (MD), not in the transverse direction [Imbalzano, 1991].

Transient sorption experiments were carried out, typically using pure aromatic solvents and dry fluoropolymers. Specifically, a pre-weighed and measured polymer film (3 inch dia. and 10 mil thickness) was suspended on a wire, then immersed in a jacketed flask filled with the solvent, of which temperature was controlled by circulating water through the jacket. At periodic time intervals, the film was removed from the liquid to be weighed. Before the film was weighed, the liquid adhering to the polymer surface was removed quickly by flushing with compressed air.

Corresponding rate data was plotted in terms of fractional mass uptake vs. square root of time. The solubility was measured by al-

lowing a pre-weighed sample to remain in contact with the solvent for an extended long period. Variables that were systematically tested include temperature (25, 45, and 65 °C), and the aromatic solvents (benzene, toluene, chlorobenzene). An Ohaus Galaxy 110 microbalance with an accuracy of ± 0.1 mg was used to measure the mass change of immersed polymer films. The dimensional changes of each sorbed sample were measured periodically using "digital electronic calipers" (sensitivity= ± 1 mil).

RESULTS AND DISCUSSIONS

1. Characteristics of Relaxational Sorption

PFA exhibited a seemingly ideal Fickian diffusion behavior with constant diffusion coefficient. That is, when viewed on "fractional mass change" versus "square root of time" coordination, the data is roughly linear initially and then approaches saturation asymptotically, in congruence with Fick's law. PVDF film produced a typical sigmoidal sorption curve with a single inflection point. After a short linear period, the curve became convex with respect to time axis, indicating that uptake was accelerating followed by an asymptotic approach to saturation. ECTFE film produced even more unusual sorption curves that exhibited a drastic acceleration until saturation was attained (see Fig. 1).

The volume change during transient sorption was directly measured as an increase of dimensional length of polymer film with fractional uptake of the solvent. As shown in Fig. 2, PVDF film was linearly increased in both directions (machine & transverse) with fractional uptake. On the other hand, ECTFE film increased linearly in the transverse direction and exponentially in the machine direction with fractional uptake. Therefore, it is plausible to assume that structural relaxation in ECTFE-solvent system has stronger dependence on concentration in comparison to that of PVDF-solvent system. In Fig. 2, the dimensional change is defined as L_t/L_{eq} , where L_t is the change of one-dimensional length at time of transient solvent uptake and L_{eq} is the change in length at equilibrium solvent uptake.

When the sorption curves are reported on logarithmic scales, it is easy to evaluate the power of time (or diffusional exponent), to which

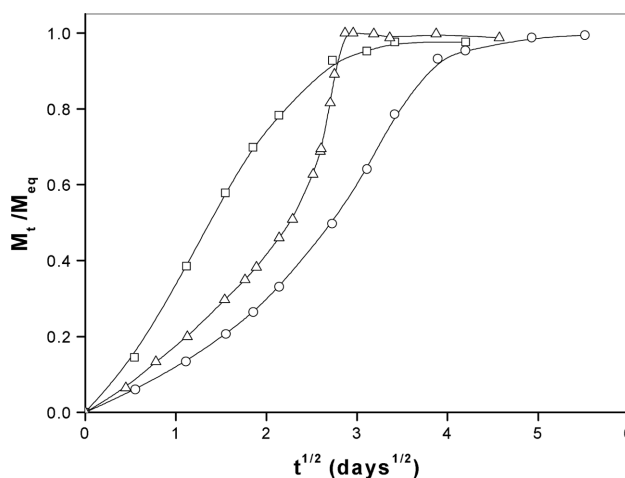


Fig. 1. Various sorption behaviors of fluoropolymer-benzene systems ($\square$: PFA, $\circ$: PVDF, $\triangle$: ECTFE).

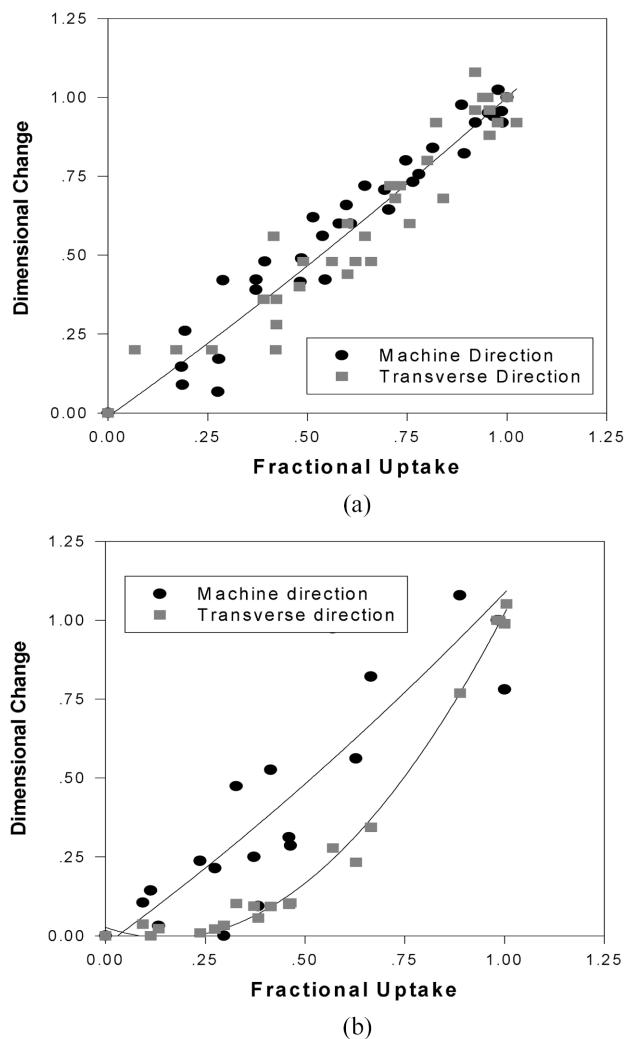


Fig. 2. Dimensional change of fluoropolymer films with fractional uptake of benzene: (a) PVDF, (b) ECTFE.

the mass uptake of the penetrant is proportional. As seen from Fig. 3, PFA film exhibited Case I sorption of which the initial slope was approximately 0.5, which is a characteristic value for Fickian diffusion. On the other hand, the initial values of diffusional exponents, n_1 , ranged in 0.6-0.7 for both PVDF and ECTFE films. The asymptotic values of diffusional exponents, n_2 , at the final stage of uptake ranged in 0.9-1.0, respectively, for PVDF and 1.2-2.0 for ECTFE (see Table 1). Anomalous sorption curves observed in PVDF and ECTFE exhibited a short linear region seemingly governed by Fickian diffusion, and a following acceleration curvature. The asymptotic diffusional exponents indicated that a rate dependence could be expressed as $M_t/M_{eq} \propto t^{n_2}$ at the final stage of uptake [Jacques et al., 1974].

It is generally accepted that the acceleration curvature is closely related to the rate at which polymer chains rearrange themselves in the presence of penetrated solvents. Dogherie and Sarti [1997] suggested that the total volume of relaxing medium is described by the sum of an elastic volume, V_E , representing the instantaneous response and a viscoelastic volume, V_v , changing in time due to structural relaxation. Therefore, it is plausible to assume that total sorption

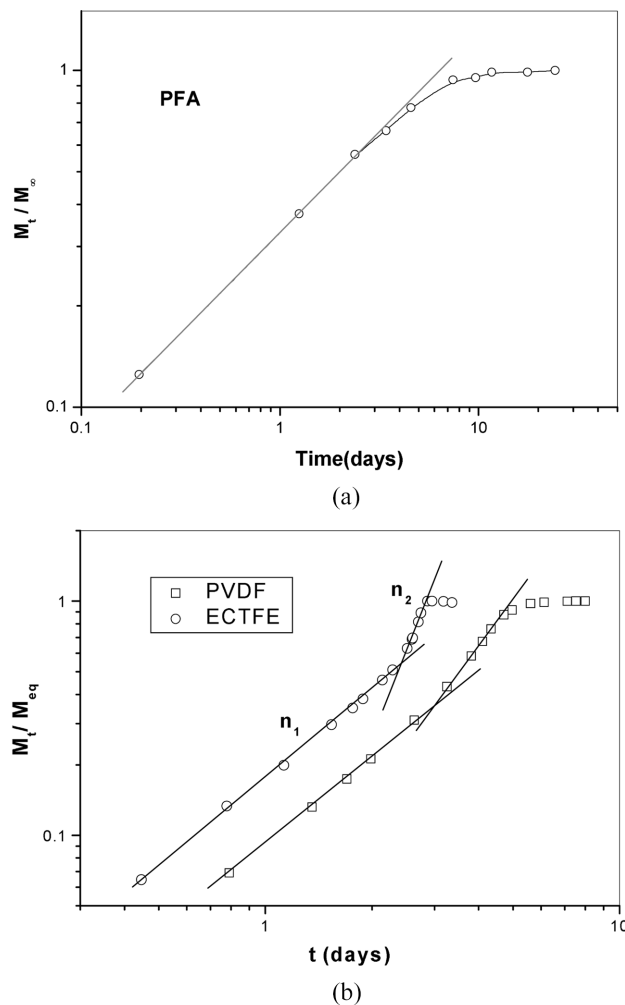


Fig. 3. Log-log plots of the kinetics of fluoropolymer-benzene system at 25 °C: (a) PFA ($\square$), (b) PVDF ($\circ$) and ECTFE ($\triangle$).

Table 1. Diffusional exponents of sorption data of fluoropolymer-solvent systems fitted by transport kinetics

Polymers		PVDF		ECTFE	
Temperature	Solvent	n_1	n_2	n_1	n_2
25 °C	Benzene	0.61	1.01	0.61	1.92
	Toluene	0.61	0.99	0.56	1.95
	Chlorobenzene	0.74	0.86	0.71	1.96
45 °C	Benzene	0.62	0.92	0.62	1.64
	Toluene	0.68	0.91	0.69	1.66
	Chlorobenzene	0.64	0.74	0.66	1.45
65 °C	Benzene	0.61	0.90	0.67	1.27
	Toluene	0.64	0.84	0.67	1.20
	Chlorobenzene	0.60	0.75	0.71	1.27

was contributed by relaxation-induced viscoelastic volume change along with the concentration-driven Fickian diffusion. We here use the asymptotic diffusional exponents, n_2 , to illustrate the relaxation-dependence on temperature. As seen from Fig. 4, the asymptotic exponents were decreased with the increase of temperature, in accordance with that sorption mechanism changed from relaxation-

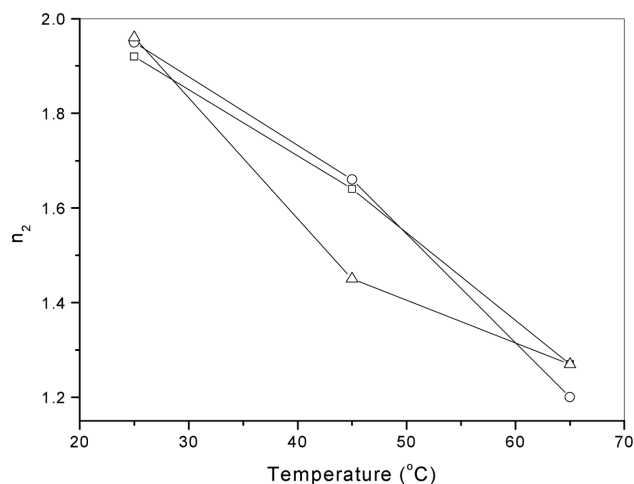


Fig. 4. Temperature dependence of n_2 slope of uptake curve in ECTFE ($\square$: Benzene, $\circ$: Toluene, $\triangle$: Chlorobenzene).

controlled diffusion into diffusion-controlled relaxation as the temperature is increased [Odani, 1961; Thomas and Windle, 1981, 1982]. In other words, relaxation time is decreased with rising temperature due to the decrease of relaxation effects on diffusion process.

2. Application of Camera-Roda and Sarti [1990] Model

A finite-difference method was applied to governing mass balance equations consisting of the viscoelastic flux equation. The Crank-Nicholson method has been adopted to integrate the equations over a time step. In the space finite differences, linear variation of the variables has been assumed between consecutive grid knots, and the grids for the diffusive flux have been staggered in order to improve stability and accuracy. Runs for different parameter values were accomplished with a uniformly spaced grid of 51 points, and assuming a time step $\Delta t^+ = 0.00038$ [Camera-Roda and Sarti, 1990].

The CMRT model for the application to transient sorption data has four adjustable parameters (such as S_o , K_T , De , R_d) with additional data of D_o and ϕ_{eq} . Then, S_o is the initial surface concentration, and K_T is the relaxation sensitivity coefficient. Also, De is the well known diffusion Deborah number, and R_d is the diffusivity ratio of D_{eq}/D_o . With pre-determined values of D_o and ϕ_{eq} , other parameter values (such as K_T , R_d , and S_o) were fitted with the stepwise increase of the diffusion Deborah number. In the evaluation of model parameters, the best-fitted parameter sets were considered to exhibit the minimum SSD (sum of least square deviations).

The numerical schemes reproduced almost the same graphs reported in Camera-Roda and Sarti [1990], as shown in Fig. 5. Fickian behavior was reproduced at very low Deborah numbers, and a larger R_d magnifies the deviation from the Fickian behavior for the intermediate values of De . Any considerable values of De and R_d generated the distinct anomalous sorption curves, especially overshoots, oscillations, and Case II sorption.

The CMRT model reproduced anomalous sorption curves by the combination of four parameter values (such as S_o , De , K_T , and R_d) with pre-determined values of D_o and ϕ_{eq} . Then, ϕ_{eq} is the equilibrium volume fraction that can be experimentally measured (Table 2). The initial diffusivity, D_o , was obtained from the first linear region of sorption curve that is assumed to be governed by Fickian diffusion [Lee and Knaebel, 1997]. The initial diffusivities of solvents

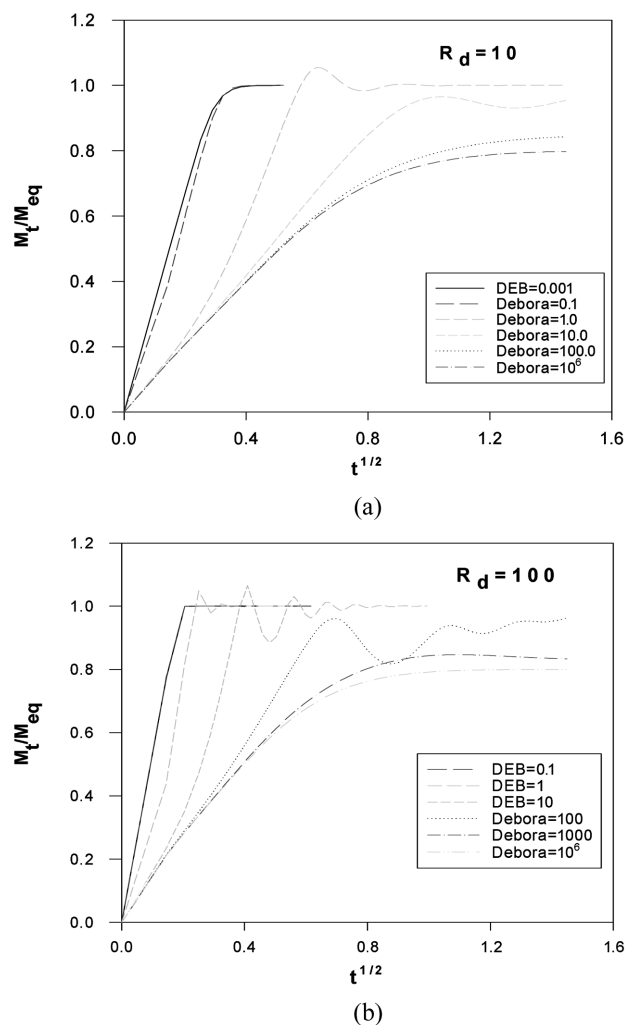


Fig. 5. Effect of various Deborah numbers on the numerical calculation of CMRT model: (a) $R_d = 10$, (b) $R_d = 100$.

Table 2. Equilibrium volume fraction of solvents in fluoropolymers at 25 °C

Polymers	Benzene	Toluene	Chlorobenzene
PVDF	0.0497	0.0423	0.0332
ECTFE	0.066	0.0593	0.0624

in PVDF are 0.942×10^{-6} , 0.588×10^{-6} , and 0.441×10^{-6} cm²/day for benzene, toluene, and chlorobenzene, respectively. The initial diffusivities of solvents in ECTFE are 2.48×10^{-7} , 1.78×10^{-7} , and 1.28×10^{-7} cm²/day for benzene, toluene, and chlorobenzene, respectively.

As seen from Fig. 6, the CMRT model almost reproduced the anomalous sorption curves observed in PVDF and ECTFE films. A slight deviation of predicted values from experimental data was also observed at the final stage of uptake, e.g., less asymptotic approach to saturation for PVDF, and slight oscillation peaks for ECTFE. The validation of the CMRT model, however, should be deferred until the fitted parameter values are proved to have physical and quantitative values.

All the parameter values fitted by the CMRT model are summarized in Table 3. The fitted Deborah numbers were in the ranges of

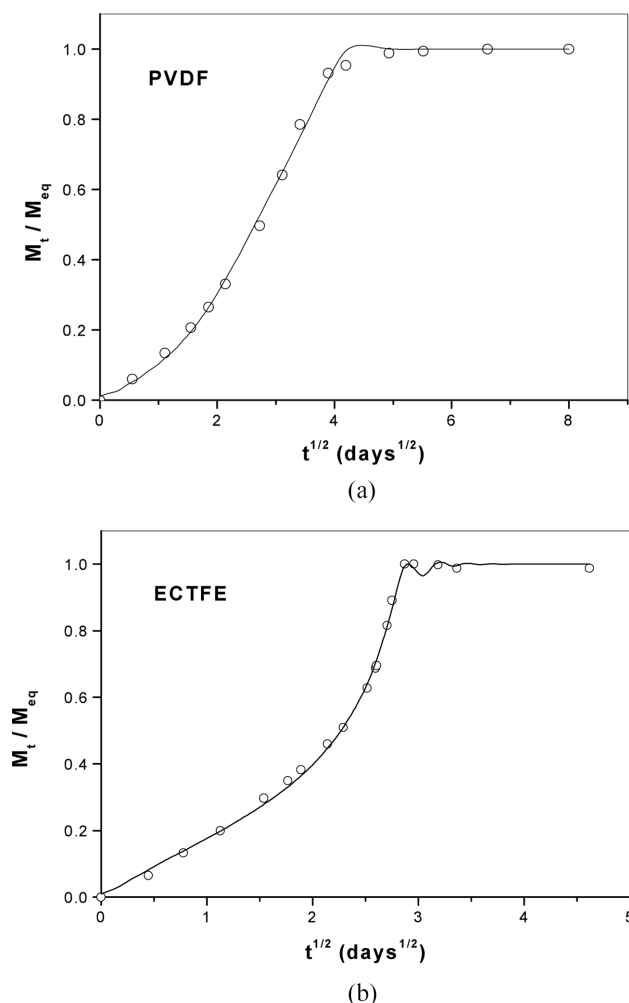


Fig. 6. The sorption curve of benzene at 25 °C reproduced by CMRT model fit: (a) PVDF, (b) ECTFE.

Table 3. Fitted parameter values of CMRT model for sorption data at 25 °C

Polymer	Parameter	Benzene	Toluene	Chlorobenzene
PVDF	S_o	0.699	0.727	0.762
	K_T	66.5	189.3	64.3
	De	0.250	0.338	0.262
	$R_d(K_D^a)$	31.3(3.44)	56.4(4.03)	29.1(3.37)
	SSD	4.59×10^{-4}	2.55×10^{-4}	2.15×10^{-4}
ECTFE	S_o	0.608	0.602	0.594
	K_T	123.0	162	114
	De	3.553	3.220	5.544
	$R_d(K_D^a)$	323(5.78)	322(5.77)	693(6.54)
	SSD	2.2×10^{-4}	2.93×10^{-4}	3.34×10^{-4}

$$^a K_D = \ln(D_{eq}/D_o)/\phi_{eq}$$

0.2-0.3 for the sigmoidal sorption of PVDF, and 2-5 for the drastic accelerating sorption of ECTFE. The diffusivity ratio, R_d , in PVDF-solvent system was also fitted as tenth order of magnitude lower than ECTFE-solvent systems. Acceleration features in the weight uptake were predicted at intermediate values of De with high values

of R_d . The initial surface concentration, S_o , was fitted in the ranges of 0.6-0.8 for both ECTFE and PVDF. The relaxation sensitivity coefficient, K_T , was fitted in the ranges of 50-200 that is quite higher than the reported values in Camera-Roda and Sarti [1990]. The high values of K_T means that initial surface concentration, S_o , is relaxed very rapidly to equilibrium value of unity.

The sensitivity factor for relaxation time, K_T , should be taken different from the sensitivity factor for the diffusivity, K_D , because these quantities are influenced by different degree of extent for the same concentration [Ferry, 1970]. The ratio of K_D/K_T usually ranges from 0.5-1.0 if the value has the same physical meaning of B_d/B_k according to Fujita's free volume theory. For instance, Kulkarni and Stern [1983] got B_d values which ranged from 0.9-1.0 based on unit value of B_k for semicrystalline PE of C_2H_4 and C_3H_6 , whereas B_d of small molecules (such as CO_2 and CH_4) ranged from 0.5-0.8. The ratio of B_d/B_k was indeed less than one and approached unity only for the larger penetrants in natural rubber. For large molecules which have sufficient interactions with the polymer molecules, it is reasonable to assume that an explicit correlation of diffusion with relaxation process i.e., the coupling parameter is approaching the upper limiting value of unity. The estimated K_D/K_T values by the CMRT model, however, were so low that the fitted K_T values were not reasonably fitted values, or rather behaving as an arbitrary adjusting parameter.

CONCLUSIONS

Transient sorption of aromatic solvents in fluoropolymers was conducted to investigate the relaxation kinetics in conjunction with diffusion behavior. PVDF film produced a typical sigmoidal sorption curve, indicating that uptake was accelerating followed by an asymptotic approach to saturation. ECTFE film produced even more unusual sorption curves that appeared to accelerate until saturation was attained. In the structural relaxation in time, PVDF film was linearly increased in both directions (machine & transverse) with fractional uptake. On the other hand, ECTFE film increased linearly in the transverse direction and exponentially in the machine direction with fractional uptake. By log-log plots of sorption curve, both PVDF and ECTFE exhibited the almost same initial slopes of $n_1=0.6-0.7$, followed by asymptotic values of $n_2=0.9-1.0$ for sigmoidal sorption and $n_2=1.2-2.0$ for a drastic accelerating sorption. The asymptotic exponents decreased with the increase of temperature, indicating that relaxation time is decreased with rising temperature due to the decrease of relaxation effects on the diffusion process, i.e., relaxation sensitivity coefficient should be decreased with rising temperature.

A rate-type viscoelastic [Camera-Roda and Sarti, 1990] model was applied to reproduce the anomalous sorption curves observed in ECTFE and PVDF. The fitted Deborah numbers ranged in 0.2-0.3 for PVDF, and 2-5 for ECTFE. The diffusivity ratio, D_{eq}/D_o , in PVDF-solvent system was fitted as tenth order of magnitude lower than ECTFE-solvent systems. The initial surface concentration, S_o , ranged in 0.6-0.8 for both ECTFE and PVDF. K_T was fitted as high values of 50-200, which means that initial surface concentration is relaxed very rapidly to equilibrium value of unity. Even though the CMRT model reproduced anomalous sorption data well in a qualitative sense except for a slight deviation at the final stage of uptake,

the validation of the model should be deferred until the parameter values are proved to be reasonably and quantitatively fitted values.

Conclusively, it is plausible to assume that diffusion coupled with comparable structural relaxation has accelerating curvature that is strongly dependent on asymptotic diffusional exponents, and total sorption is contributed by relaxation-induced viscoelastic volume change along with concentration-driven Fickian diffusion [Sarti and Doghieri, 1998].

NOMENCLATURE

B_d	: minimum hole required for a diffusional displacement of the solvent
B_k	: minimum hole required for a polymeric jumping unit
De	: diffusion Deborah number [$\tau D/l^2$]
D_r	: effective diffusivity changing in time [$D_r = D_{eq} - D_o$]
D_o	: diffusivity at the very beginning of a diffusion process
D_{eq}	: diffusivity of the completely relaxed polymer at equilibrium state
F	: fractional mass uptake, M_t/M_{eq}
f_o	: fractional free volume in the pure polymer
J	: diffusional mass flux
k, n	: constants
K_D	: sensitivity coefficient of volume fraction in the diffusivity
K_T	: sensitivity coefficient of volume fraction in the relaxation time
M_t	: mass uptake at time $[t]$
R_d	: diffusivity ratio [D_{eq}/D_o]
S_o	: initial surface concentration [ϕ_o/ϕ_{eq}]
V_v	: viscoelastic volume according to Dogherie and Sarti [1997]
V_E	: elastic volume according to Dogherie and Sarti [1997]

Greek Letters

ϕ	: volume fraction of the solvent in the polymer matrix
τ	: relaxation time
γ	: sensitivity coefficient of free volume fraction depending on temperature and concentration

Subscripts

eq	: equilibrium state
f	: Fickian
o	: initial state
r	: relaxation
t	: time

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