

Diffusion in Elongated Membranes

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ABSTRACT: The model proposed by Cohen and collaborators is used to describe the process of diffusion through polymeric membranes subjected to externally applied extensions. This continuum mechanics approach is compared with a model developed via a mesoscopic theory. Experimental data on a variety of polymer/solvent systems are

successfully described by the model. It was found that the flux-versus-time curves for deformations up to 80% elongation could be reduced to a master curve. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2746–2751, 2006

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INTRODUCTION

Polymeric materials are now widely used in protective clothing, liners, and separation processes, which has led to a growing number of investigations of the transport properties of various fluids through polymeric membranes. The diffusion process through polymers is always non-Fickian. So far, no simple model can describe the diverse time-dependent behaviors associated with non-Fickian diffusion. Stastna and De Kee¹ discussed some of the non-Fickian models. Recent developments in diffusion through polymers was reviewed by Neogi.²

Membranes may be subjected to stretching and various other forms of external deformation, and it is desirable to consider the effects of these deformations on the barrier properties of the membranes. So far, only a limited number of reports on the effects of applied deformation on the transport properties of fluids in polymers have appeared. For some polymer/solvent systems applied deformation enhances diffusion, and for other systems the opposite effect is observed. It has also been found that, for the same system, the effect of applied deformation depends on the magnitude of the deformation. Li et al.³ summarized some of the experimental observations and presented some of their results for extensions up to 20%. In this article, we consider the effects of uniaxial elongation on the transport properties of various polymer/sol-

vent systems for elongations up to 80%. The Cohen model is used to predict the experimentally obtained flux-time profiles. It is also compared with a model developed via a mesoscopic approach.

EXPERIMENTAL

The permeation measurements were obtained using a modified ASTM permeation cell (ASTM F-739-85) combined with a homemade stainless drawing apparatus. The membrane was fixed at one end by a clamp and stretched in one direction until the desired elongation was attained. The top and bottom parts of the cell were firmly clamped with the elongated membrane in between. The penetrant was introduced into the upper chamber, and after diffusing through the membrane, it was automatically sampled by a Valco programmed valve and analyzed by a GC flame-ionization detection system. Details of the experimental procedures are given in Xiao et al.⁴ and in Hinestroza.⁵

Mathematical model

We considered a rectangular Cartesian coordinate system (x,y,z) with the origin at the center of the upper surface (in contact with the penetrant) of the membrane. The diffusion process was in the x direction, and the elongation was in the z direction.

If (X,Y,Z) and (x,y,z) are the positions of a material point in the undeformed and deformed states, respectively, then for a uniaxial elongation, the relationship between (X,Y,Z) and (x,y,z) can be written as

$$x = \lambda_1 X, \quad y = \lambda_1 Y, \quad z = \lambda_3 Z \quad (1)$$

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and for an incompressible material as

$$\lambda_1^2 \lambda_3 = 1 \quad (2)$$

The draw ratio, γ_3 , is related to the extension, ε , as

$$\varepsilon = \lambda_3 - 1 \quad (3)$$

If L and l are the thicknesses of the membrane in the undeformed and deformed states, respectively, it follows from eqs. (2) and (3) that

$$l = \lambda_1 L = L / \sqrt{1 + \varepsilon} \quad (4)$$

Continuum mechanics approach (CMA)

To describe the non-Fickian diffusion, we adopted the model proposed by Cohen and White.⁶ In this model, the diffusion process is driven by a difference between concentration and internal stress, σ . The one-dimensional diffusion equation can be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + E \frac{\partial^2 \sigma}{\partial x^2} \quad (5)$$

where c is the concentration, D and E are assumed to be independent of c , D is the molecular diffusion coefficient, and E is a stress-driven diffusion coefficient.

The relationship between σ and c is assumed to be

$$\beta_1 \frac{\partial \sigma}{\partial t} + \sigma = \nu \left(\frac{\partial c}{\partial t} + \beta_2 \frac{\partial^2 c}{\partial t^2} \right) \quad (6)$$

where β_1 , β_2 , and ν are assumed to be constants.

Eq. (6) can be considered to be an analog of Jefferey's model in linear viscoelasticity but expressed differently from Chan Man Fong et al.⁷ and Hinestroza.⁵ An advantage of using eq. (6) is that it clearly

shows the physical properties of the polymer that may relate to the diffusion process. For example, in Jefferey's model, β_1 is a relaxation time and β_2 is a retardation time. The relaxation and retardation times describe the mechanical behavior of the polymer reacting to a penetrant concentration change.

We introduced the following dimensionless quantities

$$\begin{aligned} c^* &= c/c_s, \quad t^* = t/(L^2/D), \quad x^* = x/L, \\ \sigma^* &= \sigma/[\nu c_s/(L^2/D)], \quad \gamma_1 = E\nu/L^2, \\ \gamma_2 &= \beta_1/(L^2/D), \quad \gamma_3 = \beta_2/(L^2/D) \end{aligned} \quad (7)$$

Combining eqs. (5)–(7) yielded

$$\frac{\partial c^*}{\partial t^*} = \frac{\partial^2 c^*}{\partial x^{*2}} + \gamma_1 \frac{\partial^2 \sigma^*}{\partial x^{*2}} \quad (8)$$

$$\sigma^* + \gamma_2 \frac{\partial \sigma^*}{\partial t^*} = \frac{\partial c^*}{\partial t^*} + \gamma_3 \frac{\partial^2 c^*}{\partial t^{*2}} \quad (9)$$

The appropriate initial and boundary conditions are

$$\begin{aligned} c^*(x^*, 0) &= 0, \quad \sigma^*(x^*, 0) = 0, \quad c^*(0, t^*) = 1, \\ c^*(1, t^*) &= 0 \end{aligned} \quad (10)$$

The dimensionless quantities t^* , σ^* , γ_1 , γ_2 , and γ_3 also are defined differently here than in Chan Man Fong et al.⁷ and Hinestroza.⁵ The advantage of choosing these dimensionless quantities is that the dimensionless parameters γ_1 , γ_2 , and γ_3 are independent.

The solution of eqs. (8) and (9) subject to conditions in eq. (10) can be obtained by the continuum mechanics method described in Chan Man Fong et al.⁷ The penetrant concentration profile, c , inside the membrane is given as:

$$\frac{c(x, t)}{c_s} = \left(1 - \frac{x}{L} \right) + \sum_{s=1}^{\infty} \left[\frac{2}{\pi s} \frac{(\lambda_2 - \gamma_3 \lambda_2^2)(1 - \gamma_2 \lambda_1)}{(\lambda_1 - \lambda_2)(1 - \gamma_3(\lambda_1 + \lambda_2) + \lambda_1 \lambda_2 \gamma_2 \gamma_3)} e^{-\lambda_1 t/(L^2/D)} - \frac{2}{\pi s} \frac{(\lambda_1 - \gamma_3 \lambda_1^2)(1 - \gamma_2 \lambda_2)}{(\lambda_1 - \lambda_2)(1 - \gamma_3(\lambda_1 + \lambda_2) + \lambda_1 \lambda_2 \gamma_2 \gamma_3)} e^{-\lambda_2 t/(L^2/D)} \right] \sin \left(s \pi \frac{x}{L} \right) \quad (11)$$

and the flux, F , at time t at the surface $x = L$ is expressed as:

$$F = \frac{\rho D c_s}{L} \left\{ 1 - 2 \sum_{s=1}^{\infty} (-1)^s \left[\frac{(\lambda_2 - \gamma_3 \lambda_2^2)(1 - \gamma_2 \lambda_1 - \gamma_1 \lambda_1 + \gamma_1 \gamma_3 \lambda_1^2)}{(\lambda_1 - \lambda_2)(1 - \gamma_3(\lambda_1 + \lambda_2) + \lambda_1 \lambda_2 \gamma_2 \gamma_3)} e^{-\lambda_1 t/(L^2/D)} - \frac{(\lambda_1 - \gamma_3 \lambda_1^2)(1 - \gamma_2 \lambda_2 - \gamma_1 \lambda_2 + \gamma_1 \gamma_3 \lambda_2^2)}{(\lambda_1 - \lambda_2)(1 - \gamma_3(\lambda_1 + \lambda_2) + \lambda_1 \lambda_2 \gamma_2 \gamma_3)} e^{-\lambda_2 t/(L^2/D)} \right] \right\} \quad (12)$$

where

$$\lambda_1 = \frac{(W + \sqrt{W^2 - 4\pi^2 s^2 V})}{2V}$$

$$\lambda_2 = \frac{(W - \sqrt{W^2 - 4\pi^2 s^2 V})}{2V}$$

$$W = 1 + s^2 \pi^2 (\gamma_1 + \gamma_2)$$

$$V = \gamma_2 + \gamma_1 \gamma_3 s^2 \pi^2 \quad (13)$$

Note that in deriving the flux, we used the following extension of Fick's law

$$F = -\rho \left(D \frac{\partial c}{\partial x} + E \frac{\partial \sigma}{\partial x} \right) \quad (14)$$

If we simplify eq. (6) to a Maxwell-type model ($\gamma_3 = 0$), the flux becomes:

$$F = \frac{\rho D c_s}{L} \left\{ 1 - 2 \sum_{s=1}^{\infty} (-1)^s \left[\frac{\lambda_2 (1 - \gamma_2 \lambda_1 - \gamma_1 \lambda_1)}{(\lambda_1 - \lambda_2)} e^{-\lambda_1 t / (L^2/D)} - \frac{\lambda_1 (1 - \gamma_2 \lambda_2 - \gamma_1 \lambda_2)}{(\lambda_1 - \lambda_2)} e^{-\lambda_2 t / (L^2/D)} \right] \right\} \quad (15)$$

and the concentration profile is given by:

$$\frac{c(x,t)}{c_s} = \left(1 - \frac{x}{L} \right) + \sum_{s=1}^{\infty} \frac{2}{\pi s} \left[\frac{\lambda_2 (1 - \gamma_2 \lambda_1)}{(\lambda_1 - \lambda_2)} e^{-\lambda_1 t / (L^2/D)} - \frac{\lambda_1 (1 - \gamma_2 \lambda_2)}{(\lambda_1 - \lambda_2)} e^{-\lambda_2 t / (L^2/D)} \right] \sin \left(s \pi \frac{x}{L} \right) \quad (16)$$

where

$$\lambda_1 = \frac{(W + \sqrt{W^2 - 4\pi^2 s^2 \gamma_2})}{2\gamma_2}$$

$$\lambda_2 = \frac{(W - \sqrt{W^2 - 4\pi^2 s^2 \gamma_2})}{2\gamma_2}$$

$$W = 1 + s^2 \pi^2 (\gamma_1 + \gamma_2) \quad (17)$$

In the special case of Fickian diffusion ($\gamma_1 = 0$), the flux, F , becomes:

$$F = \frac{\rho D c_s}{L} \left\{ 1 + 2 \sum_{s=1}^{\infty} (-1)^s e^{-s^2 \pi^2 t / (L^2/D)} \right\} \quad (18)$$

which is an approximation of Fickian diffusion flux.

Mesoscopic theory approach (MTA)

This approach is based on the Hamiltonian formalism and uses Poisson and dissipation brackets to derive the governing equations of the diffusion process. The detailed derivation of this mesoscopic theory approach can be found in Beris and Edward,⁸ El Afif and Grmela,⁹ and Liu and De Kee.¹⁰ For the sake of simplicity, some assumptions have been made: (1) the system under consideration is composed of a solvent (small molecules or simple fluid) and a complex polymer fluid (large molecules); (2) the molecules under consideration are completely miscible; (3) the conditions considered are isothermal; (4) the density of the system is constant; (5) the system is in mechanical equilibrium, and (6) bulk flow has not been considered (that is, the mass flux is relatively small).¹⁰ The governing equations developed via this approach for a one-dimensional diffusion problem are:

$$\rho \frac{\partial c}{\partial t} = - \frac{\partial F}{\partial x} \quad (19)$$

$$F = -\rho D \left(\frac{\partial c}{\partial x} + \Gamma_{11} \frac{\partial m_{11}}{\partial x} \right) \quad (20)$$

$$\frac{\partial m_{11}}{\partial t} = \frac{F}{\rho(1-c)} \frac{\partial m_{11}}{\partial x} - m_{11} \frac{\partial}{\partial x} \left(\frac{F}{\rho(1-c)} \right) - \lambda G_0 (1-c) \left[(1-c(2-c_s)) \frac{m_{11}}{k_B T / K} - 1 \right] \quad (21)$$

where λ is a positive, real, valued phenomenological parameter, G_0 is the modulus of elasticity of the polymer, k_B is the Boltzman constant, K is the characteristic elastic constant, and T is the temperature. Note that a conformation tensor, \mathbf{m} , has been used as a state variable to represent the internal structure of the polymer, and m_{11} is a component of \mathbf{m} . Γ_{11} is a component of tensor $\mathbf{\Gamma}$, which relates the elastic and mixing parts of the free energy of the system. Eq. (19) is the mass balance equation, and eq. (20) is associated with momentum transfer.¹⁰ Eq. (21) defines the conformation of the polymer chains and is associated with polymer elasticity. The dimensionless form of eqs. (19)–(21) yielded two dimensionless parameters:

$$\Pi = \frac{k_B T \Gamma_{11}}{K C_{eq}} \quad (22)$$

and

$$De = \left(\frac{k_B T}{G_0 \lambda K} \right) / \left(\frac{L^2}{D} \right) \quad (23)$$

where De is a Deborah number, and $k_B T / G_0 \lambda K$ is a characteristic time associated with polymer structural changes. A characteristic flow time is associated with L_2 / D .

Comparison of the two models

Both approaches used modify Fick's first law to account for the effect of polymer structural change on the diffusion process [eqs. (14) and (20)]. The continuum mechanics approach uses a macroscopic variable (stress) to represent the convective flux because of the deformation of the polymer. The mesoscopic theory approach uses a mesoscopic variable (the conformation tensor) to account for the convective flux. The extra stress tensor, σ , can be expressed in terms of the conformation tensor as follows,

$$\sigma_{\alpha\beta} = 2m_{\alpha\gamma} \frac{\partial \phi}{\partial m_{\gamma\beta}} \quad (24)$$

where ϕ is the free energy density.

In eq. (6), β_1 is a polymer relaxation time used to define the dimensionless parameter, γ_2 . This parameter (γ_2) is a Deborah number (a ratio of a relaxation and a diffusion time). It has the same physical meaning as the Deborah number, De , in the mesoscopic theory approach. Thus, we can relate β_1 to $G_0 \lambda K / k_B T$.

In deriving the governing equations via the mesoscopic theory, we used a Maxwell-type model to express the free energy. The parameters γ_1 and Π both represent the influence of stress on the diffusion process. More recently, Liu and De Kee¹⁰ proved Π to be

TABLE I
Values of Calculated Thickness l_c , and Measured Thickness, l_m , for Various Values of Elongation, ε , for the Acetone Natural Rubber System

ε (%)	0	20	40	60	80
$10^2 l_m$ (cm)	7.7	7.0	6.5	6.1	5.75
$10^2 l_c$ (cm)	7.7	7.03	6.51	6.09	5.74

a negative number in a swelling polymer. We therefore expected γ_1 to be negative as well, as it was in polymer swelling.

RESULTS AND DISCUSSION

The thickness of the membrane was measured with a micrometer with an accuracy of 10^{-3} cm, and it could also be calculated from eq. (4). Table I shows a comparison of the measured thickness (l_m) and the calculated thickness (l_c) of the membrane for the acetone/natural rubber system. The agreement between l_m and l_c also was excellent for other systems.

Once the penetrant came into contact with the membrane, it took a finite time to diffuse through the membrane and to be detected at the downstream side of the membrane. This time lapse is the breakthrough time, t_b . In Table II we have listed the values of t_b and the ratio $\sqrt{t_b}/l$ for the acetone/natural rubber system. As expected, elongation lowered the value of t_b . Note also that the ratio $\sqrt{t_b}/l$ is almost constant, suggesting that the decrease of t_b was a result mainly of the thinning of the membrane.

We first tested the accuracy of eq. (18). Figure 1 shows dimensionless flux versus dimensionless time using eq. (18) and a numerical solution of Fick's laws. The prediction of eq. (18) (squares in Fig. 1) deviated slightly from the numerical solution at the initial stage. That is, eq. (18) provided a reasonable prediction of the Fickian diffusion process.

For the CMA, eq. (15) was programmed into an Excel spreadsheet, and Excel Solver was used to de-

TABLE II
Effects of Elongation on Some Parameters of the Acetone/Natural Rubber System

Acetone/natural rubber system					
ε (%)	0	20	40	60	80
t_b (min)	22	19	14	12	10
t_b/l (min ^{1/2} /cm)	60.91	62.3	57.6	56.8	55.0
γ_1	-1.93	-1.48	-0.93	-0.56	-0.067
γ_2	29.97	49.10	60.01	90.03	121.52
τ (min)	229.68	149.96	139.70	133.86	116.88
β_1 ($\times 10^3$ min)	6.88	7.39	8.38	12.05	14.20
$E\nu$ ($\times 10^{-5}$ cm ²)	-114.43	-72.52	-39.29	-20.84	-2.22
$F_s \times L$ ($\mu\text{g}^2/\text{cm}$)	1.04	0.98	0.96	1.10	1.12
Π	-1	-3	-4.2	-5.5	-7
De	0.01	10	30	32	50

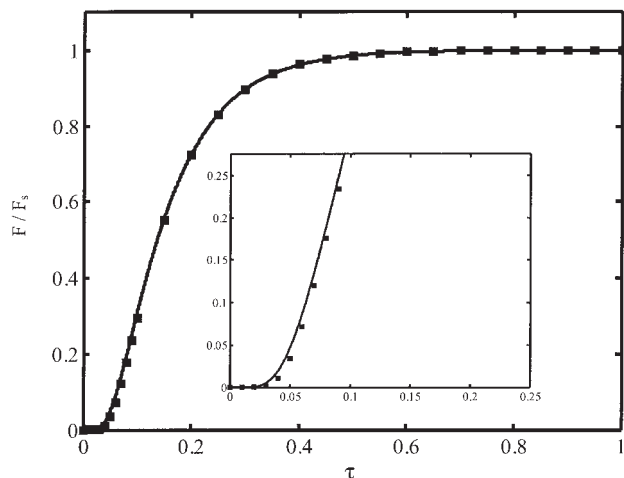


Figure 1 Figure 1 Dimensionless flux (F/F_s) versus dimensionless time, τ : (■) model prediction [eq. (18)], (—) numerical solution of Fick's laws.

termine the best-fitting parameters. The criterion was to maximize the R -squared value. The adjustable parameters were γ_1 , γ_2 , and a characteristic diffusion time, $\tau = L^2/D$. We observed that the effective diffusion coefficient, $D (= F_s L / \rho c_s)$, where F_s is the steady state flux) did not lead to an acceptable prediction of the experimental data. An apparent diffusion coefficient needs to be determined through a fitting process. For MTA, the numerical analysis of eqs. (19)–(21), described in Liu and De Kee,¹⁰ was applied to determine the best-fitting parameters.

The parameters of the acetone/natural rubber system using the continuum mechanics approach are listed in Table II. The R -squared values of this system were 0.996, 0.996, 0.997, 0.998, and 0.999 for 0%, 20%,

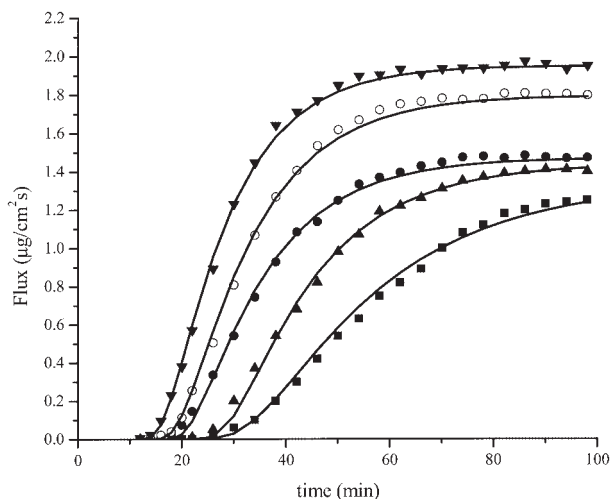


Figure 2 Flux versus time for an acetone/natural rubber system at 298 K and different elongations: (■) 0%, (▲) 20%, (●) 40%, (○) 60%, (▼) 80%, (—) predictions of eq. (15).

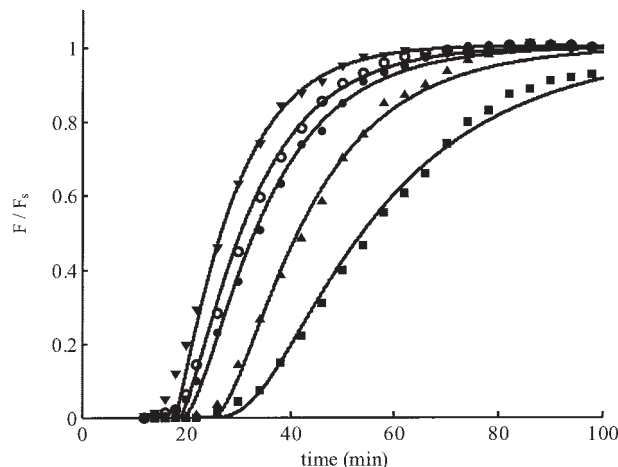


Figure 3 Flux versus time for an acetone/natural rubber system at 298 K and different elongations: (■) 0%, (▲) 20%, (●) 40%; (○) 60%, (▼) 80%, (—) predictions of eqs. (19)–(21).

40%, 60%, and 80% extension, respectively. Wolf and Fu¹¹ observed that an applied stress can either reduce the surface energy or can open sites so as to allow penetrant to enter the (stressed) region. Either case leads to an increase in c_s . In the present study, however, we considered c_s to be constant ($c_s = 0.1$ at zero deformation).

The dimensionless parameter γ_1 demonstrates the importance of stress on the diffusion process. Table II shows that the magnitude of γ_1 decreased as a result of applying an external stress. Eq. (6), which relates stress to concentration, underestimated the effect of stress. The stress was related to the deformation of the polymer chains from the swelling, which was related to the osmotic pressure. We note that eq. (6) predicted zero stress at equilibrium for a swelling polymer, which was not realistic. Table II shows that external deformation greatly reduced the effect of concentration (the magnitude of $E\nu$ decreased). When an extra stress was applied to the polymeric membrane, the polymer relaxed over time (β increased). The negative value of γ_1 means that the relaxation of the polymer decreases the flux.

Dimensionless time, γ_2 , provides an additional measure of the effect of stress on the diffusion process. The γ_2 values were very different from the De numbers obtained using the mesoscopic theory. We note that both addressed the same physical meaning and both increased with elongation.

Table II also shows that the characteristic diffusion time ($\tau = L^2/D$) decreased with elongation. However, the modified flux (which is the experimental flux times the membrane thickness) only changed slightly. The decrease in characteristic diffusion time and the increase in steady-state flux were thus mainly a result of the decreased thickness of the membrane.

Figures 2 and 3 compare the predictions of the CMA

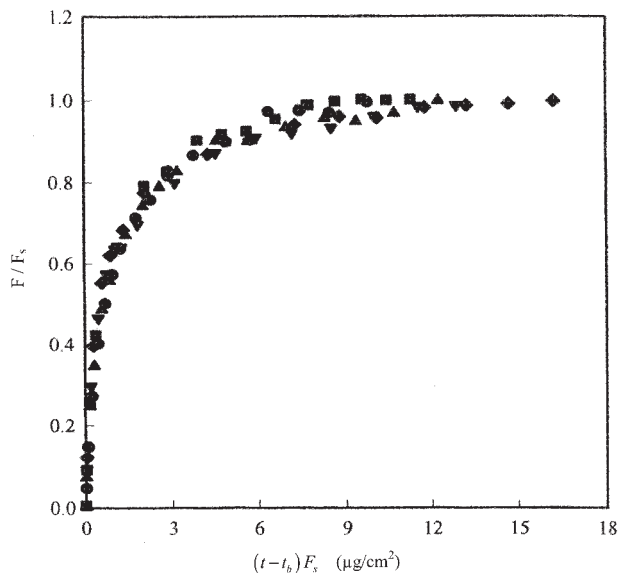


Figure 4 Plot of F/F_s versus $(t - t_b)F_s$ for a toluene/nitrile rubber system at 298 K and different elongations: (●) 0%, (■) 20%, (▲) 40%, (▼) 60%, (◆) 80%.

and MTA methods with the experimental data for an acetone/natural rubber system. The agreement between the experimental data and the model prediction was quite good.

We observed that, for several solvent/rubber pairs, the shapes of the F -versus- t curves were similar for all elongations. This suggests that it is possible to obtain

a master curve by plotting F/F_s versus $(t - t_b)F_s$. Figure 4 shows such a plot for a toluene/nitrile rubber system. This means that once F_s and t_b are known, the evolution of F can be described as a function of time.

The results of the present study were only for an extension of up to 80%, and the extension was in a direction normal to the direction of the diffusion. For higher extensions the effects of the applied extension could be more pronounced.^{11,12}

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