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Diffusion time–temperature superposition of various penetrant–adhesive systems: correlations between penetrant structure, diffusivity, and dynamic mechanical response. III

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Abstract

The effect of the transport of a series of *n*-alkane and a series of ester penetrants on the dynamic mechanical response of a polyamide-based polymer matrix has been investigated. This was done by comparing the dynamic mechanical behaviors of the polymer exposed to the penetrants for various times ranging from 0 to 10^5 min. The concept of double reduction in variables (using temperature and penetrant exposure time) was adopted to create master curves of the dynamic loss moduli of the polymer–penetrant systems that were shifted with respect to both of the above-mentioned variables. This procedure involved the introduction of a new shift factor, diffusion–time shift factor, designated as a_{Dt}. Diffusion–time shift factor plots (log a_{Dt} vs. log time) were made for each of the polymer–penetrant systems, and analysis of these curves revealed that there is no change in the polymer relaxation mechanism due to increased exposure time to a given penetrant as well as penetrant size. Differences in chemical nature between the *n*-alkanes and esters (i.e. due to ester group) were also found not to alter the mechanism of molecular relaxation. However, the chemical nature of the esters indeed influences the rate and extent of polymer relaxation. The dynamic mechanical behaviors of the polymer–penetrant systems from the present study have also been correlated with the basic relationships between the molecular structure (size, shape, and chemical nature) of the penetrants and their observed diffusion properties that were established in the previous publications [Kwan, PhD Dissertation, 1998; Polymer 44 (2003) 3061; Polymer 44 (2003) 3071]. These correlations were used to demonstrate that it is possible to obtain the diffusion parameters ($D, D_0, E_{\mathrm{d}}, M_\infty$, and concentration profiles) of the polymer–penetrant system, as well as the effect of penetrant transport on the dynamic mechanical response (G'', log a_{T}, and log a_{Dt}) of the polymer matrix, based upon knowledge of just the penetrant structure.

Keywords: DMA; Transport; Diffusion

1. Introduction

The presence of low molecular weight liquids in a polymeric adhesive may lead to a variety of physical and chemical changes that can significantly influence the overall performance of the adhesive in real applications [1]. These changes, in turn, may alter the properties of the material to a considerable extent, and may render the material unsuitable for some applications. Therefore, it is of importance to understand the diffusion of low molecular weight liquid penetrants into a polymeric system, and the changes induced in the material as a result of the diffusion process. The transport behaviors of a homologous series of *n*-alkanes and a series of esters in a polyamide-based polymeric adhesive have been investigated, and the results reported in a series of two publications [2,3]. The effects of size, shape, and chemical nature of the penetrants on their transport processes were demonstrated. Furthermore, correlations encompassing the above penetrant properties and the diffusion parameters (diffusion coefficient and activation energy of diffusion) were proposed based on the results obtained. In the present study, the effect of the transport of the *n*-alkane and ester penetrants on the mechanical response of the polyamide-based polymer matrix, is investigated. This has been achieved by means of invoking the principles of reduced variables, originally proposed by Williams–Landell–Ferry [4]. The results from this

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study, in conjunction with those from the previous publications [2,3] provide the basis of correlations between the penetrant properties and their subsequent effect on the transport process on the one hand, and the changes induced in the mechanical response of the polymer, on the other. These correlations will enable the prediction of one parameter, given a reasonable set of data on the other parameters. Such predictive capability could broaden the range of application of this scheme to many other polymers and penetrants.

2. Background

The principles of time–temperature correspondence are widely used to study the long-term behaviors of polymers. This is done by performing experiments over short, accessible time frames at a given temperature, and then repeating them over the same time frame at different temperatures. This is followed by a shifting procedure that results in a smooth continuous curve known as a master curve that extends over a large time scale. These principles for studying the long-term behavior of polymers have been eloquently explained and demonstrated [4–6]. This time–temperature correspondence is described by the empirical relationship known as the WLF equation, given as

$$\log a_\mathrm{T} = \frac{-C_1(T - T_\mathrm{g})}{C_2 + (T - T_\mathrm{g})} \tag{1}$$

where a_T, temperature shift factor, T_g, glass transition temperature, and C_1, C_2, constants.

This equation forms the basis of many accelerated testing procedures that are used to predict the behavior of polymers at a given time and temperature. Such procedures have also been extended to test variables other than time and temperature, provided those variables accelerate the process measured without changing its mechanism. Some such common variables include strain rate, humidity, filler content, pH, and chemical polarity.

In addition to the shifting procedure with respect to one pair of test variables, the concept described above may also be applied to multiple variables at the same time. Such multiple shifting results in a ‘multiply-reduced’ master curve. However, it is noted that the variables involved must be independent of each other, and their effect on the polymer behavior must be additive only. Such multi-variable shifting has been extensively used to study the mechanical properties of a variety of polymers and variables [7–11]. A few pertinent examples of previous investigations involving double reduction of a set of three test parameters are given below.

Multi-variable shifting using temperature and relative humidity has been used in a study of the mechanical behaviors of semicrystalline poly(vinyl alcohol) and nylon-6 [12]. Stress relaxation tests were performed in tension on both materials with different degrees of crystallinity, over a range of temperatures (22 to 77 °C) and humidity. $\log E(t)$ vs. time curves were shifted along the time axis using temperature and relative humidity as variables. Superposition of the variables was found to be valid except in the extremes of very high and low humidity and temperatures. It was concluded from that study that the application of time–relative humidity superposition was valid only when temperature conditions were near those of the polymer glass transition region.

Kohan [13] has shown the temperature–humidity equivalence for the yield stress of various nylons (nylon-6, -66, -610). In that study, temperatures were varied from −40 to 100 °C, and humidity levels ranged from 0 to 100%. Each of the nylon polymers showed similar trends in behavior with respect to temperature and humidity. However, the extent to which the relative humidity affected the yield stress varied from polymer to polymer. Unfortunately, no interpretation of the different humidity dependencies was made in terms of the individual polymer structures in that study.

Schausberger and Ahrer [14] have used the concept of multiple shifting using temperature and plasticizer concentration in their study on polystyrene. Frequency–temperature master curves were created for the neat polymers as well as for polymers containing various compositions of plasticizer using the WLF equation. The magnitude of relaxation strength was shown to depend upon the square of the weight fraction of the plasticizer. The authors [15] have defined a concentration shift factor based on the translation of the dynamic moduli curves of varying plasticizer concentrations along the frequency axis. These concentration shift factors were observed to roughly follow a power law relationship with the weight fraction of plasticizer.

The examples discussed above demonstrate the utility of the multiple shifting procedure based upon the principles of the WLF theory, involving common test variables such as temperature, humidity, filler content, etc. In the present study, the concept of multi-variable shifting involving the three variables—temperature, frequency, and diffusion time (i.e. penetrant exposure time)—is used to investigate the effect of penetrant transport on the mechanical properties of a polymeric matrix. The concept of a ‘diffusion–time shift factor’ will be introduced to describe the correlation between the diffusion process and the observed mechanical properties.

3. Experimental

3.1. Materials

The dynamic mechanical properties of the polymer–penetrant systems from the previous publications [2,3] have been investigated. The polymer is a polyamide-type matrix that was cured at 100 °C for 1 h followed by post-cure at 150 °C for 3 h. The penetrants used consist of a homologous series of *n*-alkanes from C_6 to C_{17}, and a series of esters from C_3 to C_{17} purchased from Aldrich Chemical Co. (99.9 + %). Another ester penetrant, isodecyl pelargonate (Emery 2911) from Emery Chemicals (99.9 + %) was also used. A list of all the penetrants used along with some of their physical properties is given in Tables 1a and b.

3.2. Experimental procedures

The dynamic mechanical experiments were performed using a Polymer Laboratories Mark II Dynamic Mechanical Analyzer Instrument with a sandwich geometry in the shear mode. The particular testing mode and geometry were chosen due to the elastomeric nature of the material. The strain on the sample from the oscillation of the shear plate was selected to be approximately 1.262%. Locking screw clamps and adjustment screws were tightened with torque wrench settings of 30 and 25 cN m, respectively. The experiments were carried out in a step-isothermal mode over a temperature range of −65 to 280 °C at intervals of 3 °C. An equilibration time of 30 s was allowed at each step. After equilibration, a series of 8 frequencies (0.1, 0.3, 1, 3, 10, 30, 50, and 100 Hz) were tested at each temperature.

The DMA tests required two circular samples, each about 0.56 mm thick and 7 mm in diameter. These samples were cut out from pre-cured polymer sheets using a die with a 7 mm inside diameter, followed by curing and testing. The cured polymer samples were then exposed to the penetrants for various times ranging from 1 to 10^5 min at room temperature. Then they were weighed, their thicknesses were measured, and they were placed between the shear plates. The plates were clamped intimately to the surface of the samples so as to ensure contact and to minimize penetrant evaporation. Samples were quickly cooled down to −65 °C and dynamic mechanical data was collected as the samples were heated to the final temperature of 280 °C.

The authors are confident that the evaporation of penetrants was kept to a minimum throughout the test temperature range of most interest (−30 to 60 °C), and that it did not have any influence on the results obtained. This was confirmed by measuring the T_g of the polymer, which was found to be a broad transition ranging from 20 to 43 °C, and comparing it to the boiling points of the penetrants (≥100 °C in general). Furthermore, separate experiments were carried out to determine the mass of penetrant within a polymer sample during the actual dynamic mechanical test, at temperatures right above the thermal transition of interest. These experiments clearly confirmed that penetrant evaporation from the samples was minimal.

The authors also confirmed that the DMA results were not affected by non-uniform penetrant distribution in the sample caused by stopping the diffusion process before equilibration was reached. This assumption was verified by first exposing polymer samples to a given penetrant for a specified time. Then, the samples were removed from the penetrant, and promptly sealed in airtight vials for various times from one minute to one month. This was done in order to provide different times for the penetrant to uniformly distribute itself within the polymer films. The sample stored in a vial for one month represents an equilibrated state (homogeneous distribution of penetrant), whereas the sample stored in a vial only for a minute represents an un-equilibrated state (non-uniform distribution of penetrant). The dynamic mechanical data for all the stored polymer films were obtained and compared. No noticeable difference was observed between the data for the different samples. The experiment described above was repeated with a number of the penetrants from the present study, and several exposure times. Similar results were obtained in all cases. This result confirms that the dynamic mechanical data are indeed average values over the entire sample thickness and that non-uniform distribution of penetrant caused by stopping the diffusion process prior to equilibrium does not affect our results.

3.3. Shifting procedure

The dynamic mechanical data obtained for a polymer–penetrant system at a given diffusion time consisted of approximately 60 isothermal curves. Using the concept of time–temperature superpositioning (tTSP), each isotherm was shifted left or right along the log frequency axis, relative to a reference isotherm $T_{\text{ref}} = 50$ °C, to yield the final master curve. $T_{\text{ref}} = 50$ °C was selected as the

Table 1a
Physical characteristics of *n*-alkane penetrants

Penetrant	Molecular weight (gram/mol)	Molar volume (cm^3/mol)	Solubility parameter (MPa$^{0.5}$)
Hexane (HX)	86.17	130.50	14.8
Heptane (HP)	100.20	147.40	15.2
Nonane (NN)	128.25	179.70	15.6
Decane (DC)	142.28	195.95	15.8
Undecane (UD)	156.30	212.47	16.0
Tridecane (TD)	184.35	244.92	16.4
Pentadecane (PD)	212.41	277.69	16.8
Hexadecane (HXD)	226.43	294.07	17.0
Heptadecane (HPD)	240.46	309.50	17.2

Table 1b
Physical characteristics of ester penetrants

Penetrant	Molecular weight (gram/mol)	Molar volume (cm^3/mol)	Solubility parameter ($MPa^{0.5}$)
Methyl acetate (MA)	74.07	79.86	19.4
Ethyl propionate (EP)	102.12	115.45	17.9
Propyl butyrate (PB)	130.19	149.97	17.2
Ethyl heptanoate (EH)	158.24	183.09	17.0
Ethyl nonanoate (EN)	186.30	216.24	16.9
Ethyl undecanoate (EU)	214.35	249.53	16.7[a]
Ethyl myristate (EM)	256.43	299.22	16.6[a]
Isodecyl myristate (IPM)	270.46	318.19	16.5[a]
Isodecyl pelargonate (IDP)	270.46	314.56	16.4[a]

[a] Calculated using Hansen's method.

reference isotherm based on the result that it was the approximate peak position of the middle-most frequency (3 Hz) for the neat material. Shifting of the isotherms was done so as to ensure that each curve matched the slope of its immediate neighbor, closest to the reference curve. The number of frequency units through which an isotherm is translated is defined as its temperature-shift factor, a_T. Shifts towards the right are designated as negative, while those towards the left are positive shifts.

Horizontal shifting along the frequency axis essentially compensates for a change in the time scale of a process induced by changes in temperature. However, it is known from the thermo-mechanical spectrum of polymers that a change in modulus co-exists with a change in temperature, and that thermal expansion decreases the amount of material per unit volume. Deviations from purely horizontal shifting may be due to both of the above factors. Such deviations would be manifested in the form of a vertical shift that involves translation of the isothermal curves along the modulus-axis. In the current study, the use of vertical shifting was kept to a minimum and when used, the magnitudes of the vertical shifts were very small.

4. Results and discussion

The dynamic mechanical behaviors of the polymer samples exposed for various times to the *n*-alkane and ester penetrants have been determined as described in the Experimental section. The shifting procedure discussed earlier was used to construct the master curves for each polymer–penetrant system. Examples of such master curves for an *n*-alkane penetrant (*n*-decane) and for an ester penetrant (propyl butyrate) are shown in Fig. 1a and b, respectively. The corresponding shift factor plots are also shown in Fig. 1c and d, respectively. The nomenclature used to refer to these systems is based on the penetrant used and the exposure time. For example, Decane-100K represents a polymer sample exposed to the penetrant decane for 100 K (10^5) minutes. This nomenclature will be used in the remainder of this paper.

The breadth of the loss modulus master curves in Fig. 1a and b indicates the broad spectrum of relaxation times due to the crosslinked nature of the polymer. Using frequency–temperature superpositioning, the range of frequencies has now been expanded by a factor of at least 3 decades, in comparison to the original range of experimental frequencies. The shift factor plots in Fig. 1c and d show smooth transitions with no discontinuities, in accordance with the general shape expected from the WLF process. The inflection in the low temperature region of these curves is due to the failure of WLF at temperatures below the glass transition temperature (T_g) and does not reflect any adverse effects resulting from penetrant diffusion.

Curves similar to the ones shown in Fig. 1a–d were obtained for the polymer samples exposed to each of the nine *n*-alkane and nine ester penetrants, for the entire range of exposure times from 10^0 to 10^5 min. All those curves are not reproduced here for the purpose of brevity. However, they are available in the original work related to this paper [1].

The shift factors, a_T, obtained for each polymer–penetrant system were used to calculate the WLF constants, $C1$ and C_2, using the linearized form of the WLF equation,

$$\frac{-1}{\log a_T} = \frac{C_2}{C_1}\left(\frac{1}{T - T_{ref}}\right) + \frac{1}{C_1} \qquad (2)$$

According to this equation, plots of $-1/\log a_T$ vs. $1/(T - T_{ref})$ were made, followed by linear regression of the data in the temperature range between T_{ref} and $T_{ref} + 100$ °C. This yielded a line of slope, C_2/C_1 and intercept, $1/C_1$. The values of C_1 and C_2 for all the polymer–penetrant systems and exposure times were calculated from the slopes and intercepts of the above-mentioned plots. In general, the values of C_1 for the systems ranged between 7 and 26, while the C_2 values were in the range 58–289. No trends were observed in the values of C_1 and C_2, with respect to penetrant size, type, or exposure time.

The effect on the dynamic mechanical properties of the polymer due to increasing exposure time to a penetrant may be seen by comparing the master curves constructed for a given polymer–penetrant system at different exposure times. Such a comparison for the polymer exposed to the penetrant, *n*-decane for two different times—10^2 and

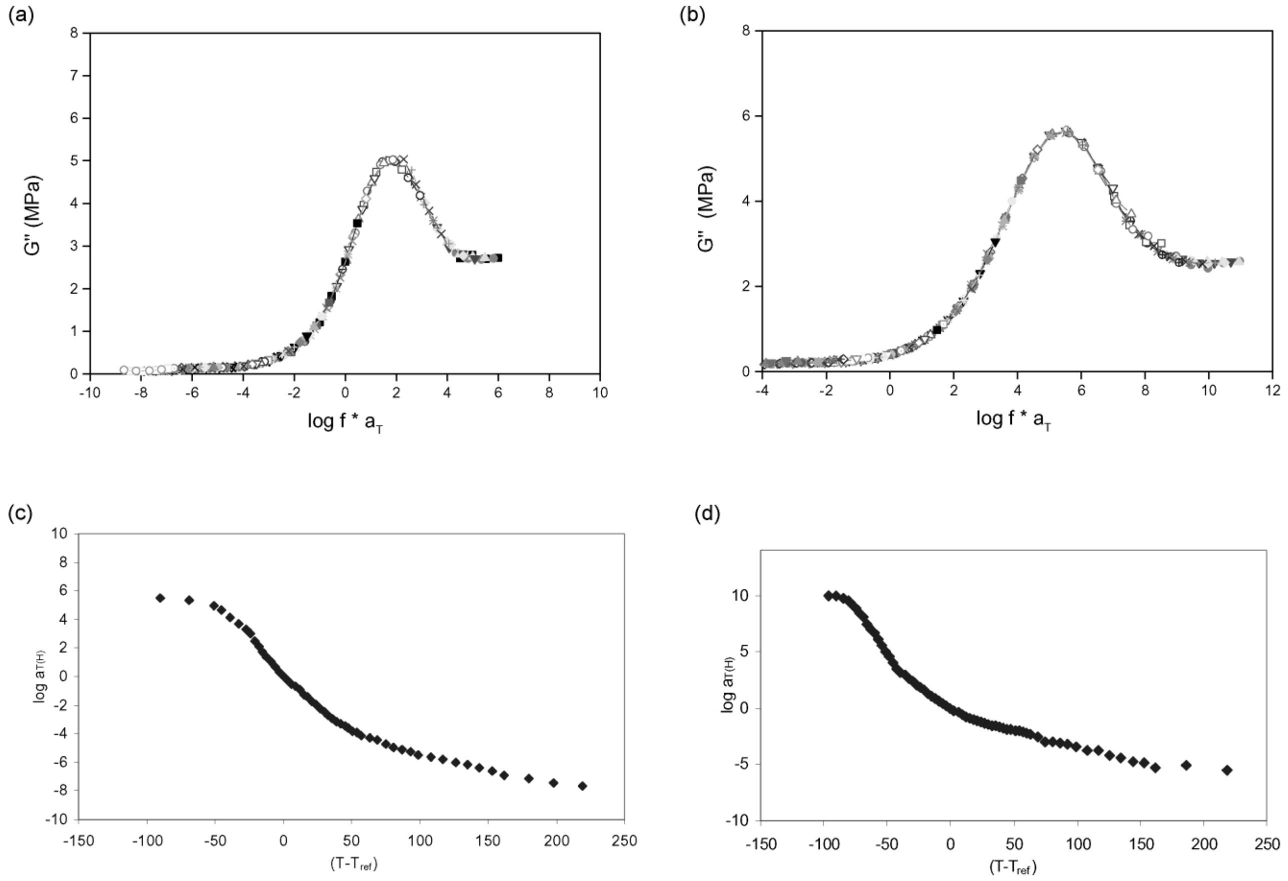

Fig. 1. (a) Frequency–temperature dynamic loss modulus master curve of polymer exposed to *n*-decane penetrant for 10^2 min. (b) Frequency–temperature dynamic loss modulus master curve of polymer exposed to *propyl butyrate* penetrant for 10^3 min. (c) Temperature shift-factor plot of polymer exposed to *n-decane* penetrant for 10^2 min. (d) Temperature shift-factor plot of polymer exposed to *propyl butyrate* penetrant for 10^3 min.

10^5 min, is shown in Fig. 2. It is seen from the figure that an increase in exposure time to the penetrant shifts the mechanical spectrum towards higher frequencies. Since higher frequencies are analogous to lower temperatures, this effect may be interpreted in terms of a depression of the T_g to lower temperatures due to plasticization by the penetrant, consistent with what is expected on the basis of the free volume theories [15–17].

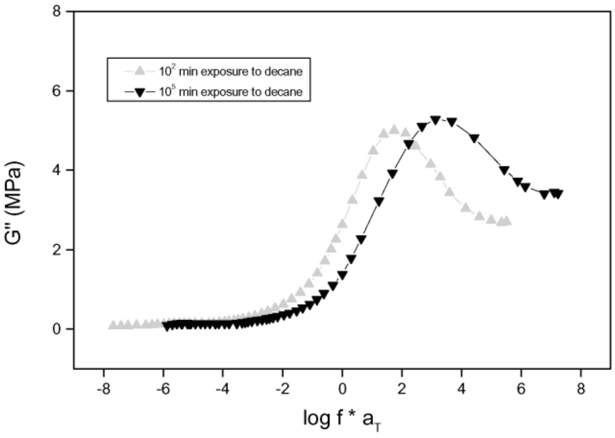

Fig. 2. Frequency–temperature master curves of polymer for exposure times of 10^2 and 10^5 min to decane penetrant.

It is also seen from Fig. 2 that the master curves for the two different exposure times exhibit similar shapes, and appear as if they may be transposable. However, before such a transposition could be achieved, a common scale that would allow proper comparison of all the curves needed to be created. This was done by first normalizing each master curve with respect to its relaxed and un-relaxed loss moduli, followed by a second normalization with respect to its $G''_{\max}$. Such a normalization procedure is widely accepted, and is extensively used by several researchers [18,19] in creating master curves of polymeric relaxations. This method is based on the assumption that the loss peaks arise predominantly from the motions of the polymer itself. Such an assumption is valid for the polymer–penetrant systems presently studied, due to the fact that the penetrants used are poor solvents (high χ_{12} values) with relatively low solubilities.

The normalized master curves constructed using the above procedure for the polymer exposed to *n*-decane (DC) and propyl butyrate (PB) are shown in Figs. 3a and 4a, respectively. These curves at different exposure times were then transposed with respect to the neat polymer, i.e. zero exposure time, to yield a single, final master curve. Such a

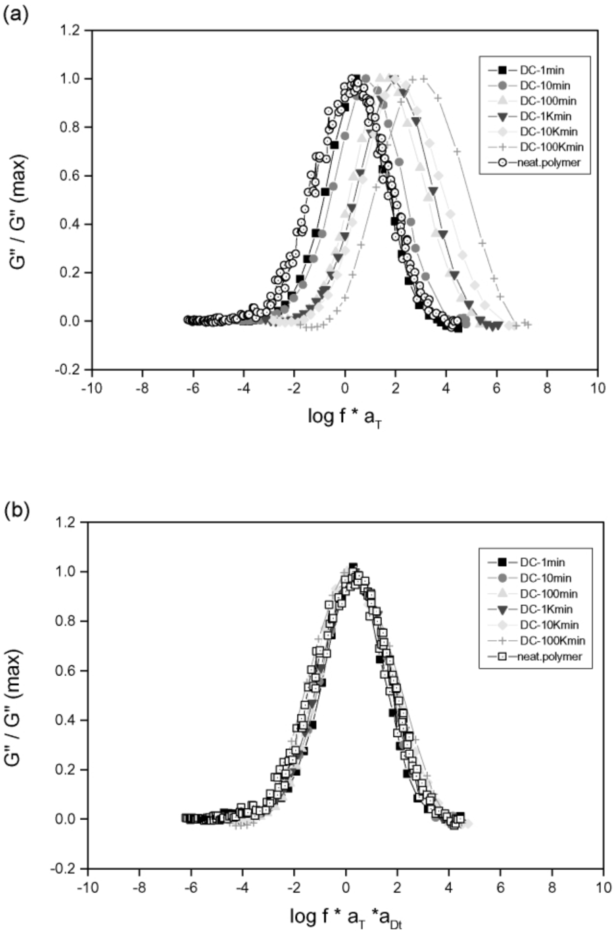

Fig. 3. (a and b) Normalized frequency–temperature master curves of polymer for various penetrant exposure times to *decane* (top). Doubly reduced temperature and diffusion–time master-master curve for penetrant, *decane* (bottom).

doubly reduced master curve for the polymer–n-decane and the polymer–propyl butyrate systems are depicted in Figs. 3b and 4b, respectively. A new term, ‘diffusion–time shift factor, a_{Dt}’ is introduced in the present study to refer to the number of log(frequency) units by which each master curve was shifted in this process. The values of log a_{Dt} determined from the multiple shifting were plotted as a function of exposure time to the penetrants as shown for n-decane and propyl butyrate in Fig. 4c, respectively. In both cases, smooth monotonic curves without any discontinuities are obtained, suggesting that there is no change in mechanism of the polymer relaxation due to increased exposure time to a penetrant. The absence of any discontinuities further confirms the validity of the shifting procedure adopted.

Curves similar to the ones discussed above were constructed for each of the nine n-alkane and nine ester penetrants. All those curves are not presented here for the purpose of briefness. However, they are available in the original work related to this publication [1].

The next step is to determine if increasing size, i.e. penetrant molecular weight, within each penetrant series influences the polymer relaxation mechanism. It was shown

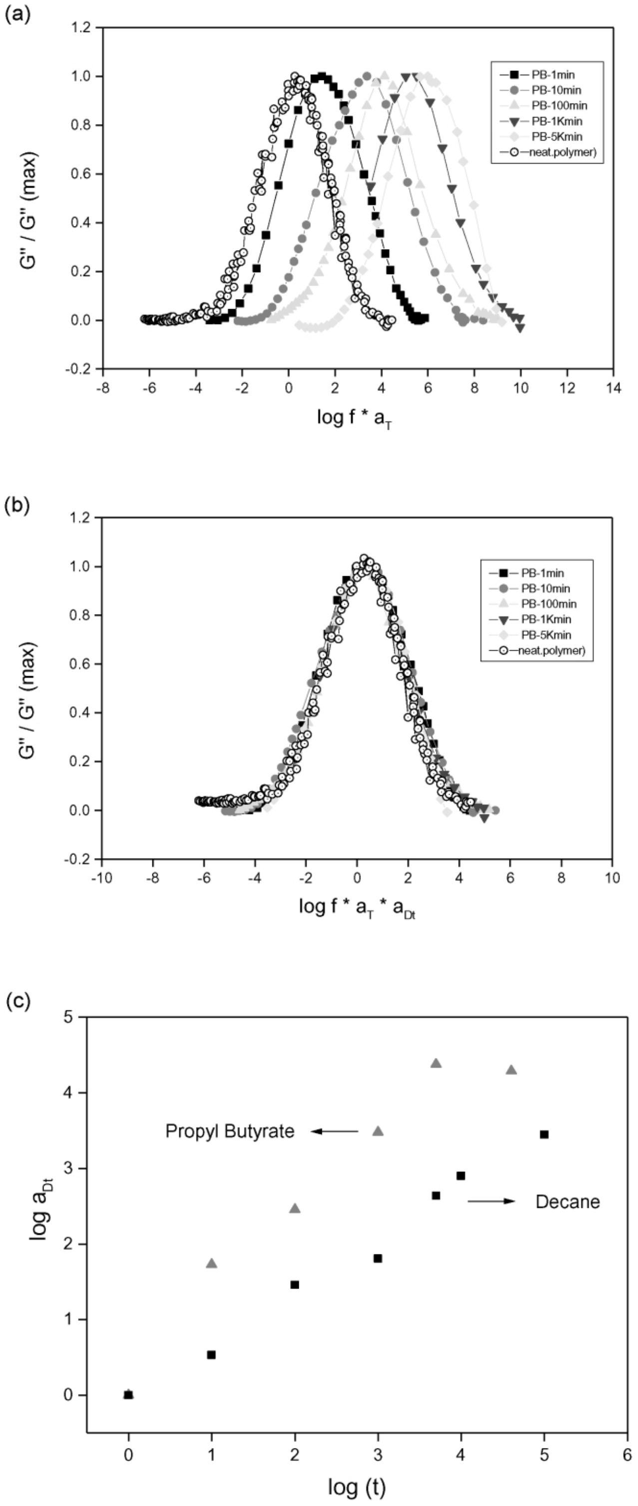

Fig. 4. (a and b) Normalized frequency–temperature master curves for various penetrant exposure times to *propyl butyrate* (top). Doubly reduced temperature and diffusion–time master-master curve for penetrant, *propyl butyrate* (bottom). (c) Diffusion–time shift factors, log a_{Dt}, for polymer exposed to *n-decane* and *propyl butyrate* for various times.

from the results of mass uptake experiments reported previously [2,3] that penetrant size varies directly as the equilibrium diffusion time, t_e, for the transport of a given penetrant through the polymer matrix. Then the influence, if any, of penetrant size on the polymer relaxation mechanism may be determined by normalization of the exposure time with respect to equilibrium sorption/diffusion time, t_e. Accordingly, the exposure times represented in the x-axis of the log a_{Dt} vs. log t plots, were reduced with respect to t_e (values obtained from mass uptake experiments reported previously [1–3]) as shown in Fig. 5a and b for the n-alkanes and esters, respectively. The curves in the figures are found to closely resemble a sigmoidal shape. This shape could possibly be related to the fact that diffusion processes are often modeled as being a result of statistical jumps via Brownian motion [20].

It is further noted from the figures that it may be possible to represent all of the ca. 40 diffusion–time shift factor curves within each penetrant series by a single curve. This observation is remarkable in view of the complex nature of these experiments. It also verifies that both exposure time and penetrant size (within each penetrant series) do not alter the relaxation mechanism of the polymer. The above result is further consistent with the principles of the WLF procedure that have been invoked in the construction of the doubly reduced master curves, and lends further validity to the concept of the newly introduced diffusion–time shift factor.

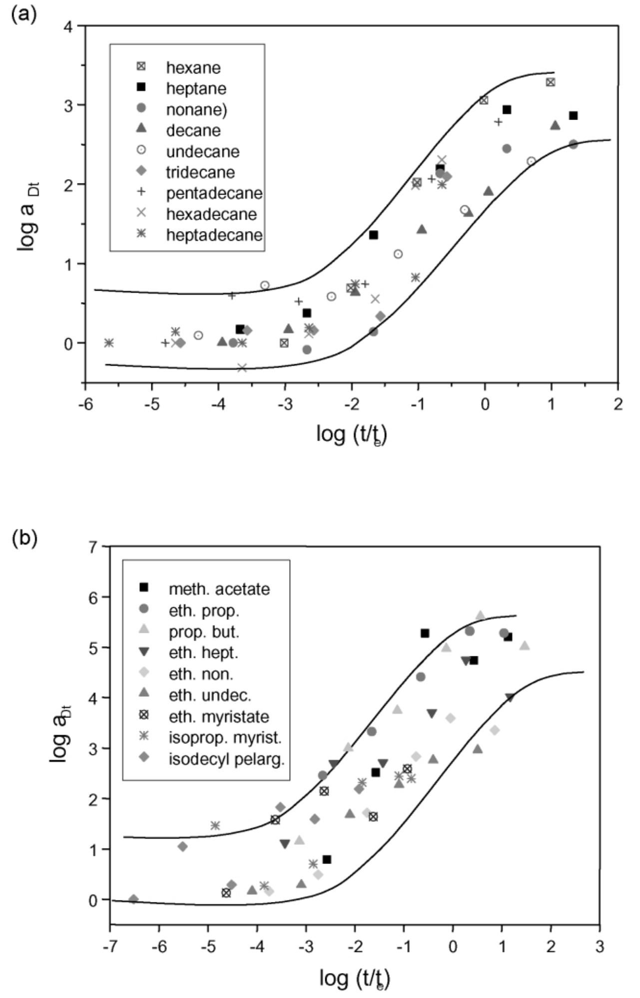

Fig. 5. (a) Diffusion–time shift factors for n-alkanes as a function of normalized time (lines drawn for visualization) (b) Diffusion–time shift factors for esters as a function of normalized time (lines drawn for visualization).

Further comparison of the diffusion–time shift factor plots for the n-alkanes and esters (Fig. 5a and b, respectively) reveals the following differences. The magnitudes of the shift factors for the ester penetrants approach higher values than those of the corresponding n-alkanes. In addition, the slope of the 'linear' portion for the esters is greater than that of the n-alkanes. These results may be attributed to the increased solubility and thereby enhanced plasticizing efficiency due to the presence of the ester functionality. The above results are also in agreement with the higher diffusion coefficients and solubilities for the ester penetrants (compared to the n-alkanes), determined from the mass uptake experiments reported previously [2,3].

The diffusion–time shift factors (log a_{Dt}) of the n-alkanes and esters may also be described as a function of the concentration (wt% uptake) of the penetrants, as shown in Fig. 6. The wt% uptakes plotted on the x-axis in this figure were determined experimentally, immediately before performing the dynamic mechanical analysis (DMA) experiments on each of the polymer samples. Such a plot provides an elegant means of correlating the diffusion–time shift factors to the fundamentals of the diffusion process, i.e. correlation of log a_{Dt} to penetrant concentration, which in turn is related to exposure time via the diffusion coefficient.

From Fig. 6, it is found that the magnitudes of both the wt% uptakes and log a_{Dt} for the ester penetrants extend to higher values than those for the n-alkanes. Furthermore, it is found that the data for both the n-alkanes and esters may be represented by a single curve, described by a power law expression, $y = ax^b$, where $a = 1.01$ and $b = 0.53$ (statistical chi$^2 = 0.39$). This result further indicates that differences in chemical nature between the two penetrant series do not alter the relaxation mechanism of the polymer. However, the chemical nature of the penetrants does indeed influence the rate and extent of polymer relaxation by determining the rate of penetrant diffusion, and thereby its concentration in the polymer matrix.

In view of the above results, the effect of a penetrant on the relaxation process in a polymer matrix may be explained as follows. The presence of a penetrant causes the polymer matrix to swell to a small extent resulting in an increase in free volume within the matrix. The effect of this free volume increase is to accelerate the rate of relaxation of the polymer, without altering its mechanism. This is analogous to the effect that may be induced by increasing the temperature.

So far, a multiple shifting procedure (double reduction) using the variables—temperature and exposure time to a penetrant—has been adopted to analyze the dynamic

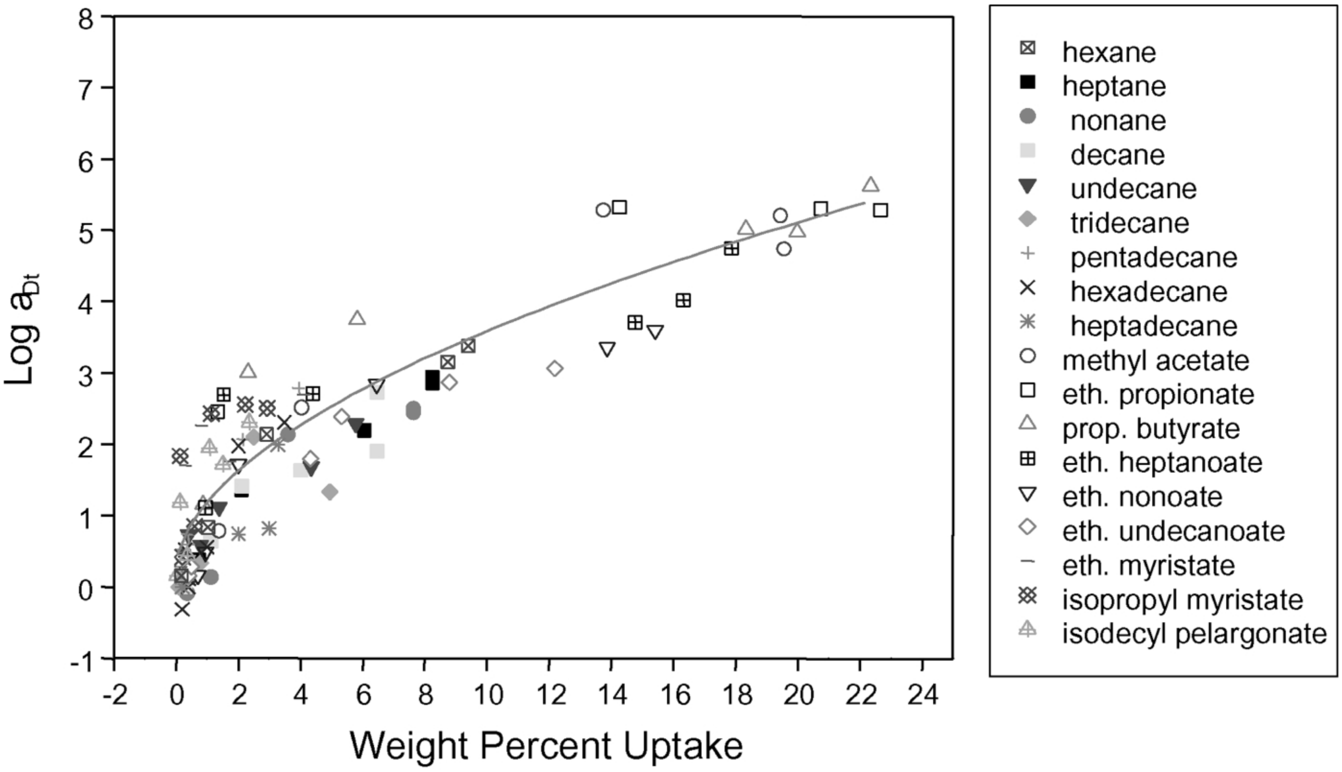

Fig. 6. Diffusion–time shift factors for both *n*-alkane and ester penetrants as a function of weight percent uptake.

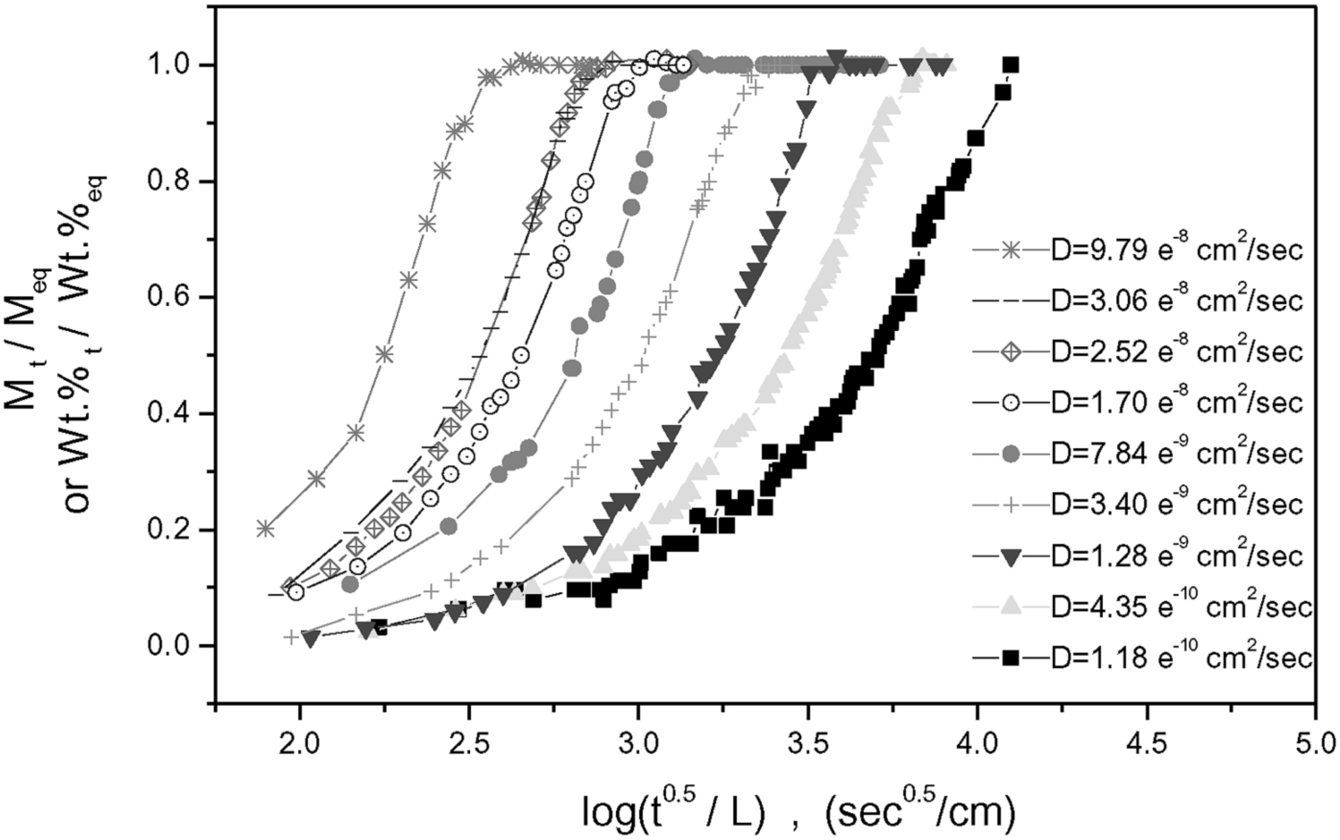

Fig. 7. Fractional composition as a function of normalized time for various diffusivities.

mechanical behavior of the polymeric adhesive exposed to a series of *n*-alkane and a series of ester penetrants. The doubly reduced master curves created here enable prediction of the mechanical response of the polymer at a given temperature and exposure time to a given penetrant. It is reminded that basic relationships between the molecular structures of penetrants and their observed diffusion properties were established in the previous publications [2,3]. The multiple shifting procedure used in the present study is used to correlate those relationships with the dynamic mechanical response of the polymer studied here. Such a correlation is possible due to the fact that the diffusion coefficient relates penetrant concentration to exposure time. And, it was demonstrated in this study that the dynamic mechanical response of a polymer is also related to the same two parameters—penetrant concentration and exposure time. The correlations so established enable prediction of the transport properties as well as the dynamic mechanical behavior of a polymer–penetrant system based upon knowledge of only the penetrant structure. The steps involved in such a prediction are outlined below.

4.1. Step 1: determination of E_d

Starting from the size (molar mass or molar volume) of a given penetrant similar to the ones in the present study, its activation energy of diffusion (E_d) through the polymer may be derived from the plot of E_d vs. molar mass or from the plot of E_d vs. $\chi \times V_m$ (where V_m is molar volume) (Figs. 4 and 8, respectively of the previous publication [3]).

4.2. Step 2: determination of Arrhenius front factor, D_0

From the value of E_d, the Arrhenius front factor (D_0) for the penetrant may then be evaluated from a plot of log D_0 vs. E_d (Fig. 5) [3].

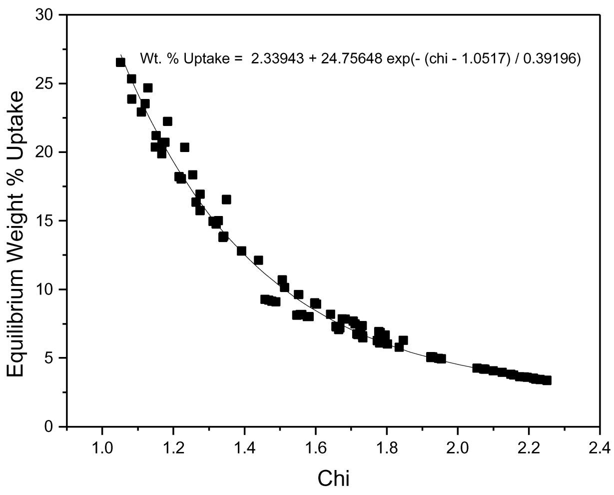

Fig. 8. Equilibrium weight percent uptake for both series of penetrants as a function of the Flory–Huggins interaction parameter χ_{12}.

4.3. Step 3: evaluation of Diffusion coefficient, D

Having calculated the values of E_d and D_0 as described above, the value of the diffusion coefficient (D) for the penetrant at any temperature is determined based on the Arrhenius expression,

$$D = D_0\, exp(-E_d/RT)$$

4.4. Step 4: determination of concentration profile

The diffusion coefficient, D from step 3 may then be used to determine the concentration–time profile for any geometry and boundary conditions, by incorporating the value of D into the appropriate solution of the Fick's law of diffusion. An example of such concentration profiles for a thin-film geometry based upon various values of diffusion coefficients is shown in Fig. 7. The fractional composition, M_t/M_{eq} or wt%$_t$/wt%$_{eq}$, of the penetrant at a given time in a polymer sample of thickness, L may be estimated from curves such as these.

4.5. Step 5: evaluation of penetrant composition

In order to determine the actual composition of the penetrant (M_t or wt%$_t$) at a given time from the concentration profiles such as those shown in Fig. 7, knowledge of the value of the equilibrium weight uptake, M_∞ is essential. M_∞ (also related to equilibrium wt% uptake) is a measure of the solubility of a penetrant in a polymer and is directly related to the Flory–Huggins interaction parameter, χ, as shown in Fig. 8 for the *n*-alkanes and esters. It is seen from this figure that both series of penetrants may be represented by a single curve of the form

$$\text{Equilibrium wt\% Uptake} = 2.34 + 24.76 \exp\left(\frac{-(\chi_{12} - 1.05)}{0.39}\right)$$

This equation may then be used to calculate the equilibrium wt% uptake values for similar types of penetrants, if their χ_{12} values are known. The wt%$_{eq}$ values thus obtained may be subsequently used to determine wt%$_t$ (the wt% uptake of a penetrant at a given time, t) from the concentration profiles (as shown in Fig. 7).

4.6. Step 6: evaluation of dynamic mechanical response

The penetrant composition, wt%$_t$ evaluated from above may then be used to predict the dynamic mechanical response of the polymer–penetrant system, taking into account the effects of both temperature and penetrant diffusion. This is done by determining the diffusion time shift factor, a_{Dt}, from a plot of log a_{Dt} vs. wt% uptake, as shown in Fig. 6 for the *n*-alkanes and esters. One could then derive the dynamic mechanical response of a polymer–penetrant system at any temperature and exposure time as follows: The first step is to obtain the dynamic mechanical data of the neat polymer, necessary to construct a temperature-shifted master curve (with respect to the desired reference temperature). That master curve is further shifted through a factor of log a_{Dt} (obtained from above) along the log (frequency) axis to result in a doubly-reduced master curve, that is shifted with respect to temperature and penetrant exposure time. This final master curve represents the dynamic mechanical response of the polymer–penetrant system, taking into account the effects of both temperature and penetrant diffusion.

Thus, it has been demonstrated that a quantitative prediction of the dynamic mechanical response of a polymer–penetrant system may be made, based upon knowledge of just the chemical structure of the penetrant. The procedure described above may also be extended to other similar polymer–penetrant systems. The predictive capability gained here could be a precursor to the development of a more concise molecular model of diffusion that takes into account all of the factors that have been considered in this study. Such a model may be able to predict the behavior of any polymer–penetrant system of interest more easily and accurately than any model currently available.

5. Conclusions

The effect of the transport of a series of *n*-alkanes and a series of ester penetrants on the mechanical response of a polyamide-based polymer matrix has been investigated. This was done by comparing the dynamic mechanical behaviors of the polymer exposed to the penetrants for various times ranging from 0 to 10^5 min. The concept of double reduction in variables (using temperature and penetrant exposure time) was adopted to create master curves of the dynamic loss moduli of the polymer–penetrant systems that were shifted with respect to both of the above-mentioned variables. This procedure involved the introduction of a new shift factor, diffusion–time shift factor, designated as a_{Dt}.

Diffusion–time shift factor plots (log a_{Dt} vs. log time) for the polymer–penetrant systems yielded smooth monotonic curves without any discontinuities, suggesting that there is no change in the polymer relaxation mechanism due to increased exposure time to a given penetrant. The time axes of these shift factor plots were further normalized with respect to the equilibrium diffusion times, t_e, for each penetrant. Such normalization revealed that it is possible to represent the ~40 diffusion–time shift factor curves within each penetrant series, by a single curve. This result further implies that penetrant size (within a penetrant series) in addition to exposure time does not alter the mechanism of polymer relaxation.

The diffusion–time shift factors of the *n*-alkane and esters were also described in terms of penetrant concentration (wt% uptake). A plot of log a_{Dt} vs. wt% uptake of the penetrants showed that the data for both the *n*-alkanes and esters (~80 master curves) could be represented by a single curve. This result implies that differences in chemical nature between the two penetrant series do not alter the polymer relaxation mechanism. However, the magnitudes of the log a_{Dt} as well as the wt% uptakes for the esters were found to extend to higher values than those of the *n*-alkanes. Similar observations regarding the higher values of log a_{Dt} for the ester penetrants were also made from the normalized log a_{Dt} plots. These results confirm that the chemical nature of the esters indeed influences the rate and extent of polymer relaxation. This was attributed to the increased solubility and thereby enhanced plasticizing efficiency due to the ester functionality.

The dynamic mechanical behaviors of the polymer–penetrant systems from the present study have also been correlated with the basic relationships between the molecular structure (size, shape, and chemical nature) of the penetrants and their observed diffusion properties that were established in the previous publications [2,3]. These correlations were used to demonstrate that it is possible to obtain the diffusion parameters (D, D_0, E_d, M_∞, and concentration profiles) of the polymer–penetrant system, as well as the effect of penetrant transport on the dynamic mechanical response (G'', log a_T, and log a_{Dt}) of the polymer matrix, based upon knowledge of just the penetrant structure. The concepts demonstrated in this study may potentially be extended to other similar polymer–penetrant systems.

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