# Kinetics of Phase Separation in Segmented Polyurethanes

K. K. CHEE* and R. J. FARRIS, *Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003*

## Synopsis

The phase-separation process in segmented copolymers is treated by first-order kinetics which couples with the Fox equation to derive an expression for describing the change of soft segment $T_g$ with the annealing time. Kinetic data of five commercial polyurethanes have been analyzed. The studies conclude that the phase-segregation mechanisms involve two elementary steps which can be characterized by two discrete relaxation times. It has been shown quantitatively that a polyether-based polyurethane (ET) recovers its original domain structure faster than a polyester soft-segment material. The average activation energy of the demixing process of an ET polyurethane is found to be about 23 kJ·mol$^{-1}$ and is not influenced by hydrogen bonding.

## INTRODUCTION

Basically, segmented polyurethanes are two-phase systems consisting of hard-segment domains distinctly dispersed within a soft-segment matrix.[1,2] This domain model has been playing an important role in understanding the unique thermal and mechanical properties of these materials.

Recent work has revealed that the domain morphology is susceptible to thermal treatment.[3,4] Specifically, Wilkes and Emerson[5] have demonstrated that considerable phase mixing in segmented polyurethanes takes place at 160°C. However, upon cooling, phase separation occurs gradually until the original domain structure is restored. This thermally reversible process can be studied kinetically by a variety of techniques such as small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), mechanical methods, and others. This paper deals extensively with the time dependence of the glass-transition temperature of the soft segments which effectively measures the degree of phase separation.[6]

## Kinetics of Phase Separation

One of the striking features of the domain model for multiblock copolymers is the retractive forces arising from the extended flexible soft segment. These forces tend to pull the hard segments out from the adjacent domains so as to facilitate the mixing process. Since the retractive forces of the soft segments and the compatibility of soft and hard segments increase with increasing temperature, substantial segmental mixing is possible at elevated temperatures where the hydrogen bonding and crystallinity are disrupted. However, due to the decrease in the restoring forces exerted by

---

* On leave from Department of Chemistry, University of Malaya, Malaysia.

the stretched soft segment, and the incompability of the two distinct segments at low temperatures, the above process may be reversed by lowering the temperature. The kinetic behavior of this phase-separation process may also be affected by the hydrogen bonding between the various functional groups in the system, the viscosity of the medium as well as the distribution of sizes of the hard segments departing from the system.[7]

Although the model has been successfully employed to interpret the variation of glass transition of soft segments, Young's modulus, and SAXS intensity with annealing time,[3] it is too sophisticated to be realized for quantitative description of these kinetic studies. In view of this, we introduce herein a characteristic parameter, $\tau$, to take care of these physical variables operating in the model. We assume that during a phase-separation process, the rate of decrease in the volume fraction of the $i$th hard segment in the mixed structure, $-\partial\phi_{2i}/\partial t$, follows a kinetics which is first-order with respect to the volume fraction of this particular segment, $\phi_{2i}$, at time $t$ and annealing temperature, $T_a$. This means

$$\left(\frac{\partial\phi_{2i}}{\partial t}\right)_{T_a} = -\frac{\phi_{2i}}{\tau_i} \tag{1}$$

where $\tau_i$ is a characteristic time known as the relaxation time of the $i$th hard segment. Integration of eq. (1) yields

$$\phi_{2i} = \phi'_{2i} \exp(-t/\tau_i) \tag{2}$$

where $\phi'_{2i}$ is the volume fraction of the $i$th hard segment in the mixed structure at zero time. By additive rule, we obtain the overall volume fraction of the hard segments in the mixed structure at time $t$ as

$$\phi_2(t) = \sum_i \phi_{2i} = \int_0^\infty f(\tau) \exp(-t/\tau) \, d\tau \tag{3}$$

where $f(\tau)$ is a normalized distribution function which defines the concentration (volume fraction) of the hard segments with the relaxation times between $\tau$ and $\tau+d\tau$ at $t = 0$ in the system. However, if the relaxation time spectrum is discrete, eq. (3) can be written in a series form:

$$\phi_2(t) = \phi'_{21} \exp(-t/\tau_1) + \phi'_{22} \exp(-t/\tau_2) + \cdots \tag{4}$$

where $\tau_1$ and $\tau_2$ are the longest and second longest relaxation times, respectively; $\phi'_{21}$ and $\phi'_{22}$ are, respectively, the initial volume fractions (at $t = 0$) of the hard segments associated with $\tau_1$ and $\tau_2$. This implies that the phase-separation mechanisms consist of individual elementary processes.

The change of volume fraction $\phi_2$ in eq. (4) will result in the decay of the glass-transition temperature of soft-segment phase, $T_g$. A number of theoretical equations has been developed to correlate these two parameters for compatible copolymers and polyblends.[8,9] In this study, we choose the Fox equation[10] given as

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{5}$$

where $w_1$ and $w_2$ are, respectively, the weight fractions of the soft and hard segments in the system. Accordingly, $T_{g1}$ and $T_{g2}$ are the values of $T_g$ when $w_2$ is equal to zero and unity, respectively. Since $T_{g1}$ may be represented by $T_g$ at infinite time, $T_{g\infty}$, where the hard segments are presumably completely segregated from the soft-segment matrix in the sense that $w_2 = 0$, we have from eq. (5)

$$\frac{1}{T_{g\infty}} - \frac{1}{T_g} = k\phi_2 \tag{6}$$

where

$$k = \left(\frac{1}{T_{g\infty}} - \frac{1}{T_{g2}}\right)\frac{\rho_2}{\bar{\rho}_{12}} \tag{6'}$$

Here $\rho_2$ and $\bar{\rho}_{12}$ are the density of the hard segments and the average density of the mixed segments, respectively. Both quantities are considered as constants. This assumption is valid if the amount of hard segments mixed with soft segments is not considerably large as justified by the present analysis. Obviously, eq. (6) and (6') demonstrate that the parameter $T_g$ is intimately related to a thermal property of the soft segments $T_{g\infty}$, as well as the nature of the hard-segment domain characterized by a distinct glass-transition temperature $T_{g2}$. Combining eqs. (4) and (6) leads to

$$\left(\frac{1}{T_{g\infty}} - \frac{1}{T_g}\right) = K_1 \exp(-t/\tau_1) + K_2 \exp(-t/\tau_2) + \cdots \tag{7}$$

where

$$K_1 = k\phi'_{21} \tag{7a}$$

$$K_2 = k\phi'_{22} \tag{7b}$$

If the discrete relaxation times differ significantly from one another (i.e., $\tau_1 >> \tau_2 >> \cdots$), then the contributions from the higher exponential terms in eq. (7) will be negligibly small at long annealing times. Hence, we have

$$\ln\left(\frac{1}{T_{g\infty}} - \frac{1}{T_g}\right) = \ln K_1 - \frac{t}{\tau_1} \text{ for } t > t_1 \tag{8}$$

where $t_1$ is the threshold time beyond which the equation is valid. The general form of eq. (8) is expressed by

$$\ln\left(\frac{1}{T_{g\infty}} - \frac{1}{T_g} - \sum_{l=1}^{n-1} A_l\right) = \ln K_n - \frac{t}{\tau_n} \text{ for } t > t_n \qquad (9)$$

where

$$A_l = K_l \exp\left(-\frac{t}{\tau_l}\right) \qquad (9')$$

and $t_n$ is the critical time over which this linear relationship holds. Equations (8) and (9) allow the experimental results to be processed graphically by plotting the variables on the left-hand side of these equations versus time. The values of $K_n$ and $\tau_n$ are derived from the intercepts and slopes of the straight lines resulted from the above manipulation, respectively. In fact, this graphical method has been practised in the analysis of the stress–relaxation of rubbery polymers.[11]

## RESULTS AND DISCUSSION

Wilkes and Wildnauer[7] have examined the kinetic aspects of domain formation of four commercial polyurethanes. Samples were preannealed at 170°C for 5 min and then quenched to room temperature at which the $T_g$ was monitored as a function of time by DSC. For the present purposes, data of $T_g$ were interpolated from the curves in Figures 5 and 8 of Ref. 7 at appropriate time intervals. Figure 1(a) displays the plots of $\ln(1/T_{g\infty} - 1/T_g)$ vs. annealing time for samples T480 and R53, which are polyester-segmented polyurethanes with different amounts of hard segments on 4,4'-diphenylmethane diisocyanate (MDI). The straight lines which conform to eq. (8) provide the values of $K_1$ and $\tau_1$ listed in Table I. At short annealing time the rate of change in $T_g$ is more rapid in that it follows a different elementary step that corresponds to a shorter relaxation time $\tau_2$ as shown in Figure 1(b). The values of $A_1$ are based on the predetermined data of $K_1$ and $\tau_1$ from Figure 1(a). It is noted that sample R53 which contains less hard segments has longer relaxation times $\tau_1$ and $\tau_2$, about four and eight times those of T480, respectively.

Table II also includes the results obtained likewise for the other two thermoplastic elastomers. Evidently, the demixing rate in the polyether segmented polyurethane (2-ET-38-1) decreases by about sixfold if the soft component of the polymer is replaced by an equivalent amount of polyester soft segment (2-ES-38-1). This finding coincides with the theory that the ester linkages form stronger hydrogen bonding with the urethane groups.[12] Further attempts to correlate the kinetic values collected in the table are unfruitful, because the molecular structures and morphological states of these samples are less understood. Nevertheless, these figures serve to represent the phase separation kinetics remarkably well. In any case, the computed values of $T_g$ via eq. (7) do not deviate more than 0.6°C from the experimental data which are reproducible to ± 1.0°C.
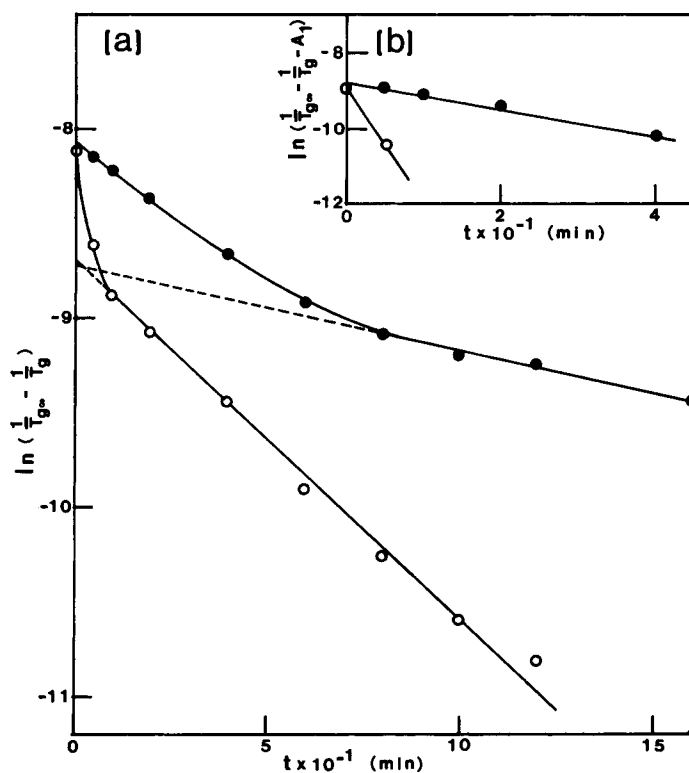
Fig. 1. (a) Kinetic curves for determining the longest relaxation times of T480 (○) and R53 (●); (b) kinetic curves for determining the second longest relaxation times of T480 and R53.

TABLE I
Kinetic Parameters of Commercial Polyurethanes

| Sample | $T_{g\infty}$ (K) | $K_1 \times 10^4$ (K$^{-1}$) | $\tau_1 \times 10^{-4}$ (S) | $K_2 \times 10^4$ (K$^{-1}$) | $\tau_2 \times 10^{-3}$ (S) |
|---|---|---|---|---|---|
| T480 | 243.2 | 1.666 | 0.316 | 1.313 | 0.201 |
| R53 | 227.2 | 1.617 | 1.352 | 1.507 | 1.716 |
| 2-ES-38-1 | 248.2 | 1.878 | 1.321 | 2.613 | 0.528 |
| 2-ET-38-1 | 210.0 | 2.587 | 0.221 | 12.390 | 0.226 |

TABLE II
Kinetic Parameters of PTMO/MDI/BD(ET)-Segmented Polyurethane at
Various Annealing Temperatures ($T_a$)

| $T_a$ (K) | $T_{g\infty}$ (K) | $K_1 \times 10^5$ (K$^{-1}$) | $\tau_1 \times 10^{-4}$ (S) | $K_2 \times 10^5$ (K$^{-1}$) | $\tau_2 \times 10^{-3}$ (S) |
|---|---|---|---|---|---|
| 363.2 | 213.0 | 4.108 | 1.652 | 2.983 | 1.728 |
| 353.2 | 212.0 | 4.632 | 2.498 | 3.792 | 2.340 |
| 333.2 | 210.4 | 5.545 | 4.187 | 4.276 | 3.672 |
| 295.2 | 208.3 | 6.773 | 12.204 | 4.820 | 9.108 |

Recently, Kwei[13] has conducted some precise DSC measurements in connection with the phase separation in an MDI-based polyurethane with polyether soft segment at various annealing temperatures after preannealing at 190°C for 15 min. This work establishes that the $T_g$ drops logarithmically with annealing time to a steady value at each annealing temperature, and as such the data of $T_g$ can be readily calculated from these empirical relationships at any preset time $t$.

The foregoing computation procedure was repeated to produce the results summarized in Table II. Again, two discrete relaxation times are required to depict the time-dependent $T_g$ behavior adequately in each of these cases. The activation energy, $E_a$, for these elementary processes can be evaluated by the Arrhenius equation

$$\ln \tau = C + E_a/RT_a \tag{10}$$

where $C$ is an empirical constant and $R$ is the ideal gas constant. Figure 2 illustrates the Arrhenius plots for the relaxation times of this particular material. The activation energy for $\tau_1$ is found to be 25 kJ · mol$^{-1}$, which agrees reasonably well with the value of 21 kJ · mol$^{-1}$ for $\tau_2$. In the same studies, Kwei discovered that if the logarithm of time at which the equilibrium $T_g$ value was reached was plotted against the reciprocal of annealing temperature, two straight lines intercepting at $T = 73$°C would be observed. The change in gradient was attributed to the different mechanisms assumed by the long and short hard segments at temperatures below and above this particular transition point. However, our results suggest that the distribution of sequence lengths might change the relaxation time spectrum appreciably, but it should not alter the segmental segregation mechanisms anyway, as the two individual relaxation processes have about the same $E_a$ over a wide range of annealing temperatures from 22°C to 90°C.
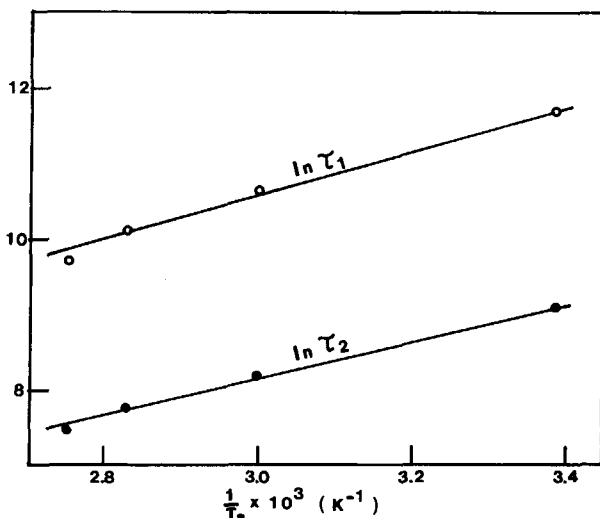


Fig. 2. Linear plots ln $\tau_1$ and ln $\tau_2$ vs. the reciprocal of annealing temperature.

Our results conclude that the relaxation time spectrum is conveniently resolvable. For the first approximation, we may assume that the long and short hard segments are partially responsible for the relaxation times $\tau_1$ and $\tau_2$, respectively. It follows from eqs. (7a) and (7b) that the fraction of long hard segments in the mixed structure at zero time, $X_l$, is given by

$$X_l = \frac{\phi'_{21}}{\phi'_{21} + \phi'_{22} + \cdots} = \frac{K_1}{K_1 + K_2 + \cdots} \tag{11}$$

which is sensitive to the preannealing conditions. The values of $X_l$ for the polymer in Table II are estimated by this equation and found to be independent of the annealing temperatures, which reportedly have a common $T_g$ equal to $-54°C$ at zero time.[13] These two results are indeed compatible.

## References

1. R. Bonart, *J. Macromol. Sci. Phys.*, **B2**, 115 (1968).

2. R. W. Seymour, G. M. Estes and S. L. Cooper, *Macromolecules*, **3**, 579 (1970).

3. J. W. C. Van Bogart, A. Lilaonitkul, and S. L. Cooper, in *Multiphase Polymers*, Advances in Chemistry Series No. 176, S. L. Cooper and G. M. Estes, Eds., American Chemical Society, Washington, D.C., 1979, pp. 1–30.

4. Z. H. Ophir and G. L. Wilkes, in *Multiphase Polymers*, Advances in Chemistry Series No. 176, S. L. Cooper and G. M. Estes, Eds., American Chemical Society, Washington, D.C., 1979, pp. 53–67.

5. G. L. Wilkes and J. A. Emerson, *J. Appl. Phys.*, **47**, 4261 (1976).

6. N. S. Schneider and C. S. Paik Sung, *Polym. Eng. Sci.*, **17**, 73 (1977).

7. G. L. Wilkes and R. Wildnauer, *J. Appl. Phys.*, **46**, 4148 (1975).

8. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).

9. P. R. Couchman, *Macromolecules*, **11**, 1156 (1978).

10. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**(3), 123 (1956).

11. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.

12. W. J. MacKnight and M. Yang, *J. Polym. Sci.*, **C42**, 817 (1973).

13 T. K. Kwei, *J. Appl. Polym. Sci.*, **27**, 2891 (1982).