

Phase Segregation and Viscoelastic Behavior of Poly(ether urethane urea)s

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ABSTRACT: Two poly(ether urethane urea)s were synthesized, one based on poly(propylene glycol) and another one on poly(tetramethylene glycol). Hydrogenated MDI was used as the diisocyanate and propylenediamine as the chain extender. The diisocyanate : polyol : diamine molar ratio was 2 : 1 : 1 for both copolymers. Data from stress-relaxation tests were adjusted to a power law and to the Kohlraush–William–Watts equation. Phase separation and viscoelastic behavior were correlated through the calculation of the time-relaxation spectrum, the steady-state tensile compliance, and the tensile viscosity. The results indicated that the material based on poly(tetramethylene glycol) was the more effectively phase-segregated block copolymer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2227–2236, 1997

Key words: viscoelasticity; stress relaxation; polyurethanes; phase segregation

INTRODUCTION

It is well established that poly(ether urethane) elastomers are phase-segregated copolymers, consisting of a hard phase, rich in urethane groups, a soft phase, rich in ether groups, as well as an interface abundant in all the involved functionalities.¹ This morphology is responsible for the behavior of these block copolymers as crosslinked elastomers,² due to a virtual crosslinking, resulting from the strong cohesion of the hard phase.

Moreland et al. extensively studied the viscoelastic behavior of polyurethane foams as a function of temperature and relative humidity.^{3,4}

Kutty and Nando⁵ used *procedure X*, developed by Murakami and Tobolsky,⁶ to determine the relaxation times involved in the relaxation process of fiber-reinforced polyurethanes. Huang and Gibson modeled the linear and nonlinear creep of polymeric foams, characterizing their behaviors as linear viscoelastic for stress levels less than half the yield strength of the foam.⁷ Reynolds et al. analyzed the behavior of poly(ether urethane)s under relaxation stress using FTIR spectroscopy.⁸ Their work, in conjunction with the work of Desper et al. on the characterization of microstructure deformation of polyurethanes by SAXS,⁹ constitutes a comprehensive study on the mechanisms of deformation and relaxation of these block copolymers. None of these works, however, tried to comparatively correlate phenomenological viscoelastic behavior of polyurethane block copolymers to the extent of phase segregation.

Such an approach, however, was already used by Sung and Smith.¹⁰ In their work, polyurethane

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block copolymer stress-relaxation data were fitted to the power law

$$E(t) = At^{-b} \quad (1)$$

where $E(t)$ is the Young's modulus at a time t , and A and b are constants. Phase segregation was then characterized as a function of the time spent to relax half of the initial stress of a given sample. Since a higher occurrence of phase segregation implies the presence of a purer and more cohesive hard phase, the longer this time was, the more phase-segregated the copolymer in question was considered to be.

In the present work, the viscoelastic behavior of poly(ether urethane urea)s based on poly(propylene glycol) and poly(tetramethylene glycol) is correlated to the occurrence of phase segregation. Such a correlation is carried out from the a priori knowledge that the copolymer based in the latter polyol is more phase-segregated (as it has fewer ether groups, which can undergo weak hydrogen bonding to N—H groups from the hard segment¹). The macroscopic, phenomenological, manifestation of the phase segregation is then analyzed through the use of data from stress-relaxation tests, which are fitted to the power law as well as to the Kohlraush–William–Watts (KWW) equation:

$$E(t) = E_0 e^{-(t/\tau_c)^c} \quad (2)$$

where c is a constant between 0 and 1; E_0 , the Young's modulus at $t = 0$, and τ_c , a characteristic relaxation time. This equation, although being a quite old phenomenological one (it is related to a Kohlraush work from 1866¹¹), was deduced by Gaylord and DiMarzio^{12,13} as a result of the application of a continuous-time random walk (CTRW) description to the stress relaxation of crosslinked rubbers; it has also been used to study dipolar orientational relaxation in amorphous polymers for nonlinear optics.¹⁴

To verify the correlation between stress relaxation and phase segregation in these elastomers, use is made of the following quantities, which come from phenomenological theory of viscoelasticity: D_e^0 , the steady-state tensile compliance, and η_t , the tensile viscosity. Additionally, use is made of the relaxation spectrum, $H(\tau)$, which is related to the Young's modulus variation with time by the following expression:

$$E(t) = \int_{-\infty}^{\infty} H(\ln \tau) e^{-t/\tau} d(\ln \tau) \quad (3)$$

where τ is the relaxation time.

EXPERIMENTAL

Copolymer Synthesis

The synthesis was carried out in two steps:

- (i) *Prepolymer synthesis*: It was carried out through the reaction of polyol with diisocyanate with $(n_{\text{NCO}}/n_{\text{OH}}) = 2$, where n_{NCO} is defined as the number of NCO groups in the system, and n_{OH} , as the number of OH groups in the system (since one molecule of water is capable of consuming two NCO groups, n_{OH} also accounted for water molecules present in the polyols—each molecule corresponding to two OH groups). The reaction was run at 80°C, using tin dibutyl-dilaurate (DABCO T12, 99 wt %, Air Products) due to the low reactivity of aliphatic diisocyanates.¹⁵ The polyols poly(propylene glycol) (PPG, Voranol 2110, hydroxyl number = 114 mgKOH/g, Dow) and poly(tetramethylene glycol) (PTMG, Terathane 1000, hydroxyl number = 112 mgKOH/g, du Pont Nemours) were purified from volatile impurities (basically moisture) using a vacuum oven ($P = 10^{-2}$ Torr) at 100°C for 3 h. The resultant water percentages were 0.06 wt % (PPG) and 0.07 wt % (PTMG). The diisocyanate, 4,4'-dihexylmethane diisocyanate (H_{12}MDI , Mobay, 99 wt %), was used without further purification.
- (ii) *Extension of the prepolymer in solution*: The fully converted prepolymer was solubilized in tetrahydrofuran (THF), at a concentration of 20 wt %. A solution of propylenediamine (98 wt %, Bayer) in THF, 20 wt %, was added to the reactional system at room temperature and under effective stirring. At this stage, the ratio $n_{\text{NH}_2}/n_{\text{NCO}}$ was 1.01, where n_{NH_2} is the number of NH_2 groups initially present in the reactional system. The copolymers based on PPG and PTMG were designated as PUPPG and PUPTMG, respectively.

Solid material was obtained using an adapta-

tion of a procedure already established by Cooper and Tobolsky.¹⁶ About 20 g of the resultant solution in THF was cast over a glass slide ($10 \times 10 \text{ cm}^2$). After 2 days evaporating at room temperature, the films were stripped from the slides and left in a desiccator with silica for 2 days under a vacuum at 60°C.

Copolymer Characterization

The intrinsic viscosities of the copolymers were determined using an Ostwald-Fenske viscometer (#2) at a temperature $T = 30.0 \pm 0.5^\circ\text{C}$. Their molecular weights (M_w and M_n) and polydispersities were determined by GPC (Shimadzu; solvent—THF; concentration—0.5%; temperature—25°C; columns—400, 3000, and 3,000,000 Å; pressure—60 psi).

Infrared spectra of the solid materials were obtained using a Nicolet FTIR spectrometer (Model 740) with a resolution of 2 cm^{-1} and 50 scans. A solution of the copolymer to be analyzed (5 wt %) was cast on a KBr crystal. The crystal was left for 24 h at 60°C under a vacuum before the analysis was carried out at room temperature.

Hardnesses were measured using a Shore hardness tester (type A2). The samples used in these tests were made in the same way as were the ones used in stress-relaxation experiments (the preparation is described below). Tensile strength and elongation at rupture were determined using an Instron dynamometer Model 1105. Samples were made by pressing the solid material between aluminum foils using a proper spacer at 100°C for 10 min, the system being cooled under pressure. The thicknesses of the samples varied from 0.07 to 0.1 cm; their widths and lengths were 0.5 and 7 cm, respectively, 10% being the associated experimental error. The crosshead speed was 20 cm/min.

Before starting any experiment designed to measure mechanical properties, the sample was left in contact with the experimental conditions—RH = $65 \pm 2\%$, $T = 23.5 \pm 0.5^\circ\text{C}$ —for at least 48 h. All the samples destined to stress-relaxation experiments received the same treatment.

Relaxation Tests

Experimental Setup

Among the main requisites needed to perform relaxation tests, there is the shape of the sample. Besides being regular, it must prevent the occur-

rence of the sample slipping from the clamps during the test. Tschoegl et al.¹⁷ solved this problem by making the extremities of the samples rigid with the application of a cyanoacrylate adhesive; this procedure was proved to be effective for strains up to 200%. Since the deformation used in our stress-relaxation tests was $10 \pm 1\%$, such a procedure was assumed to be adequate. The samples used in the tests were the result of pressing the elastomers at 100°C, 1000 psi, for 30 min and cooling them under pressure. Their thicknesses varied from 0.35 to 0.40 cm (within an experimental error below 5%); their lengths and widths were, respectively, 2.45 ± 0.05 and $8.00 \pm 0.05 \text{ cm}$.

When deformed to 10%, the materials were assumed to have nonlinear viscoelastic behavior. Equations describing the nonlinear viscoelastic behavior of polyurethanes in creep experiments can be found in the work of Huang and Gibson.⁷ For stress-relaxation experiments, use was made of the following equation¹⁸:

$$E(t, \lambda) = \frac{\sigma(t)}{f(\lambda)} \quad (4)$$

where $\sigma(t)$ is the stress at a time t , $f(\lambda)$ is a function of the sample strain λ , being $\lambda = L/L_0$, L_0 the original length of the test specimen, and L is the length of the strained sample. In other words, the mathematical description of the viscoelastic behavior was factorized into two independent functions, one of the time, $\sigma(t)$, and another one of the strain, $f(\lambda)$. When $\lambda \rightarrow 1$, $f(\lambda) \rightarrow \lambda - 1$ (linear viscoelasticity). For strains up to 10%, it follows that¹⁸

$$f(\lambda) = 3 \left(\lambda - \frac{1}{\lambda^2} \right) \quad (5)$$

In this way, if one analyzes $E(t, \lambda)/E(t', \lambda)$, rather than $E(t, \lambda)$, where t' is any particular time, the resultant data can be treated using ordinary linear viscoelasticity, since the former expression does not depend on the strain. A typical run consisted of, after being properly placed in the dynamometer, stretching the sample at 100 cm/min and then collecting the data [$\sigma(t)$] associated to the process.

The resultant data were fitted to the power law [eq. (1)] and to the KWW equation [eq. (2)]. In the latter case, that was done using the Levenberg–Marquardt nonlinear regression method.¹⁹

Table I Copolymers Values of M_n , M_w , and n , Determined by GPC

| | PUPPG | PUPTMG |
|---------------|--------|--------|
| M_n (g/mol) | 15,000 | 12,000 |
| M_w (g/mol) | 70,000 | 60,000 |
| n | 4.7 | 5.0 |

Determination of the Time Spent to Relax Half of the Initial Stress— $t_{1/2}$

Since, when using the power law, when $t \rightarrow 0$, $E \rightarrow \infty$, the concept of an initial time $t_0 = 0$ does not apply. Therefore, it is more convenient to express $t_{1/2}$ as a function of t_0 ; the modulus would decrease to half of its initial value, according to eq. (6):

$$\frac{t_{1/2}}{t_0} = \left(\frac{1}{2}\right)^b \quad (6)$$

Differently from the power law, the KWW equation has a value of the initial modulus (E_0) when $t_0 = 0$. In this particular case, $t_{1/2}$ is expressed by

$$t_{1/2} = (\ln 2)^c \tau_c \quad (7)$$

Relaxation Spectrum Calculation

When using the power law, the relaxation spectra can be analytically expressed by

$$H(\tau) = A \frac{\tau^{-b}}{\Gamma(b)} \quad (8)$$

where $\Gamma(b) = \int_0^\infty x^{b-1} e^{-x} dx$.

On the other hand, when working with the KWW equation, the relaxation spectra can be expressed through a series. However, this series has the inconvenience of not converging well for longer relaxation times.²⁰ Thus, it was numerically calculated using the inversion formula, given by Doetsch,²¹ for the Laplace transform associated to eq. (3):

$$H(\tau) = \lim_{k \rightarrow \infty} \frac{(-1)^k k^{k+1} \tau^k}{k!} \left. \frac{d^k \sigma(t)}{dt^k} \right|_{t=k\tau} \quad (9)$$

For each value of τ , a k was chosen so that the numerical error involved in the calculation was below 1%.

Table II Copolymer Limiting Viscosity Numbers, $[\eta]$, Before and After Pressing

| | $[\eta]$ (dL/g) | |
|--------|-----------------|-----------------|
| | Before Pressing | After Pressing |
| PUPPG | 0.65 ± 0.02 | 0.64 ± 0.02 |
| PUPTMG | 0.57 ± 0.02 | 0.59 ± 0.02 |

Tensile viscosity and steady-state tensile compliance were calculated using eqs. (10) and (11), respectively²²:

$$\eta_t = \int_0^\infty E(t) dt = \frac{E_0 \tau_c \Gamma\left(\frac{1}{c}\right)}{c} \quad (10)$$

$$D_e^0 = \frac{1}{\eta_t^2} \int_0^\infty t E(t) dt = \frac{E_0 \tau_c^2 \Gamma\left(\frac{2}{c}\right)}{c \eta_t^2} = \frac{c \Gamma\left(\frac{2}{c}\right)}{\left(\Gamma\left(\frac{1}{c}\right)\right)^2} \quad (11)$$

RESULTS AND DISCUSSION**General Characterization**

The copolymers' molecular weights (M_n and M_w) as well as their polydispersities (n) are shown in Table I. Although the values were obtained using a calibration curve for polystyrene (and the soft segments must have different gyration radii), they show that both copolymers can be considered as having M_n , M_w , as well as n , in the same range. Since when analyzing the viscoelastic behavior of elastomers, M_n , M_w , and n are important parameters,²³ one can say that the viscoelastic behavior of the elastomers can be connected mainly to the occurrence of phase segregation.

Limiting viscosity numbers, determined before and after preparing the samples for stress-relaxation tests, are shown in Table II. Based on these

Table III Tensile Strength (σ_r), Elongation at Rupture (e_r), and Hardness of Block Copolymers

| | σ_r (MPa) | e_r (%) | Hardness (°Shore) |
|--------|------------------|--------------|-------------------|
| PUPPG | 26 ± 3 | 680 ± 30 | 27 ± 3 |
| PUPTMG | 39 ± 8 | 440 ± 30 | 59 ± 2 |

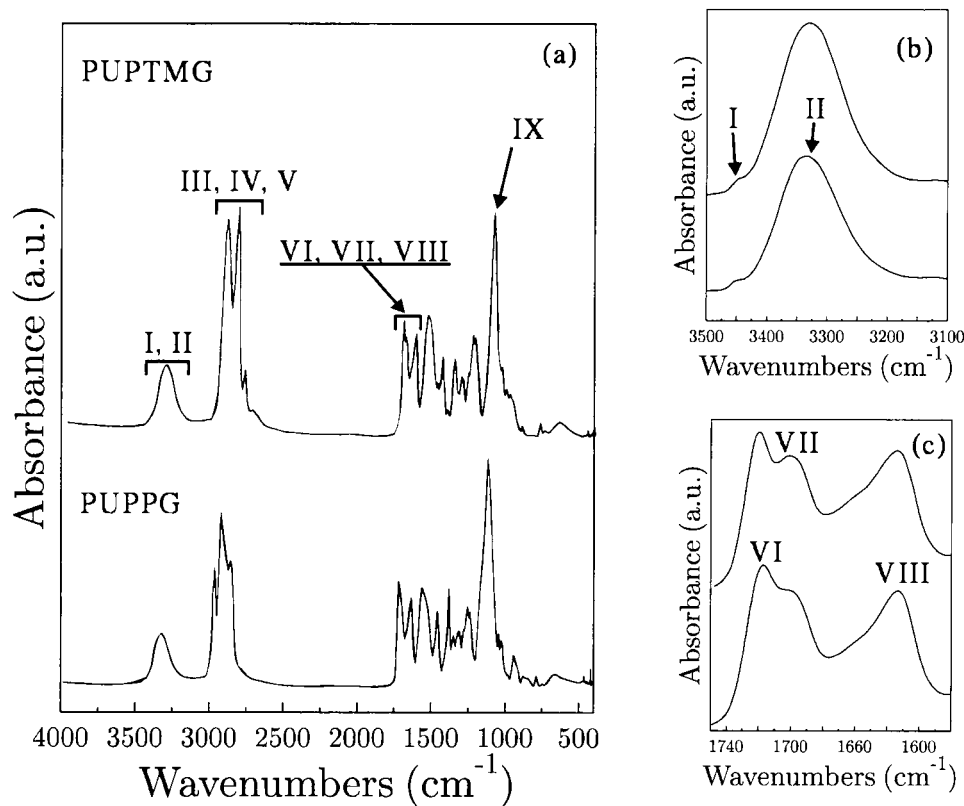


Figure 1 FTIR spectra of poly(ether-urethane-urea)s: (a) whole spectra; (b) N—H stretching region; (c) C=O stretching region.

results, it is correct to say that the process of making the test samples did not alter the elastomers' molecular weights.

Table III shows the copolymer values of tensile strength, elongation at rupture, and hardness. Since virtual crosslinking of urethane block copolymers is directly linked to their phase segregation,²⁴ the more pronounced it is, the higher the virtual crosslinking will be and, as a consequence, the stiffer and harder the material will be. The obtained results suggest that PUPTMG is more phase-segregated, since its hardness and tensile strength values are larger than the PUPPG ones. In the same way, a smaller value of elongation at rupture, in the case of PUPTMG, indicates a higher degree of virtual crosslinking. Another cause of this behavior may be the occurrence of stress crystallization of the poly(tetramethylene glycol) from the soft segment of PUPTMG.

Figure 1 depicts the infrared spectra of PUPPG and PUPTMG. The characteristic bands related to polyurethaneureas can be readily identified^{25,26} as shown in Table IV. Regarding the carbonyl region [Fig. 1(c)], it can be seen that the PTMG-

based copolymer spectrum presents a better resolution of the associated and nonassociated C=O bands. Once more, this is another indication of PUPTMG being the most phase-segregated copolymer.

Stress Relaxation

Data from PUPPG and PUPTMG stress-relaxation tests are shown in Figure 2. All data were normalized in relation to $E(t')$, the modulus at $t' = 5$ s. The constants related to eqs. (1) and (2) are shown in Table V. The best fit, in both cases, occurred when the KWW equation was used.

Still regarding Table V, it can be seen that both η_i and D_e^0 have larger values for PUPTMG. One could correlate these results to the cohesion of rigid domains (higher difficulty in flowing, implying a higher viscosity); it could be considered another indication of a higher phase separation for PUPTMG. Analogously, with D_e^0 being correlated to the existence of virtual crosslinking within the copolymers (the higher its occurrence, the more reversible the deformation will be), it

Table IV Band Assignments of Copolymer IR Spectra

| Label | Assignment | Wavenumber (cm ⁻¹) | |
|------------|---|--------------------------------|------------------|
| | | PUPPG | PUPTMG |
| I | NH stretching, without occurrence of hydrogen bonding | 3448 | 3447 |
| II | NH stretching, with occurrence of hydrogen bonding | 3333 | 3339 |
| III, IV, V | CH stretching | 2925, 2863, 2820 | 2919, 2844, 2811 |
| VI | C=O stretching (urethane), not hydrogen-bonded | 1717 | 1720 |
| VII | C=O stretching (urethane), hydrogen-bonded | 1700 | 1700 |
| VIII | C=O stretching (urea) | 1633 | 1634 |
| IX | C—O—C stretching (ether) | 1113 | 1088 |

could also be correlated to a higher occurrence of domain separation in the case of PUPTMG.

One could also correlate D_e^0 to the occurrence of phase segregation following Desper et al.'s approach to the problem, using SAXS.⁹ They found that, when stretching amine-cured polyurethanes, hard segments lamellae tilted away from the stretch direction, while the soft-segment microphase deformed in the shear. The reversibility of the deformation (high value of D_e^0) is, then, a consequence of the occurrence of a pure soft phase. Since phenomenological viscoelasticity per se cannot yield proof of what exactly is the mechanism of stress relaxation at the molecular level, the au-

thors assume that the most important processes occurring in the hard phase (whatever they are) take much longer times than do the most important ones which occur in the soft phase.

The values of $\log(t_{1/2}/t_0)$ indicate the PTMG-based copolymer as the more phase-segregated, if one has in mind Sung and Smith's criteria¹⁰ (the longer $t_{1/2}$, the higher the phase segregation will be). However, it can be seen that when using the KWW equation $t_{1/2}$ is longer in the case of the PPG-based elastomer. Obviously, it can be seen that Sung and Smith's criteria is not consistent when using two different expressions. It indicates these criteria to be rather subjective.

If one plots $t_{1/2}/t_0$ against t_0 for the KWW equation (Fig. 3), this ambiguity becomes clearer. It can be seen that at $t_0 \approx 10^{-1}$ min the value of $t_{1/2}/t_0$ is the same for PUPPG and PUPTMG. If one chooses t_0 to be above or below this value, one can reach opposite conclusions.

The relaxation spectra of PUPPG and PUPTMG, using the power law, are depicted in Figure 4. If one analyzes the spectra for longer relaxation times, there is a higher contribution of these times in the relaxation process of PUPTMG. As assumed before, when one refers to rigid domains, one considers longer relaxation times (slower relaxation process); thus, the more pronounced occurrence of large values of τ for PUPTMG is considered evidence of higher domain segregation in the case of PUPTMG. A and b were determined from data already published for the copolymers used in Sung and Smith's work¹⁰ and their relaxation spectra calculated. These spectra are also depicted in Figure 4. Comparing them with the spectra obtained in our work, it can be seen that the copolymer with $M_n = 2000$ g/mol is the most phase-segregated, followed by the copolymer with $M_n = 1000$ g/mol. Since the diisocyanate used in that work (2,4-toluene diisocyanate—

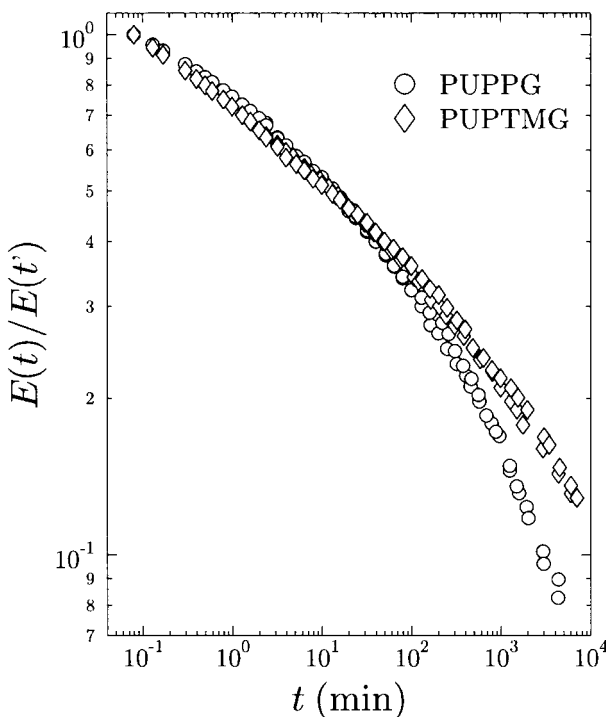
**Figure 2** Data from stress-relaxation experiments.

Table V Constants Related to Stress-relaxation Tests

| | PUPPG | PUPTMG |
|--|-------------------|---------------------|
| $\log[A/(\text{MPa}\cdot\text{min}^b)]$ | -0.50 ± 0.03 | -0.06 ± 0.02 |
| b | 0.254 ± 0.001 | 0.1994 ± 0.0003 |
| $\log(E_0/\text{MPa})$ | -0.20 ± 0.07 | 0.6 ± 0.1 |
| $\log(\tau_c/\text{min})$ | 0.4 ± 0.1 | -3.0 ± 0.6 |
| c | 0.151 ± 0.003 | 0.082 ± 0.003 |
| $\log(t_{1/2}/t_0)$ (power law) | 1.185 ± 0.009 | 1.549 ± 0.002 |
| $\log(t_{1/2}/\text{min})(t_0 = 0)$ (KWW equation) | -0.7 ± 0.2 | -4.9 ± 0.6 |
| $\log(D_e^0 \cdot \text{MPa})$ | 4.4 ± 0.2 | 5.8 ± 0.3 |
| $\log(\eta_t/P)$ | 14.0 ± 0.3 | 18 ± 1 |

TDI) as well as the diamine (ethylenediamine—EDA) provide a copolymer with a more compact, rigid, and cohesive hard phase, the later is more phase-segregated than is PUPTMG, its counterpart made with hydrogenated MDI and propylene-diamine.

In the same fashion that the process of rigid domain interactions is associated to longer relaxation times, the process of soft-segment relaxation can be related to the occurrence of shorter relaxation times (less intense interactions, implying a faster relaxation). However, in both spectra, $\lim_{\tau \rightarrow 0} H(\tau) = \infty$. This together with the already-

mentioned impossibility of calculating η_t and D_e^0 are the main limitations of the power law in this kind of analysis. It turns out to be unfeasible, as a consequence of the analysis of the spectra in terms of soft-segment relaxation.

The spectra of both copolymers, when obtained using the KWW equation, are depicted in Figure 5. It can be seen that both spectra tend to 0 when $\tau \rightarrow \infty$ and $\tau \rightarrow 0$, which is due to the existence of a defined value of $E(t)$ when $t = 0$. Now, the spectra are analyzed from a different perspective. In

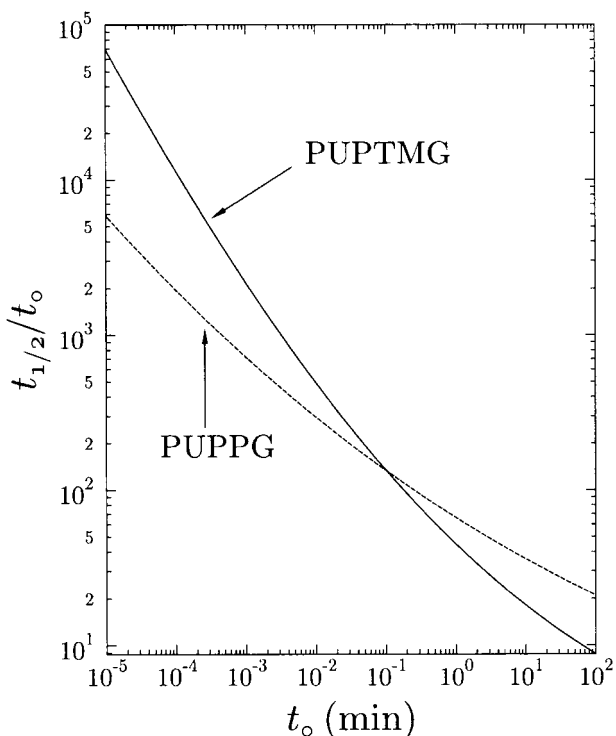


Figure 3 $t_{1/2}/t_0$ as a function of t_0 for the KWW equation.

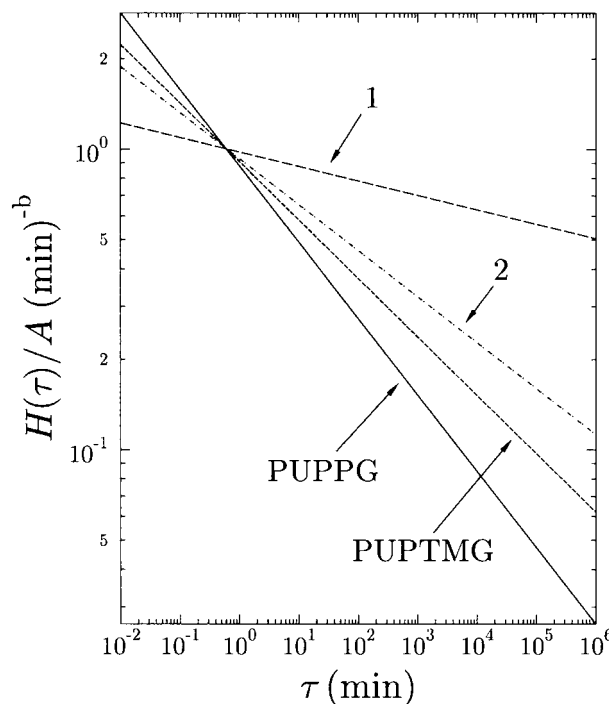


Figure 4 Relaxation spectra of PUPPG, PUPTMG, and the copolymers studied by Sung and Smith: (1) $M_{nPTMG} = 2000$ g/mol (TDI : EDA : PTMO = 4 : 3 : 1) and (2) $M_{nPTMG} = 1000$ g/mol (TDI : EDA : PTMO = 2 : 1 : 1)—using the power law.

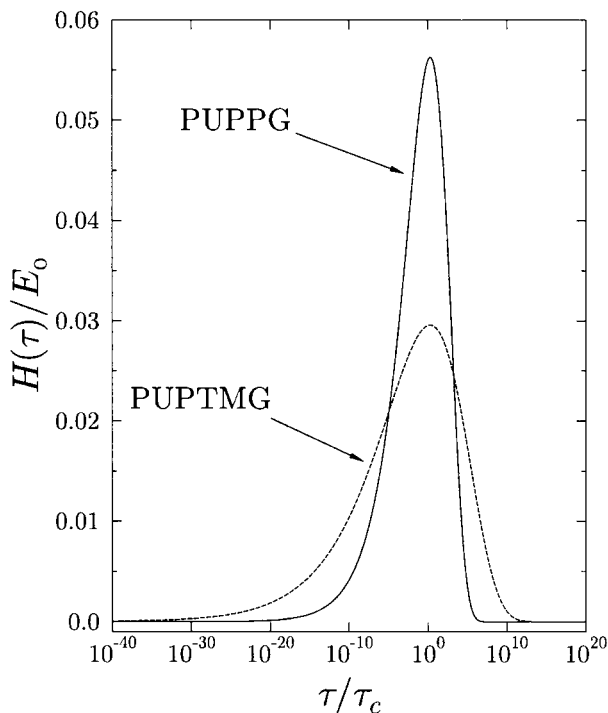


Figure 5 Copolymer relaxation spectra using the KWW equation.

the way that they are represented, it is possible to have an idea of the heterogeneity of the relaxation process. A stronger interaction within rigid domains would imply a shift of the relaxation spectrum to longer times. A higher occurrence of a purer soft phase would imply a higher occurrence of weaker interactions within soft segments, resulting in a shift to lower values of τ , the widening of the spectrum being the net result. In other words, the wider the spectrum, the more heterogeneous the process is; the more heterogeneous the process is, the higher the phase segregation is. If one analyzes Figure 5, it is clear that the PTMG-based copolymer is the most phase-segregated one.

Having examined the relaxation spectra, it is possible to set new insights from the results obtained from the calculation of $t_{1/2}/t_0$. As said before, the relaxation spectra yield information solely useful in terms of rigid domains, when the power law is used. Thus, the better associated these domains are, the larger $t_{1/2}/t_0$ will be. With the KWW equation, information is obtained which is related to the soft phase as well: The higher the phase segregation, the faster will be the relaxation process at shorter times and on the other hand, the slower will be the stress decrease at longer times, agreeing with the power law. That

can explain the ambiguity of Sung and Smith's criteria, when using the KWW equation, which, in fact, derives from the power law limitations.

This kind of analysis can also explain some data already published in the literature. It has been found that, concerning polyurethane elastomers, c decreases when the temperature is increased²⁷; it is known that the higher the temperature is, the higher the miscibility between the phases is²⁸ and that a smaller value of c results in a broader spectrum.²⁹ These results agree, consequently, with the analysis used in this work: A broader relaxation spectrum implies a more phase-segregated system.

Table VI presents values for some constants related to the KWW equation from previously published work in the literature, for the sake of comparison with calculated results from our work. The materials are polyisobutylene³⁰ (PIB, $M_v = 665,000$ g/mol) at 50°C ($T_g = -73^\circ\text{C}$), the styrene-butadiene-styrene block copolymer (SBS; $T_g = 100^\circ\text{C}$ and -58°C , for the hard and soft phases, respectively)³¹ at room temperature, and soda-lime glass³² at 450°C ($T_g = 540^\circ\text{C}$).³³ The constants related to PIB and SBS were calculated from graphically displayed experimental data and their values related to glass were directly reported in the mentioned reference.

If one analyzes the variation of c with the material, one can see that glass has the largest value. It indicates it to be the most homogeneous material. Then comes the PIB elastomer, which is a homopolymer, but has inhomogeneity in the form of a molecular weight distribution. Finally, SBS, the phase-segregated material, has the smallest value, indicating the highest occurrence of inhomogeneity.

When the object of analysis is η_t , it can be seen that both SBS and glass have larger values, which indicate the presence of a hard phase in both of them. However, D_e^0 shows that the reversibility of the deformation of glass is the lowest among the three materials. It follows that, although glass has a very hard phase (in fact, it is purely made

Table VI Data Related to the KWW Equation Taken from the Literature

| | c | $\log(\eta_t/P)$ | $\log(D_e^0 \cdot \text{MPa})$ |
|---------------------|------|------------------|--------------------------------|
| PIB ³⁰ | 0.3 | 8.5 | -1.5 |
| SBS ³¹ | 0.07 | 21 | 4.9 |
| Glass ³² | 0.5 | 19 | -6.4 |

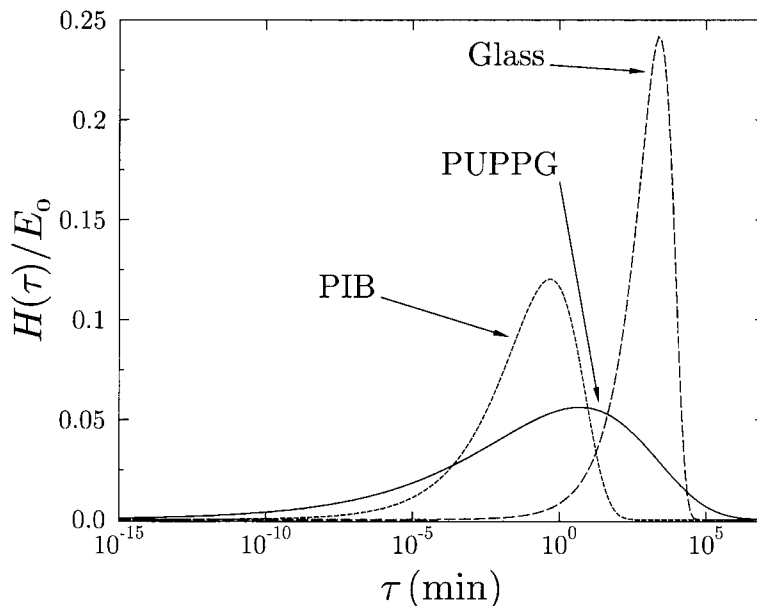


Figure 6 Comparison among the relaxation spectra of a phase-segregated copolymer (PUPPG), glass, and polyisobutylene (PIB), using the KWW equation.

of it), the absence of a soft phase, which is present in SBS, differentiates these two materials: The presence of both virtual crosslinking and the soft phase is essential to a high occurrence of reversible deformation.

Finally, Figure 6 depicts the relaxation spectra of PUPPG at room temperature, soda-lime glass below its T_g , and polyisobutylene above its T_g . This figure clearly shows the poly(ether urethane urea) spectrum as a result of the contributions of a soft phase (PIB elastomer) and a hard phase (soda-lime glass).

CONCLUSIONS

Although it has the serious limitation of not providing a molecular description of the stress relaxation of block copolymers (in fact, of any material), basic phenomenological viscoelasticity theory can be used to compare the behavior of materials with different degrees of phase separation, provided that other variables (such as molecular weight and polydispersity) are within an acceptable range. This phenomenological description can be qualitatively correlated to the occurrence of phase separation through the calculation of some quantities given by this theory.

When comparing PPG- and PTMG-based poly(ether urethane urea)s, it was found that the

PTMG-based copolymer presented larger values of tensile viscosity (reflecting, perhaps, stronger interactions between rigid segments) and steady-state compliance (higher reversibility for a given applied strain, which is the product of the existence of a more cohesive rigid phase as well as a soft phase with weak interactions). Relaxation spectra calculated from the KWW equation were wider in the case of the PTMG-based copolymer; from this fact, it was inferred that the relaxation spectrum of this material showed a higher contribution of both the soft phase (shorter relaxation times) and the hard phase (longer relaxation times).

The use of a simple power law to describe stress relaxation, although useful in the analysis of long-term relaxation interactions, was unsatisfactory to analyze the short-term behavior of these materials. The KWW equation was found to be more adequate for the analysis of both soft- and hard-phase behavior.

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