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# Tensile Creep Measurements of Glassy VOC-Loaded Polymers

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ABSTRACT: The paper describes a new apparatus to measure tensile creep curves of polymer/volatile organic compound (VOC) systems, especially designed for measurements of small VOC loadings in glassy polymers. For the first time creep curves for glassy polymer/VOC systems are recorded. The measurements were performed for the system polystyrene/toluene at different toluene loads up to $w_{\text{toluene}} = 0.13$ and at temperatures of 30, 50, and 70 °C. It was found that increasing VOC mass fractions qualitatively influence the mechanical properties of a polymer in the same way like increasing temperature does. Since at isothermal conditions these properties are affected by the glass transition of the system, this information for the polystyrene/toluene mixtures was used to modify and to verify the correlation of Kelly and Bueche to predict the glass-transition temperature of polymer/solvent systems.

## Introduction

To characterize the physical properties of polymer films, creep measurements are usually performed to estimate the time-dependent increase of film deformation at constant stress. Those measurements provide information about the viscoelastic behavior of polymers and therewith also allow the determination of viscosity and Young's modulus.[1]

During the past decades, creep measurements have be mainly performed for VOC-free polymers, characterizing the mechanical properties of neat polymers as a function of temperature.[1−3] However, it is also qualitatively known that dissolved VOCs have a great impact on the glass-transition temperature as well as on the mechanical parameters of polymers.[4] Apart from tensile strength, these parameters have a great influence on the diffusion process, especially if the sorption or diffusion of solvent takes place below the polymer glass transition.[5,6] Apparently for all applications in which a VOC is dissolved in a polymer film, such as membrane separations or investigations of sorption isotherms[5] as well as during the drying processes,[8] the determination of the mechanical parameters of the polymer/VOC system is of high interest.[7]

Although several setups for creep measurements are commercially available, none of these are capable of measuring the mechanical properties of VOC-loaded polymer films. To the best of our knowledge, the only work published are the papers of Majsztrik et al.[9] and Satterfield et al.,[10] who built an apparatus that allowed for measuring the creep behavior of polymers as a function of relative humidity. However, no measurements were reported at very low pressures (corresponding to very small loadings).

Within this work we developed and built a novel experimental setup for creep experiments under a defined VOC atmosphere, especially for measurements at very low and constant VOC pressures and in glassy polymers. Moreover, we will show that this also allows to estimate the glass-transition temperature of the VOC-loaded polymer and to verify approaches to predict the glass-transition temperature in these systems.[11−14]

## Experimental Section

Two different experimental setups were used for determining the mechanical properties of neat polymers as well as of VOC-loaded polymers. These are the TA dynamic mechanical analyzer 2980 (DMA 2980) for performing creep measurements of neat polystyrene films at different temperatures and the novel setup which was designed for creep measurements of VOC-loaded polymer films. Moreover, a gravimetric sorption equipment[5] was used to determine the sorption behavior of polystyrene/toluene systems required for interpretation of the creep experiments.

**Novel Setup for Creep Measurements.** The central device of the novel creep apparatus is a measuring chamber which is arranged in an air thermostat (see Figure 1). Within this chamber, two film-tension clamps are positioned which fasten the polymer film. The upper clamp is connected to a VOC-resistant force transducer (WI; Althen) which measures the force of up to 20 N with a reproducibility of ±0.003 N. The force is applied to the clamped polymer film by a linear drive (Physik Instrumente) that is connected via a shaft to the lower clamp. The linear drive is able to perform linear steps with a minimum step size of 100 nm in a range of up to 50 mm with a maximum force of 120 N. This large force is needed to move the bellow, which divides the low-pressure area (inner measuring cell) from the mechanical actuator which is situated outside the measuring cell. Since the lower clamp is directly connected to linear drive, the latter directly measures the position of the clamp. Because of isothermal conditions, the heat expansion of the shaft can be neglected. The control of the linear drive and therewith of the constant force applied to the polymer sample is performed by a LabView program.

The measuring chamber and the earlier designed sorption apparatus[5] are built in a vapor-flow-through design to solve the problem of inevitable leakage into the equipment. Thus, the pressure in the cell can be kept constant over long times better than ±0.1 mbar between 0.1 and 1330 mbar. The temperature of the cell is controlled by means of an air thermostat bath, which is equipped with heating and cooling devices to keep the temperature constant between 20 and 85 °C better than ±0.03 K. The temperature gradient within the air thermostat was determined to be about 0.1 K; the one within the measurement cell is even

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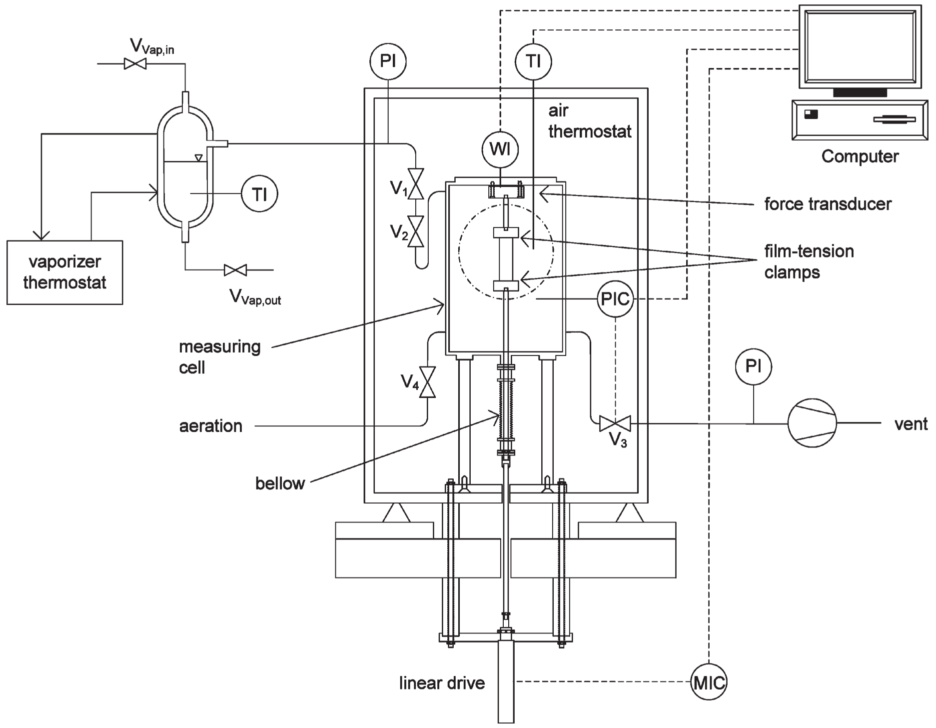

**Figure 1.** Flow sheet of the novel creep apparatus for isothermal and isobaric vapor measurements especially at low pressures.

lower. The temperature in the double-wall VOC vaporizer is controlled by means of a conventional liquid thermostat. Temperatures in the vaporizer and in the measuring chamber (next to the sample) are measured using a calibrated resistance thermometer (PT100). The measuring chamber as well as vaporizer can each be evacuated by means of a vacuum pump (Pfeiffer).

**Materials and Film Preparation.** Atactic polystyrene (aPS) was obtained from Gefinex GmbH with $M_w$ = 240 000 g/mol and $M_w/M_n$ = 5.65. The glass-transition temperature was determined at 105 °C by differential scanning calorimetry (DSC TA Q 100; heating rate: 10 K/min). Toluene of 99.9% purity was obtained from Merck & Co., Inc., and was degassed by three successive freezing–evacuation–melting steps before being filled into the evacuated VOC vaporizer.

The polymer films were prepared by casting from toluene/polystyrene solutions on a glass surface with subsequent flattening by means of an applicator exhibiting a slit of defined height between glass and applicator surface. Afterward, the films were stored in a vacuum oven to enhance the toluene removal from the films with a temperature and pressure routine, as earlier described elsewhere.[5] Using this procedure, the thickness of the polystyrene films varied at maximum by about ±1 μm. For any experiments below the glass-transition temperature, the polymer is in a nonequilibrium state which depends on the history of the sample. Therefore, all polystyrene samples were prepared under exactly the same conditions and stored as short as possible before the measurements.

**Procedure.** To compare the influence of VOC loading on the mechanical properties of a polymer with that of temperature, creep measurements of neat polymers at different temperatures were performed using the DMA 2980 and measurements at various VOC loadings were performed with the novel experimental setup.

*Creep Measurements at Different Temperatures.* Single creep curves of polystyrene films at different temperatures (85–115 °C) were recorded with the DMA 2980. A film tension clamp was used to supply a constant stress in the range of $2.3 \times 10^4 - 1.8 \times 10^6$ N/m². The temperature could be kept constant better than ±0.05 K, and the accuracy of the force applied to the samples was better than ±0.001 N. The sizes of the polystyrene films were 20 mm × 7 mm while the thickness for the different experiments varied in the range of 50–80 μm. The general experimental procedure of the creep experiments in the DMA 2980 is equal to that of the isothermal creep experiments with VOC loaded-polymer films, which are described in the following section.

*Creep Measurements at Different VOC Loadings.* For determination of the creep compliance of VOC-loaded polymers, the increasing strain was measured under constant stress. For that purpose, a VOC-free film was attached to the clamps within the measuring chamber. After heating and evacuation of the apparatus, the vaporizer was filled and subsequently heated up to a temperature of 2 K below the temperature of the measuring chamber to avoid condensation in the piping and in the valves. After that, the pressure in the measurement chamber was increased by opening valves V1 and V2 and closing valves V3 and V4 (Figure 1). After reaching the desired pressure, the inlet valve V2 was set to achieve a desired flow of 0.1 (mbar L)/s, and the pressure control was set into operation. These isothermal and isobaric conditions were maintained for the whole measurement. The time needed to reach equilibrium loading is accessible from sorption experiments which were performed earlier with the gravimetric sorption apparatus[5] (see Appendix). It depends on the particular temperature, film thickness, and concentration and took up to 7 days for the measurements performed within this work. After reaching the equilibrium, the lower clamp was carefully driven downward by the linear drive until the film was tightly strained. A small, reproducible pretension (10% of the total tension) was applied, and the tightly strained film length was recorded as the starting length $L_0$ before accomplishing the force leap. To ensure reproducibility, creep curves at 50 °C and different toluene loadings were measured at least twice.

## Results and Discussion

**Creep Experiments.** The time-dependent elongation $\varepsilon(t)$ determined in creep experiments with or without VOC loading is given by

$$\varepsilon(t) = \frac{L(t) - L_0}{L_0} \tag{1}$$

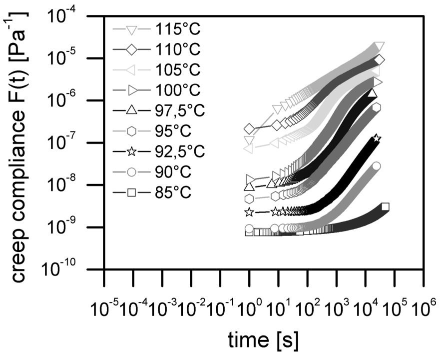

**Figure 2.** Creep curves of polystyrene films at different temperatures recorded with the DMA 2980.

$L(t)$ represents the film length at time $t$ and $L_0$ the film length of the straight-strained state at time zero. The creep compliance $F(t)$ is defined as

$$F(t) = \frac{\varepsilon(t)}{\sigma_0} \tag{2}$$

The stress $\sigma_0$ which is required is assumed to be constant during the whole creep experiment. $\sigma_0$ is required which is assumed here to be constant during the whole creep experiment. This is valid for small elongations since $\sigma_0$ is obtained by

$$\sigma_0 = \frac{F_0}{A_0} \tag{3}$$

where $F_0$ is the applied (constant) force and $A_0$ is the cross-sectional area of the polymer film which might decrease at high elongations. However, for the experiments performed in this work the film elongation was below 2%.

*Temperature Effect*. Figure 2 shows the results obtained from the measurements performed for the neat polystyrene at different temperatures. As it can be seen, temperature has a huge effect on shape and position of the single creep curves.

Because of the time−temperature superposition principle,[4] one can shift the creep curves in time. Since all molecular motions are accelerated at higher temperatures, the same compliance value will be reached earlier, resulting in a shift of the whole creep curve to smaller values of time. Assuming that all relaxation processes are influenced by temperature in the same way, the shape of the creep curves at various temperatures remains unchanged, allowing for the construction of a master curve.[15] By shifting the single curves (Figure 2) to a certain temperature (here $T_g$ = 105 °C), one obtains the so-called master creep curve (Figure 3).

The master creep curve differs for each polymer and shows its long-time creep behavior at constant temperature. To develop the master curve, it is important to consider only experimentally meaningful ranges of the single creep curves.[3,16] Because of starting effects, the first values of each single creep curve are not physically meaningful. Thus, depending on the applied stress, each creep curve was shifted to the master curve by neglecting the running-in effects. Moreover, one needs to consider that the stress is assumed to be constant which is especially not the case at high elongations.

Figure 4 shows the master creep curve of polystyrene obtained in this work compared to another one from the literature.[16]

It can be seen that the shape and the magnitude of the creep compliances are very similar. The differences can be explained by the different molecular weights of the polymers. While in this work polystyrene was characterized by a molecular mass of 240 000 g/mol and $M_w/M_n$ = 5.65, Schwarzl used a polystyrene having a molecular mass of 385 000 g/mol and $M_w/M_n$ = 2.12. A polymer with a higher molecular mass contains more entanglements leading to a higher Young modulus in the rubbery area (at long times in Figure 4), where the polymer is already above its glass-transition temperature. This explains the flatter shape of Schwarzl's creep curve in this region.

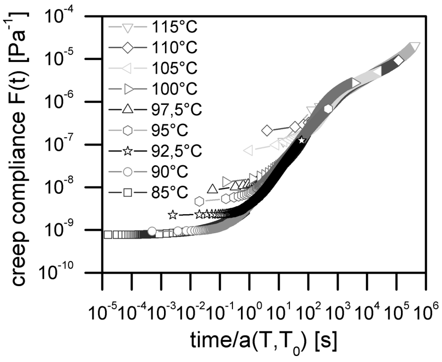

**Figure 3.** Master creep curve of neat polystyrene reduced to 105 °C. All single creep curves (shown in Figure 2) were shifted along the logarithmic time scale to the curve at 105 °C.

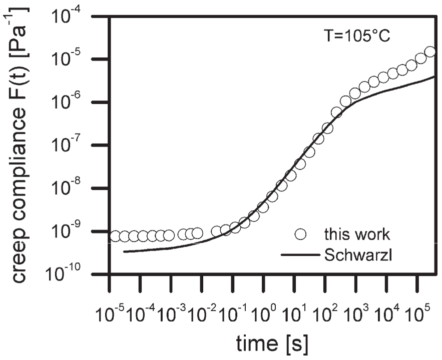

**Figure 4.** Experimental master creep curve for polystyrene at 105 °C obtained in this work compared to the one obtained from Schwarzl.[16] The experimental data from Schwarzl were transformed by using the correlation between creep compliance under constant stress $F(t)$ and under constant shear rate $J(t)$: $F(t) = {}^1/_3 J(t)$.[1]

The difference in the compliances at short times might be caused by the assumption $F(t) = {}^1/_3 J(t)$ used here for converting the data measured by Schwarzl. This is strictly valid only for a Poisson's ratio of 0.5 which applies for rubbers and molten polymers. In the glassy state (short times in Figure 4) the Poisson's ratio is between 0.3 and 0.4, resulting in a smaller conversion factor of 2.6−2.8 instead of 3.

The shifting factors log $a(T,T_0)$ applied to each single creep curve are determined by the following connection between the original experimental time $t$ at experimental temperature $T$ and the reference time $t_0$ at reference temperature $T_0$

$$\log a(T, T_0) = \log t(T) - \log t_0(T_0) \tag{4}$$

The shifting factors obtained in this work are plotted in Figure 5 versus the temperature difference $(T - T_0)$, whereas the glass-transition temperature of the polystyrene (105 °C) was chosen as the reference temperature. The shifting factors for creep curves below the glass transition are positive, which is equivalent to a reduction of the time scale for single creep curves below the glass-transition curve (105 °C). In contrast, shifting factors for creep curves above the glass transition are negative, which means an increase in time scale compared to

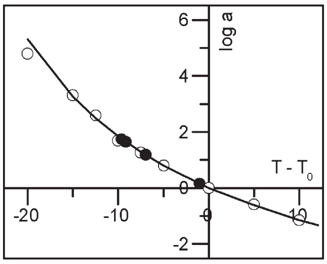

**Figure 5.** WLF shifting factors for polystyrene for different temperatures (determined by DMA 2980) and different toluene concentrations (novel creep apparatus) as a function of the temperature difference ($T - T_0$). Unfilled circles represent the experimentally obtained shifting factors of VOC-free samples, and filled circles represent shifting factors of toluene-loaded samples at 50 °C. The solid line represents the fitted WLF calculation with $c_1 = 6.1$ and $c_2 = 43$ K.

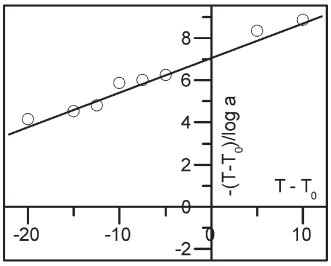

**Figure 6.** Plot of $-(T - T_0)/\log a$ vs $(T - T_0)$ for polystyrene for different temperatures (determined by DMA 2980). Circles represent experimentally obtained values, and the solid line represents calculated values using eq 5 with fitted constants $c_1$ and $c_2$.

**Table 1. Experimentally Determined Shifting Factors log *a* for Polystyrene at Different Temperatures ($T_0 = T_g = 105$ °C)**

| $T$ [°C] | $T - T_0$ [°C] | log $a$ |
|---|---|---|
| 85 | −20 | 4.8 |
| 90 | −15 | 3.3 |
| 92.5 | −12.5 | 2.6 |
| 95 | −10 | 1.7 |
| 97.5 | −7.5 | 1.25 |
| 100 | −5 | 0.8 |
| 105 | 0 | 0 |
| 110 | 5 | −0.6 |
| 115 | 10 | −1.15 |

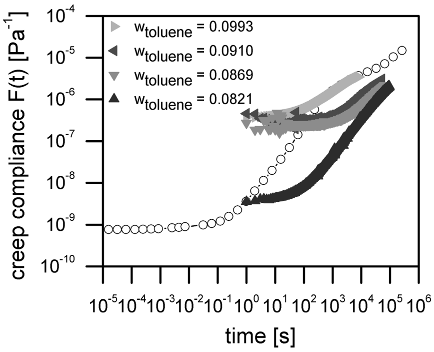

**Figure 7.** Position and shape of single creep curves of polystyrene films at 50 °C and at different toluene loadings $w_{\text{toluene}}$. Unfilled circles represent the obtained master curve (Figure 3) for the neat polystyrene reduced to 105 °C.

measurements at the reference temperature. The results obtained in this work are listed in Table 1.

In the region of the glass-transition temperature, the WLF function[4] in the form of

$$\log a(T, T_0) = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \qquad (5)$$

can be used to calculate the shifting factors log $a$. In this equation, $c_1$ and $c_2$ are material-specific constants. The reference temperature is, as already stated, the glass-transition temperature of the neat polystyrene $T_0 = T_g = 105$ °C. In addition to the experimentally determined shifting factors, Figure 5 also shows the results of eq 5 by using the two fitted constants $c_1 = 6.1$ and $c_2 = 43$ K.

Figure 6 shows a more critical plot to verify the two obtained constants $c_1$ and $c_2$. In the case that the WLF equation can be strictly applied, plotting $-(T - T_0)/\log a$ vs $(T - T_0)$ should result in a straight line as can be seen from Figure 6. This means that eq 5 describes the experimental data very well and therewith justifies the applicability of the WLF equation.

*VOC Effect.* After analysis of the well-known temperature effect on the creep compliance and determination of the WLF parameters $c_1$ and $c_2$ for the polystyrene, the effect of dissolved toluene on the single creep curves was investigated. Isothermal single creep curves at 50 °C and for different VOC loadings were recorded using the novel creep apparatus. As already mentioned above, the toluene loadings $w_{\text{toluene}}$ are available from vapor−liquid equilibrium measurements (see Appendix). The position and the shape of the obtained single creep curves are shown in Figure 7. For the determination of the compliance, film swelling could be neglected. It can be seen that VOC loadings indeed have an influence on the creep curves comparable to that of temperature. Similar to higher temperatures, higher VOC pressures, which mean higher VOC loadings, shift the creep compliances to higher time values (see also Figure 2), whereas the shape of the curves hardly differs from those of the neat polystyrene at higher temperatures. This gives rise to the assumption that the mechanical properties of the polystyrene film qualitatively change with increasing toluene loading like they do with increasing temperatures.

Thus, the WLF eq 5 should be in principle also valid for VOC-loaded polystyrene films in the vicinity of their glass transitions.

Thus, the single creep curves of the VOC-loaded polymers were shifted again to the master curve at $T_g = 105$ °C (Figure 7), and the shift factors log $a(w_{\text{toluene}}, T_g)$ were determined. In analogy to neat polymers, the WLF equation can now be reformulated:

$$\log a\,(w_{\text{toluene}}, T_g) = -\frac{c_1(T - T_{g,\,\text{mixture}}(w_{\text{toluene}}))}{c_2 + (T - T_{g,\,\text{mixture}}(w_{\text{toluene}}))} \qquad (6)$$

Here log $a(w_{\text{toluene}}, T_g)$ presents the shifting factor for shifting a single creep curve of a VOC-loaded polymer film (Figure 7) to the master creep curve of neat polystyrene at $T_g$. The reference temperature of the original eq 5 is now set to $T_0 = T_{g,\text{mixture}}(w_{\text{toluene}})$, i.e., to the glass-transition temperature of the polymer/VOC system. This glass-transition temperature of the mixture is a function of the VOC mass fraction $w_{\text{toluene}}$. All determined values of log $a(w_{\text{toluene}}, T_g)$ for the measurements at 50 °C are listed in Table 2 and are also plotted in Figure 5 (filled circles). As can be seen, fitting of these data is possible using the same constants $c_1$ and $c_2$ as determined before for the neat polystyrene.

By knowing log $a(w_{\text{toluene}}, T_g)$, one can now use eq 6 to determine the distance of a polymer/VOC system from its glass-transition $(T - T_{g,\text{mixture}}(w_{\text{toluene}}))$. At this point we introduce an apparent temperature $T_{\text{apparent}}$ at which the VOC-free polymer film mechanically behaves like a VOC-loaded polymer film at current temperature (here 50 °C).

**Table 2. Experimentally Determined Shifting Factors of Polystyrene Films at 50 °C and at Four Different Toluene Mass Fractions; Calculated Apparent Temperatures and Prediction of the Glass-Transition Temperature of the Polymer/VOC System Mixture**

| $T$ [°C] | $p$ [mbar] | $w_{\text{toluene}}{}^{a}$ | log $a$ | $T_{\text{apparent}} - T_g$ [°C] | $T_{\text{apparent}}$ [°C] | $T_{\text{g,mixture}}$ [°C] |
|---|---|---|---|---|---|---|
| 50 | 37 | 0.0821 | 1.75 | −9.6 | 95.4 | 59.6 |
| 50 | 38.5 | 0.0869 | 1.65 | −9.2 | 95.8 | 59.2 |
| 50 | 40 | 0.0910 | 1.18 | −7.0 | 98.0 | 57.0 |
| 50 | 43 | 0.0993 | 0.15 | −1.0 | 104.0 | 51.0 |

[a] From vapor−liquid equilibrium measurements; see Appendix.

**Table 3. Comparison of the Original and the Modified Kelley−Bueche Equation for the Estimation of the Glass-Transition Temperature of Polystyrene/Toluene Mixtures**

| | | | | eq 9 with $\alpha_2 = 4.8 \times 10^{-4}$ | | eq 9 with $\alpha_2 = 5.73 \times 10^{-4}$ | |
|---|---|---|---|---|---|---|---|
| $T$ [°C] | $p$ [mbar] | $w_{\text{toluene}}{}^{a}$ | estimation of $T_{\text{g,mixture}}$ [°C] | predicted | deviation (%) | predicted | deviation (%) |
| 50 | 37 | 0.0821 | 59.6 | 53.0 | 11 | 60.0 | 0.7 |
| 50 | 38.5 | 0.0869 | 59.2 | 50.4 | 14.9 | 57.6 | 2.7 |
| 50 | 40 | 0.0910 | 57.0 | 48.3 | 15.3 | 55.6 | 2.5 |
| 50 | 43 | 0.0993 | 51.0 | 43.9 | 14 | 51.7 | 1.4 |

[a] From vapor−liquid equilibrium measurements; see Appendix.

Using this apparent temperature, the WLF eq 6 can be rewritten as

$$\log a(w_{\text{toluene}}, T_g) = -\frac{c_1(T - T_{g,\text{mixture}}(w_{\text{toluene}}))}{c_2 + (T - T_{g,\text{mixture}}(w_{\text{toluene}}))} = -\frac{c_1(T_{\text{apparent}} - T_g)}{c_2 + (T_{\text{apparent}} - T_g)} \qquad (7)$$

The temperature difference on the abscissa ($T - T_0$) in Figure 5 is therefore equal to the temperature difference ($T_{\text{apparent}} - T_g$) and represents the temperature distance to the glass transition of the neat polymer. For example a polystyrene film at 50 °C and VOC pressure of 37 mbar (which corresponds to a toluene weight fraction of $w_{\text{toluene}} = 0.0821$) is characterized by a shifting factor log $a$ = 1.75 and behaves mechanically like a neat polystyrene film at $T_{\text{apparent}} = 95.4$ °C, i.e., like a polystyrene film which is 9.6 K below its glass transition (see also Table 2).

Moreover, it becomes clear from Figure 5 that all shifting factors for toluene-loaded polystyrene films obtained in this work are positive, which indicates that all considered polystyrene films were still below their glass transition. To obtain the values of $T_{\text{g,mixture}}$, one just needs to know the shifting factor log $a(w_{\text{toluene}}, T_g)$ of each VOC-loaded creep curve and transpose eq 7 to

$$T_{g,\text{mixture}}(w_{\text{toluene}}) = T + \frac{c_2 \log a(w_{\text{toluene}}, T_g)}{c_1 + \log a(w_{\text{toluene}}, T_g)} \qquad (8)$$

For the given example, the glass-transition temperature of the mixture at 50 °C and $w_{\text{toluene}} = 0.0821$ can therewith be obtained to a value of $T_{\text{g,mixture}}(w_{\text{toluene}} = 0.0821) = 59.6$ °C. This offers the opportunity to estimate the glass-transition temperature of a polymer/VOC mixture only by comparing creep curves at different temperatures with those at different VOC loadings. The results of the so-determined glass-transition temperatures for the four different VOC loadings can be found in Table 2.

**Verification of the Kelley−Bueche Equation.** Using the results of Table 2, we are for the first time able to validate equations for estimating the glass-transition temperature of polymer/VOC mixtures from the literature.[11−14] One of these is the approach of Kelley and Bueche[14]

$$T_{g,\text{mixture}} = \frac{4.8 \times 10^{-4}(1-\phi_1)T_{g2} + \alpha_1\phi_1 T_{g1}}{4.8 \times 10^{-4}(1-\phi_1) + \alpha_1\phi_1} \qquad (9)$$

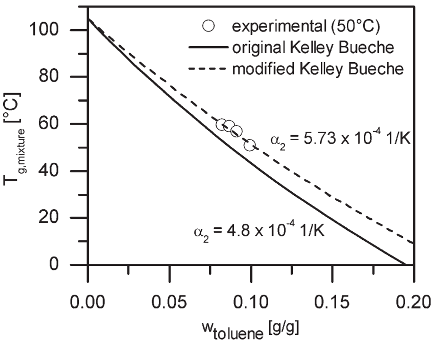

**Figure 8.** Glass-transition temperatures of the polystyrene−toluene mixture as a function of the toluene loading. The solid line represents the original equation by Kelley and Bueche, the unfilled circles are estimations of $T_{\text{g,mixture}}$ based on the experimental data at 50 °C, and the dotted line represents the modified Kelley−Bueche equation.

wherein $T_{g1}$ and $T_{g2}$ are the glass-transition temperatures of the VOC and the neat polymer, respectively. $\alpha_1$ is the thermal expansion coefficient of the pure VOC, and $\phi_1$ is the VOC volume fraction, which is related to the VOC weight fraction $w_1$ as follows:

$$w_1 = \frac{v_{01}{}^{-1}(T,p)\phi_1}{v_{02}{}^{-1}(T,p) + \phi_1(v_{01}{}^{-1}(T,p) - v_{02}{}^{-1}(T,p))} \qquad (10)$$

$v_{01}$ and $v_{02}$ are the specific volumes of pure VOC and polymer, respectively. They are calculated at the pressure $p$ and temperature $T$ of the mixture using an empirical correlation[17] for $v_{01}$ and the Tait equation[18] for $v_{02}$. More details as well as the used expressions and constants can be found elsewhere.[5]

The comparison of the glass-transition temperatures $T_{\text{g,mixture}}$ estimated by eq 9 with the experimentally obtained values is listed in Table 3 and can be seen in Figure 8. The solid line shows the predicted glass-transition temperature of a polystyrene−toluene mixture (eq 9), and the unfilled circles represent the experimentally obtained values of $T_{\text{g,mixture}}$. It is obvious that Kelley's and Bueche's prediction differs remarkably from the experimentally obtained data. A possible reason for this might be the fact that Kelley and Bueche are using an averaged heat-expansion coefficient of $\alpha_2 = 4.8 \times 10^{-4}$ 1/K for any polymer in eq 9 which results in a deviation from the glass-transition temperature of up to 15% (Table 3).

However, the experimentally obtained values for $T_{\text{g,mixture}}$ according to Table 3 can be calculated satisfactorily by eq 9 after fitting the heat-expansion coefficient $\alpha_2$ to a value

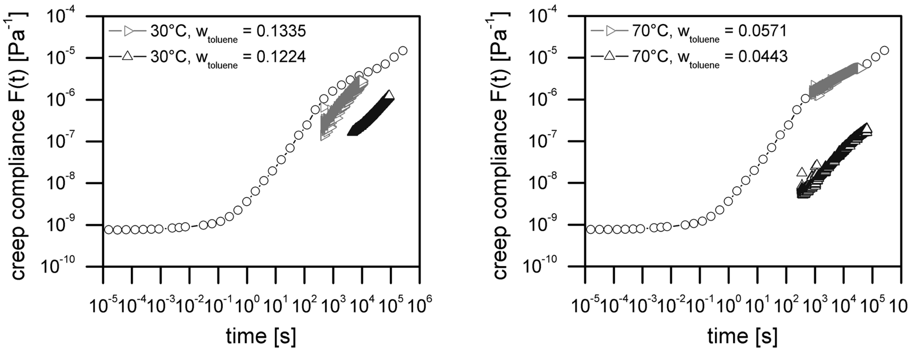

**Figure 9.** Single creep curves of VOC-loaded polystyrene films at various VOC concentrations at 30 (left) and 70 °C (right). Unfilled circles represent the obtained master curve (Figure 3) for the neat polystyrene at 105 °C.

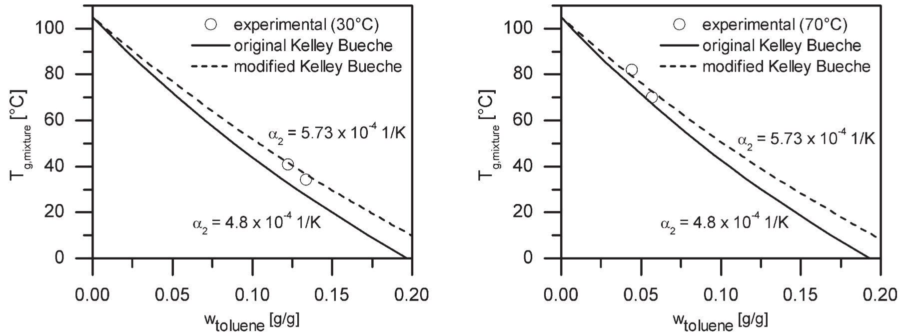

**Figure 10.** Comparison of predicted glass-transition temperatures of the polystyrene/toluene mixture using the original and the modified Kelley–Bueche equation with experimental obtained values of $T_{g,\mathrm{mixture}}$ at 30 (left) and 70 °C (right).

**Table 4. Comparison of the Original and Modified Calculation of the Glass-Transition Temperature of Polystyrene/Toluene Mixtures at 30 and 70 °C**

| | | | | | eq 9 with $\alpha_2 = 4.8 \times 10^{-4}$ | | eq 9 with $\alpha_2 = 5.73 \times 10^{-4}$ | |
|---|---|---|---|---|---|---|---|---|
| $T$ [°C] | $p$ [mbar] | $w^a_{\mathrm{toluene}}$ | log $a$ | experimental $T_{g,\mathrm{mixture}}$ [°C] | predicted | deviation (%) | predicted | deviation (%) |
| 30 | 20.8 | 0.1224 | 2.1 | 41.0 | 32.8 | 20 | 41.7 | 1.7 |
| 30 | 22.2 | 0.1335 | 0.7 | 34.4 | 27.5 | 20.1 | 36.8 | 7 |
| 70 | 50.0 | 0.0443 | 2.4 | 82.1 | 74.9 | 8.8 | 79.3 | 3.4 |
| 70 | 60.0 | 0.0571 | 0.0 | 70.0 | 67.0 | 4.3 | 72.4 | 3.4 |

[a] From vapor–liquid equilibrium measurements; see Appendix.

of $5.73 \times 10^{-4}$ 1/K. A comparison with the literature data (*Polymer Data Handbook*[19]) shows that this value is in good agreement with the volumetric heat-expansion coefficients published for neat polystyrene ($\alpha = 5.1 \times 10^{-4}$–$6.0 \times 10^{-4}$ 1/K). Thus, the new estimated value of $5.73 \times 10^{-4}$ 1/K does perfectly fit into that range (whereas the original one does not).

Figure 8 shows that the choice of a polymer-specific heat-expansion coefficient $\alpha_2$ remarkably increases the accuracy of the glass-transition prediction of a polymer/VOC mixture. With this conclusion, the Kelley and Bueche equation can be modified to

$$T_{g,\,\mathrm{mixture}} = \frac{\alpha_2(1-\phi_1)T_{g2} + \alpha_1\phi_1 T_{g1}}{\alpha_2(1-\phi_1) + \alpha_1\phi_1} \tag{11}$$

with $\alpha_2$ being the heat-expansion coefficient of the neat polymer.

**VOC Influence at Other Temperatures.** After performing measurements at 50 °C, additional creep experiments were performed at 30 and 70 °C and different VOC loadings in the vicinity of the glass-transition temperature of the mixture. The single creep curves were again shifted to the master curve, and the shifting factors log $a(w_{\mathrm{toluene}}, T_g)$ were obtained for the different temperatures and concentrations. This offered the opportunity to verify the modified Kelley and Bueche equation also at other temperatures and other VOC loadings. Figure 9 shows the obtained single creep curves for various VOC concentrations at 30 and 70 °C.

Figure 10 and Table 4 summarize the results of the experimental data set. Moreover, the results of the original as well as of the modified Kelley–Bueche equation for the prediction of the glass transitions are listed. In all cases the modified Kelley–Bueche equation predicts the glass transition of the mixture better than the original one. It can also be seen from Figure 10 that the modified Kelley–Bueche equation (dotted line) is able to predict both the 30 °C and the 70 °C measurements better than the original equation (solid line).

## Conclusion

In this work, an experimental equipment for creep measurements of VOC-loaded polymer films is presented, which combines the simplicity of a creep experiment with the complexity of the sorption process. For the first time it allows creep experiments of a polymer in an atmosphere of a saturated VOC vapor at low and well-defined VOC concentrations. The temperature range may vary between 20 and 85 °C; the pressure ranges from 0.1 up to 1333 mbar.

Using these measurements it is now possible to quantitatively compare the effect of VOC loading on the mechanical

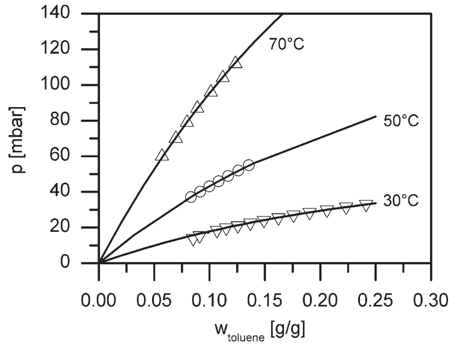

**Figure 11.** Experimental vapor−liquid equilibrium data (vapor pressure as a function of VOC weight fraction) for polystyrene/toluene mixtures at 30, 50, and 70 °C. Data at 30 °C were taken from ref 5.

**Table 5. Experimental VLE Data for the Polystyrene/Toluene System at 30, 50, and 70 °C**[a]

| 30 °C | | 50 °C | | 70 °C | |
|---|---|---|---|---|---|
| $p$ [mbar] | $w_{toluene}$ | $p$ [mbar] | $w_{toluene}$ | $p$ [mbar] | $w_{toluene}$ |
| 14.0 | 0.0853 | 37.0 | 0.0833 | 60.0 | 0.0571 |
| 15.5 | 0.0911 | 40.0 | 0.0917 | 70.0 | 0.0695 |
| 18.5 | 0.1068 | 43.0 | 0.1000 | 79.0 | 0.0797 |
| 19.8 | 0.1151 | 46.0 | 0.1083 | 87.0 | 0.0890 |
| 21.1 | 0.1256 | 49.0 | 0.1169 | 96.0 | 0.1012 |
| 22.6 | 0.1368 | 52.0 | 0.1261 | 104.0 | 0.1121 |
| 24.1 | 0.1491 | 55.0 | 0.1355 | 112.0 | 0.1235 |
| 25.6 | 0.1622 | | | | |
| 27.1 | 0.1759 | | | | |
| 28.6 | 0.1905 | | | | |
| 30.0 | 0.2061 | | | | |
| 31.6 | 0.2234 | | | | |
| 33.1 | 0.2414 | | | | |

[a] Data at 30 °C were taken from ref 5.

properties of a polymer directly to the well-known effect of temperature. The shapes of the single creep curves of toluene-loaded polystyrene films approve the assumption that VOC affects the mechanical properties of a polymer in the same way as temperature does.

Using this assumption and applying the time−temperature superposition principle to polymer-loaded films, the glass-transition temperature of the polymer/VOC mixture was determined based on the creep experiments. Comparing these values to those obtained from the Kelley and Bueche equation revealed that this equation in principle gives reasonable results but should be modified to improve the accuracy. Instead of using a universal constant $4.8 \times 10^{-4}$ 1/K for all polymers, the heat-expansion coefficient of the neat polymer should be used, which was determined to a value of $5.73 \times 10^{-4}$ 1/K for the polystyrene used in this work. By doing so, a much better prediction of the glass-transition temperature as a function of the VOC loading was obtained.

## Appendix. Vapor−Liquid Equilibria

Isothermal gravimetric sorption experiments were performed at 30, 50, and 70 °C to determine the vapor−liquid behavior of the polystyrene/toluene system at different temperatures. Therefore, the toluene pressure was varied between 14 and 70 mbar, and the changing in weight of the polymer sample was recorded. The constant thickness of the polystyrene films varied between 15 and 50 μm. A detailed description of the experimental procedure can be found elsewhere.[5]

**Table 6. χ-Parameters and Toluene Vapor Pressures Used for the Modeling of the VLE of the Polystyrene−Toluene System**

| $T$ [°C] | χ-parameter | $p_{01}^{LV}$ [mbar] |
|---|---|---|
| 30 | 0.296 | 48.7 |
| 50 | 0.238 | 122.7 |
| 70 | 0.223 | 271.5 |

The vapor−liquid equilibrium (VLE) results of the gravimetric sorption experiments at 30, 50, and 70 °C are shown in Figure 11 and are listed in Table 5. The information on the individual loading times which were required to reach the equilibrium conditions is accessible by the sorption isotherms, which are shown for example by Krueger.[5]

To model the VLE behavior of the polystyrene/toluene system, the Flory−Huggins equation was chosen.[20] The Poynting correction $\Pi_{01}^{LV} = 1$ and the ratio of the fugacity coefficients $\varphi_i^{V}/\varphi_{0i}^{LV} = 1$ were neglected. The resulting phase-equilibrium equation is

$$p = p_{01}^{LV}\phi_1 \exp\{(1-\phi_1)+\chi(1-\phi_1)^2\} \qquad (12)$$

$\phi_1$ is the VOC volume fraction, which is directly related to the VOC weight fraction $w_1$ under the assumption that there is no excess volume (see eq 10). As can be seen from Figure 11, the Flory−Huggins equation is able to model the VLE behavior very well when choosing a temperature-dependent χ-parameter (listed in Table 6).

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