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# The influence of sorption of small molecules on the yield stress of glassy polymers

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## Abstract

Uniaxial stress–strain measurements have been performed on two glassy polycarbonates and one polyimide in an atmosphere of $CO_2$, $H_2O$-vapour or acetone-vapour. The yield stress has been determined as a function of the concentration of sorbent molecules. In all observed cases the polymer is softened due to the sorption. The depression of the yield stress at a given concentration is dependent on the size of the sorbent molecules and of interchain volume sites within the polymer. For $H_2O$ and $CO_2$ a unique relation is found between the softening and the volume dilatation accompanying the sorption. This dilatation has been associated with an internal isotropic stress via Hooke's law. That enables us to explain the softening as a consequence of the well known dependence of the yield stress on the isotropic stress component.
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*Keywords:* Yield stress; Glassy polymers; Small molecules

## 1. Introduction

Plasticisation of glassy polymers due to sorption of small molecules plays major role in the application of polymeric materials in the presence of gases and liquids [1]. Investigating the effect, researchers found a depression of the glass transition temperature [2] $T_g$ and of the tensile modulus [3], an increase of the creep compliance [4] and of the loss modulus in mechanical spectroscopy [5]. The mechanisms of the softening are not yet understood, and it is the purpose of the present paper—besides adding new experimental data on the yield behaviour of sorbent-softened glassy polymers—to offer a new interpretation of the effect.

Uniaxial stress–strain measurements have been chosen to determine the yield stress at different concentrations of the sorbent. The dependence of the yield stress of glassy polymers on other parameters such as strain rate, temperature, stress field, molecular structure, physical ageing has been investigated in the past [6]–[8]. A phenomenological approach to fit measured data of the yield stress $\tau_0$ as a function of the applied strain rate $\dot{\varepsilon}$ and temperature $T$ is to employ a rate equation that stems from an early work by Eyring [9] and that has been used frequently since [6]:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left[-\frac{\Delta G - \Omega\tau_0}{kT}\right] \tag{1}$$

with the material parameters zero-stress strain rate $\dot{\varepsilon}_0$, activation free enthalpy barrier $\Delta G$ and stress activation volume $\Omega$. The dependence on the stress field can be expressed by an isotropic stress-dependent von Mises yield criterion [6]:

$$\tau_0 = \tau_{oct} + \alpha\sigma_i \tag{2}$$

where $\tau_0$ is the yield stress for zero isotropic stress $\sigma_i$, and $\alpha$ is the isotropic stress activation coefficient. The octahedral shear yield stress $\tau_{oct}$ is defined in terms of the principal components $\sigma_{y1}$, $\sigma_{y2}$, $\sigma_{y3}$ of the yield stress tensor as [6]:

$$\tau_{oct} \equiv \frac{1}{3}\left[\left(\sigma_{y1}-\sigma_{y2}\right)^2 + \left(\sigma_{y2}-\sigma_{y3}\right)^2 + \left(\sigma_{y3}-\sigma_{y1}\right)^2\right]^{1/2} \tag{3}$$

Attempts have been made to modify Eyring's theory [10], or to replace it with a physically better founded theory [11], [12]. However, the simple Eyring equation can be successfully applied in a moderate parameter range [13], and secondly, the proposed models contain severe idealisations and their molecular interpretations have become questionable through the results of computer simulations [14].

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One aim of the present study was to modify Eyring's theory to take into account the dependence of the yield stress on the concentration $c$ of small sorbent molecules. Surprisingly, we found that Eqs. (1) and (2) are already adequate to account for that dependence, if we include an internal isotropic stress $\sigma_i^{\mathrm{sor}}$ in the yield criterion (2) to account for the effect of sorbent molecules.

A second aim was to investigate the sorption mechanism of small molecules in glassy polymers. One of us has suggested a model [15], [16], in the following referred to as the *site distribution model*, to describe concentration–pressure isotherms assuming a Gaussian distribution $n(V_h)$ of site volumes:

$$n(V_h) = \frac{1}{\sigma_V \sqrt{\pi}} \exp\left( - \frac{\left(V_h - V_h^0\right)^2}{\sigma_V^2} \right) \tag{4}$$

with the average molar site volume $V_h^0$ and the width $\sigma_V$.

Occupying the sites, molecules that have larger molar volume $V_g$ than the molar site volume $V_h$ will elastically stress the polymer matrix, giving rise to a term in the occupation free enthalpy that depends on the partial molar volume defined as: $V_g - V_h$. In a continuum elastic approximation the occupation free enthalpy is then given as:

$$G = G_r + \frac{2\mu_s}{3\gamma} \frac{\left(V_g - V_h\right)^2}{V_h}, \tag{5}$$

where $G_r$ is the occupation free enthalpy independent of the volumes, $\mu_s$ and $\gamma$ are elastic constants. From Eq. (4) we can calculate an occupation free enthalpy distribution $n(G)$ and finally determine the concentration $c'$ in units of molecules per site and the sorption induced volume dilatation $\Delta V$:

$$c' = \int_{-\infty}^{\infty} n(G) \cdot f(G, \mu)\, \mathrm{d}G \tag{6}$$

$$\Delta V = \int_{-\infty}^{\infty} \left(V_g - V_h(G)\right) \cdot n(G) \cdot f(G, \mu)\, \mathrm{d}G \tag{7}$$

where $f(G, \mu)$ is the thermal occupancy function of the Fermi–Dirac statistics. The chemical potential $\mu$ is directly related to the gas pressure $p$. Using the above statistics, it is further assumed that every site can only be occupied by a single molecule. Within the framework of the site distribution model concentration–pressure isotherms [17] $c(p)$ and volume changes caused by sorption [18] $\Delta V(p)$ have been described for $H_2O$, Ar, $N_2$, $CO_2$, $CH_4$ and acetone in bisphenol-A polycarbonate, and for $CO_2$ in various polycarbonates and one polyimide.

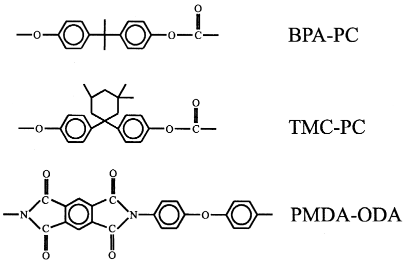

Fig. 1. Monomer units of the tested polymers.

We would like to check the underlying hypothesis of the model, that the relevant contribution to the occupation free enthalpy stems from the elastic deformation of the polymer matrix. The question arises if the elastic stress caused by the occupation of sites can be observed directly. As expressed in the isotropic stress-dependent yield criterion in Eq. (2), the yield stress is sensitive to the isotropic stress state of the sample. We will show that it can serve as an indicator for sorption-induced stress.

## 2. Experimental

### 2.1. Materials and samples

BPA-PC (bisphenol-A polycarbonate) foil and wire and PMDA-ODA (pyromellitic-acid–dianhydride–oxidianiline polyimide or Kapton-H) foil were purchased as commercial products from manufacturers listed in Table 1. The TMC-PC (tetramethyl-cyclohexane polycarbonate) foil was provided by Bayer AG prepared from a solution in methylene chloride and dried in air for 4 h at 120°C. For tensile testing, ribbons of 10 mm width and 40 mm gauge length were cut from the foils. Cylinder shaped samples of 6 mm length and 3.22 mm diameter were cut from the wire and used for testing in compression. Fig. 1 displays the monomer structure and Table 1 contains some thermal and mechanical data of the polymers. The glass transition temperatures, $T_g$, of

Table 1
Thermal and mechanical data of the tested polymers. The yield stress $\sigma_r$ of PMDA-ODA cannot be directly compared with those of BPA-PC and TMC-PC because it was obtained using a different definition

| Polymer | BPA-PC | | TMC-PC | PMDA-ODA |
|---|---|---|---|---|
| Glass transition temperature $T_g$ (K) | 425 | | 504 | 693 |
| Tensile elastic modulus $E'$ (GPa) | 2.21 | – | 2.71 | 3.55 |
| Tensile yield stress $\sigma_r$ (MPa) | 50.8 | – | 65.8 | 153 |
| Shape: thickness $d$, | foil | wire | foil | foil |
| diameter $\phi$ | $d = 125\ \mu$m | $\phi = 3.22\ \mu$m | $d = 90\ \mu$m | $d = 25\ \mu$m |
| Manufacturer | Bayer Macrofol<br>DE 6-2, 1-1 | Goodfellow PC<br>LS156065 | Bayer (R. Plaetschke)<br>P 50 | Goodfellow Kapton-H<br>LS103790 BG |

BPA-PC and TMC-PC were obtained by differential scanning calorimetry at a heating rate of 20 K/min with a calorimeter (Perkin-Elmer); the $T_g$ of PMDA-ODA was given by the manufacturer. Young's elastic modulus $E'$ was determined from the initial slope ($\varepsilon < 0.01$) of the stress–strain curve, and the reference tensile yield stress $\sigma_r$ of the two polycarbonates was taken as the upper yield stress. The stress–strain curve of the polyimide PMDA-ODA does not show a maximum stress followed by strain softening. Therefore, the yield stress was defined differently, namely as the intersection of initial elastic slope ($\varepsilon < 0.01$) and the strain hardening slope at high strains ($\varepsilon > 0.35$), adopting a convention suggested by Argon [19]. All mechanical data were measured at a strain rate of $\dot{\varepsilon} = 8.33 \times 10^{-4}\ \mathrm{s}^{-1}$ and at room temperature.

### 2.2. Tensile tests

In situ measurements of tensile stress–strain curves of the polymer ribbons were performed in an atmosphere of the sorbent molecules. For this purpose, we constructed a testing machine working in a closed chamber which can be evacuated and filled with gas. The strain was determined counting the angular steps of the motor that drives the machine, the stress was obtained by force measurement via a piezoelectric force sensor (Kistler).

For each recording of a curve a new sample was installed in the apparatus and brought into equilibrium with a gas atmosphere of a defined pressure. The equilibrium pressures ranged from 0 kPa to 100.0 kPa $CO_2$, to 2.2 kPa $H_2O$ and to 2.0 kPa acetone. The diffusion times until equilibrium was reached were estimated using the diffusion coefficients from previous measurements [20]. From each stress–strain curve a yield stress was determined as described above. The pressure–concentration isotherms of the same materials [17] were used to convert gas pressure into concentration. The average of at least three independent measurements of the yield stress were then plotted versus the concentration of the sorbent molecule.

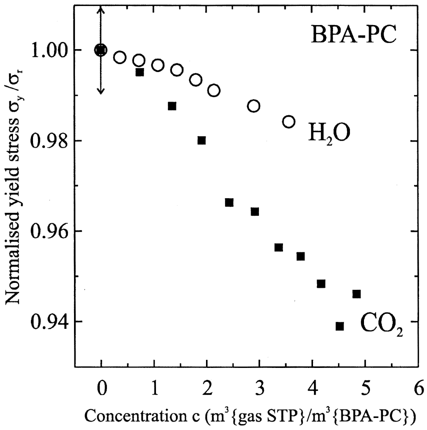

Fig. 2. Normalised tensile yield stress of BPA-PC plotted versus concentration of sorbent molecules. Comparison of $CO_2$ sorption (■) and $H_2O$ sorption (○). In all diagrams, the arrows at the data point of zero concentration correspond to the average error for all data points.

### 2.3. Compression tests

The in situ testing machine allowed $CO_2$ pressures up to 100.0 kPa, yielding a maximum concentration of about 5 m$^3${$CO_2$ STP}/m$^3${BPA-PC}. In order to reach higher concentrations, additional ex situ tests on the system $CO_2$ in BPA-PC were conducted. The samples were equilibrated with a $CO_2$ atmosphere in a pressure tube and then transferred into a conventional Zwick testing machine. To minimise the concentration loss during the time between opening of the pressure tube and testing, the sample geometry of a cylinder was chosen for having a smaller surface to volume ratio than the ribbon shape. Consequently, the kinetics of diffusion for the cylinder shape—calculated using the diffusion coefficient from measurements by Jordan et al. [21]—were much slower (1–2 weeks) than those for the ribbons (minutes–hours). The cylinder-shaped samples allowed deformation in compression to avoid shear banding and necking. The concentration was determined weighing the sample with a microbalance (Sartorius) before and after the gas loading. For the concentration loss $c(t) - c_0$ between weighing time ($t = 0$) and testing time $t$, a correction was applied according to the solution of the diffusion problem for a cylinder geometry given by Crank [22]:

$$\frac{c(t)}{c_0} = 1 - \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{r^2}\right)^{\frac{1}{2}} + \left(\frac{Dt}{r^2}\right) + \ldots, \tag{8}$$

where $c_0$ is the concentration at the weighing time, $r$ is the radius of the cylinder ($r = 1.61$ mm) and $D$ is the diffusion coefficient. By this method, at 3.0 MPa $CO_2$ loading pressure a concentration of 28 m$^3${$CO_2$ STP}/m$^3${BPA-PC} at the time of testing was reached. As in the case of the tensile tests, the yield stresses were extracted from the stress–strain curves and plotted versus the concentration.

## 3. Results

In Figs 2–4 the results of the tensile tests on the polymer ribbons are displayed, except the data for acetone sorption which will be presented and discussed later. In the diagrams the yield stress $\sigma_y$ is normalised by a reference yield stress $\sigma_r$ at zero concentration. Therefore, the influence of sorption on the yield stress of the two polycarbonates can be compared, even though the pure polymers have different yield stresses (see Table 1). However, the yield stresses of PMDA-ODA in Fig. 3 should not be directly related to those of the polycarbonates in Figs 2 and 4, since they were obtained using a different definition. Error bars at the data point of zero concentration represent the average error for all other data points in the diagram.

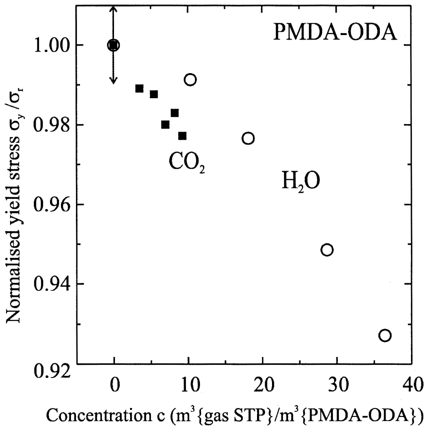

Fig. 3. Normalised tensile yield stress of PMDA-ODA plotted versus concentration of sorbent molecules. Comparison of $CO_2$ sorption (■) and $H_2O$ sorption (○).

In all systems a *depression of the normalised yield stress* $(1 - \sigma_y/\sigma_r)$, in the following also referred to as *softening*, of the polymer due to the sorption of small molecules is observable. The normalised yield stress decreases slightly stronger than linear with the sorbent concentration. The total softening is of the order of a few percent. In BPA-PC (see Fig. 2) as well as in PMDA-ODA (see Fig. 3) the $CO_2$ molecules cause greater softening than the $H_2O$ molecules at a fixed concentration. The maximum softening also depends on the solubility of the molecule in the polymer. In both of the above mentioned polymers, the solubility of the small and polar $H_2O$ molecule is significantly higher than the $CO_2$ solubility, taking into account that the maximum equilibrium pressures in these measurements were 2.2 kPa $H_2O$ and 100.0 kPa $CO_2$. In the case of PMDA-ODA with its four polar carbonyl groups per monomer unit the difference in solubility is more pronounced than for BPA-PC. Comparing the effects of $CO_2$ sorption in the two polycarbonates in [17], we observe a higher solubility in TMC-PC, but at a fixed concentration the softening is less than in BPA-PC (see Fig. 4).

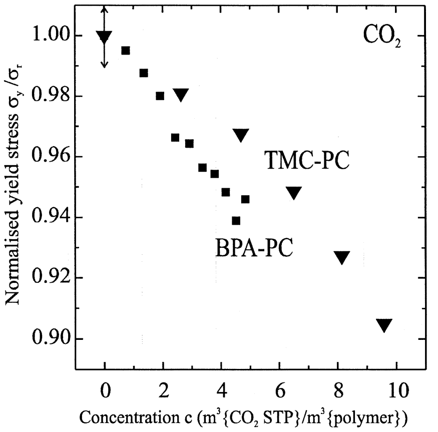

Fig. 4. Normalised tensile yield stress of polycarbonates plotted versus concentration of $CO_2$ molecules. Comparison of BPA-PC (■) and TMC-PC (▼).

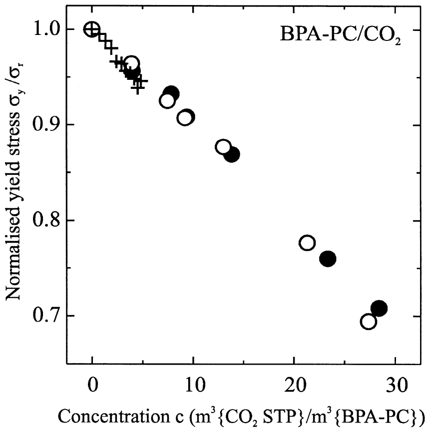

Fig. 5. Normalised yield stresses of BPA-PC plotted versus $CO_2$ concentration using the upper yield stress from compression tests (●), the lower yield stress from compression tests (○), and the upper yield stress from tensile tests ( + ).

The results of the compression tests of the high pressure loaded samples demonstrate the strong influence of $CO_2$ sorption on the deformation behaviour of BPA-PC, as displayed in Figs 5 and 6. At the highest loading pressure of 3.0 MPa $CO_2$ the compression yield stress is lowered by 30%. For comparison, the results of the low pressure tensile measurements have been plotted in Fig. 5. In spite of the different yield stresses of the two deformation modes, the normalised yield stress depends in a similar manner on the concentration.

It could be preferable to characterise the flow behaviour of glassy polymers by the lower yield stress, since according to Nanzai [10], it fulfils the condition of steady state flow better than the upper yield stress. With respect to the softening due to sorption of small molecules, both upper and lower normalised yield stress lead to the same results, as seen in Fig. 5.

It is instructive to look at the stress–strain curves themselves in Fig. 6 to study the effect in more detail. Owing to

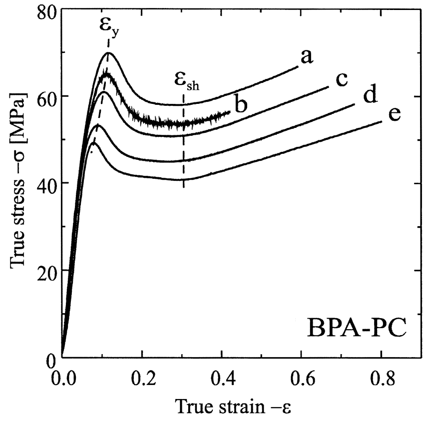

Fig. 6. Stress–strain curves from compression tests of BPA-PC loaded with $CO_2$ at various loading pressures: (a) 0 MPa; (b) 0.4 MPa; (c) 1.0 MPa; (d) 2.0 MPa; (e) 3.0 MPa. The dashed lines mark the strains at the upper yield point $\epsilon_y$ and at the onset of strain hardening $\varepsilon_{sh}$.

$CO_2$ sorption the yield strain is decreased from $\varepsilon_r = 0.13$ to $\varepsilon_y = 0.08$. However, the onset strain of strain hardening remains rather unaffected by the $CO_2$ sorption and is always around $\varepsilon_{sh} = 0.30$. As a consequence, a plateau region evolves in the lower yield range with increasing loading pressure and $CO_2$ concentration. Furthermore, the $CO_2$ sorption lowers the strain hardening modulus, i.e. the slope in the range of large strains $\varepsilon > 0.40$.

Sorption induced crystallinity could lead to an opposite effect usually referred to as antiplasticisation [3], [23]. Employing DSC, crystallinity was not observable in any of the polymer/sorbent systems in the concentration ranges and time scales of this study.

## 4. Discussion

### 4.1. Influence of molecule and polymer properties

In BPA-PC and in PMDA-ODA a $CO_2$ molecule causes greater softening than an $H_2O$ molecule (see Figs 2 and 3). We make the assumption that this is mainly due to the different molar volumes $V_g$. The softening at a given concentration increases with the molar volume of the sorbent $V_g$. The latter can be estimated from the density of the liquids as $V_g(H_2O) = 18\ cm^3/mol$ and $V_g(CO_2) = 37\ cm^3/mol$. The difference in shape, nearly spherical in the case of $H_2O$ and stretched in the case of $CO_2$, should only give rise to a second order effect. Another noteworthy molecular property, in which the two molecules differ, is the permanent electric dipole moment: $CO_2$ has zero moment while $H_2O$ has a non-vanishing moment. The interaction of the $CO_2$ molecule with the surrounding polymer matrix is mainly of the Van-der-Waals or induced-dipole-moment type, whereas for the $H_2O$ sorption dipole–dipole interactions are possible. The bond type has a strong effect on solubility—as stated in the previous section to account for the high $H_2O$ solubility in PMDA-ODA—but it is irrelevant with respect to the amount of softening at a fixed concentration. Compared with BPA-PC, the softening by $H_2O$ sorption relative to that of $CO_2$ sorption is *not* increased for PMDA-ODA, in spite of its strong dipole–dipole bonding to $H_2O$.

The dependence of the softening at a fixed concentration on the molar volume of the sorbent is noteworthy, because the glass transition temperature depression can be successfully described disregarding molecular properties [2], [24], [25]. In an equation proposed by Chow [24], the relative depression of the glass temperature is a function of two parameters $\theta$ and $\beta$, where $\beta$ is solely dependent on polymer properties, and $\theta$ is the ratio of the number of sorbent molecules and the number of possible sites. In fact, $\theta$ is proportional to the concentration $c$ ($m^3\{gas\ STP\}/m^3\{polymer\}$) used in this paper. We have attempted to adopt Chow's equation for the description of our results. It was assumed that the softening is proportional to the relative change of the glass transition temperature. The relations obtained were of the correct order of magnitude; however, they could not correctly describe the influence of molecular or polymer properties [26]. This failure indicates that the underlying mechanisms of $T_g$-depression and low temperature yield stress depression are different. The basic idea in Chow's theory is a change of configuration entropy of the liquid state with the concentration of sorbent molecules, whereas in the glassy state the entropy is assumed to be independent of the concentration. The sorption energy is given by nearest neighbour interactions only. This concept is successful in the temperature regime close to glass transition, but it is not applicable at low temperatures. Far below $T_g$ the configurational entropy can be disregarded but the energy becomes important. As our results suggest, it is the elastic deformation energy that governs the softening in the low temperature regime.

The influence of the polymer properties will be discussed with regard to $CO_2$ sorption in the two polycarbonates. At a given concentration the softening in TMC-PC is less than in BPA-PC (see Fig. 4). The monomer unit of TMC-PC differs from that of BPA-PC by an additional tetramethyl-cyclohexyl side group (see Fig. 1) that reduces the packing density of the polymer chains. In other words, TMC-PC has a larger interchain volume fraction than BPA-PC. In a previous work [17] pressure–composition isotherms of $CO_2$ in the two polycarbonates were measured and the volumes of interchain sites were described in terms of the site distribution model (4)–(7) with the parameters:

$$V_h^0\{BPA-PC\} = 18.5\ cm^3/mol,$$

$$\sigma_V\{BPA-PC\} = 6.6\ cm^3/mol \tag{9}$$

$$V_h^0\{TMC-PC\} = 22.2\ cm^3/mol,$$

$$\sigma_V\{TMC-PC\} = 7.9\ cm^3/mol \tag{10}$$

In the observed range of low concentrations, $c < 10\ m^3\{gas\ STP\}/m^3\{polymer\}$, which resembles number concentrations of $c' < 0.075$ molecules per site [27], predominantly the largest—and energetically most favourable—sites are occupied. Therefore, the average volume of the *occupied* sites in TMC-PC is significantly larger than in BPA-PC, due to the larger average site volume $V_h^0$ and to the larger width $\sigma_V$ of the distribution. This is also in agreement with results obtained by positron lifetime spectroscopy [27]. We state: the softening at a fixed concentration decreases with the molar volume of occupied interchain sites $V_h$. The nonlinearity of the concentration dependence of the normalised yield stress is interpreted in the same way: at low concentrations, additionally sorbed molecules occupying large volume sites cause less incremental softening than at higher concentrations when they must occupy smaller sites.

### 4.2. Volume dilatation

Summarising the findings of the previous paragraph, the softening increases with the partial molar volume $V_g - V_h$

of the occupied sites. It is fruitful to relate the softening to the sorption induced volume dilatation, which is directly related to the partial molar volume via Eq. (7). For each equilibrium gas pressure of our tensile experiments the volume dilatation $\Delta V/V$ was obtained from pressure–dilatation isotherms [18]. Plots of the normalised yield stress versus volume dilatation are depicted in Figs 7 and 8. At the same volume dilatation, $CO_2$ and $H_2O$ in BPA-PC and $CO_2$ in TMC-PC lead to an equal amount of softening. Similarly, $CO_2$ and $H_2O$ in PMDA-ODA cause the same softening at the same dilatation. Within the error ranges there is a linear relation between the normalised yield stress and the volume dilatation. We define a softening coefficient $\eta$ as the negative slope in the dilatation–yield stress diagrams:

$$\eta \equiv -\frac{\partial(\sigma_y/\sigma_r)}{\partial(\Delta V/V)} \tag{11}$$

Least square fitting yields:

$\eta\{\text{BPA-PC, TMC-PC}\} = 23 \pm 1$
$\eta\{\text{PMDA-ODA}\} = 12 \pm 1$

A correspondence between the polycarbonates on one side and the polyimide on the other side cannot be expected because of the difference in the definitions of the yield stress.

We conclude that the sorption induced volume dilatation $\Delta V/V$ is a good measure to characterise the softening for various polymer/sorbent systems by a single parameter $\eta$. One could now try to modify the yield criterion in Eq. (2) to account for the effect of sorption induced volume dilatation on the yield stress, but we will follow a different path.

### 4.3. Internal isotropic stress

If the volume dilatation of a polymer observed during sorption of small molecules is caused by an elastic deformation of the polymer matrix, one can calculate an isotropic stress $\sigma_i^{sor}$ via Hooke's law:

$$\sigma_i^{sor} = K \cdot \frac{\Delta V}{V} \tag{12}$$

where $K$ is the bulk modulus of the polymer. We make the assumption that this internal isotropic stress $\sigma_i^{sor}$ induced by sorption causes the softening in our experiments. Internal stresses are so far not included in the classical version of Eyring's model in Eqs. (1) and (2), but, according to Argon et al. [14], they play an important role in the flow behaviour of disordered materials. The results of this work support the above assumption. We will discuss two reasons; one interpreting the data of acetone sorption, the other one comparing the stress $\sigma_i^{sor}$ with an external mechanical stress $\sigma_i^{mech}$.

In all cases discussed in the previous section, the volume dilatation $\Delta V/V$ and the stress $\sigma_i^{sor}$ serve equally well to describe the softening, since they are proportionally coupled via Eq. (12), where BPA-PC and TMC-PC have similar bulk moduli $K$. The idea is to investigate a case in which Hooke's law is violated. This could be achieved by increasing the concentration to reach macroscopic volume dilatations beyond the elastic regime. However, there is an upper limit to the dilatation. For $CO_2$ in BPA-PC the dilatation–pressure isotherm at 35°C measured by Wissinger and Paulaitis [25] levels off at approximately 7 MPa $CO_2$ pressure and 9% volume dilatation. Hooke's law can be violated in another way at relatively moderate concentrations and dilatations, if the sorbent molecule is large enough. To understand this, let us interpret the stress $\sigma_i^{sor}$ on a microscopic level as the sum over the isotropic components of the stress fields due to each sorbent molecule occupying an interchain site. If plastic rearrangements of the polymer chains occur in the neighbourhood of a large sorbent molecule the assumption of elasticity is locally violated, and Eq. (12) can no longer be globally applied. The acetone molecule has a large molar volume of $V_g\{\text{acetone}\} = 74\ \text{cm}^3/\text{mol}$ as determined from the density of the liquid. This must be compared with the volumes of the interchain sites in the polymer, see

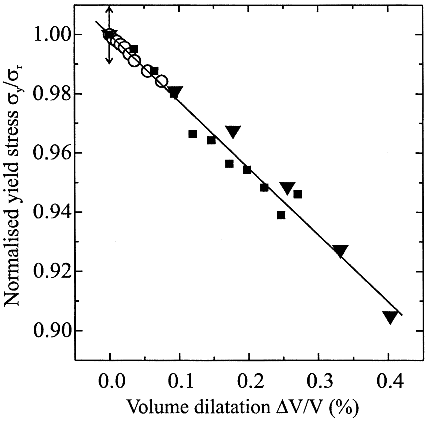

Fig. 7. Normalised yield stress of polycarbonates plotted versus volume dilatation induced sorption: $CO_2$ in BPA-PC (■), $H_2O$ in BPA-PC (○) and $CO_2$ in TMC-PC (▼). The solid straight line represents a linear least square fit to the data.

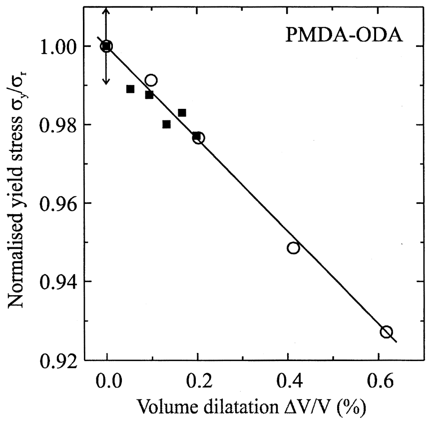

Fig. 8. Normalised yield stress of PMDA-ODA plotted versus volume dilatation induced sorption of $CO_2$ (■) and $H_2O$ (○). The solid straight line represents a linear least square fit to the data.

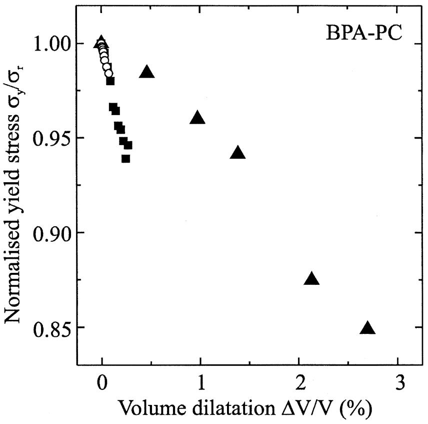

Fig. 9. Normalised yield stress of BPA-PC plotted versus volume dilatation induced by sorption of acetone (▲), $CO_2$ (■) and $H_2O$ (○).

Eqs. (9) and (10). Treating pressure–concentration isotherms in the framework of the site distribution model quoted in Eqs. (4)–(7), Grüger et al. [17] found deviations for large molecules like ethylene and acetone, which they attributed to a viscoelastic distortion of the polymer. The same explanation will be given with regard to our results displayed in Fig. 9. For equal volume dilatations, acetone causes significantly less softening than the smaller molecules. The true internal stress due to acetone sorption is less than the stress $\sigma_{\mathrm{i}}^{\mathrm{sor}}$ calculated from Eq. (12) assuming elasticity, and therefore results in a weaker softening effect.

Any isotropic stress should effect the yield stress according to the yield criterion Eq. (2). By means of comparing the changes in yield stress caused by the internal stress $\sigma_{\mathrm{i}}^{\mathrm{sor}}$ and by an external mechanical stress $\sigma_{\mathrm{i}}^{\mathrm{mech}}$, we can check the plausibility of our concept. This is done in Fig. 10. Christiansen et al. [28] recorded the tensile yield stress $\sigma_{\mathrm{y}}$ of BPA-PC subjected to a nondissolving high pressure environment. They plotted the octahedral shear yield stress $\tau_{\mathrm{oct}}$, defined in Eq. (3), versus the total isotropic stress. The latter is the sum over the isotropic stress component $\sigma_{\mathrm{i}}^{\mathrm{def}}$ in the uniaxial deformation mode and the mechanical stress $\sigma_{\mathrm{i}}^{\mathrm{mech}}$ produced by the nondissolving environment acting with a pressure $p$:

$$\sigma_{\mathrm{i}}^{\mathrm{def}} = \sigma_{\mathrm{y}}/3 \tag{13}$$

$$\sigma_{\mathrm{i}}^{\mathrm{mech}} = -p \tag{14}$$

The slope of the fitted linear function is the pressure activation coefficient $\alpha$ of the yield criterion Eq. (2), reported [28] as $\alpha = 0.072$. For comparison with sorption induced changes of the yield stress, our results from the compression tests, given in Fig. 5, are taken, since they cover a wide enough concentration range. From the measured concentrations, $c$, we determined the volume dilatation $\Delta V/V$ using swelling and sorption data reported by Wissinger and Paulaitis [25]. A volume dilatation of approximately 3% was found for the maximum concentration of 28 $\mathrm{m}^3\{\mathrm{CO}_2\ \mathrm{STP}\}/\mathrm{m}^3\{\mathrm{polymer}\}$. We applied a correction to account for the mechanical effect of the gas pressure. The literature data on volume dilatation were measured within the gas atmosphere, whereas the compression tests in this work were done at atmospheric pressure. Finally, the sorption induced stress $\sigma_{\mathrm{i}}^{\mathrm{sor}}$ was obtained according to Eq. (12) with a bulk modulus of $K = 5.0$ GPa [29].

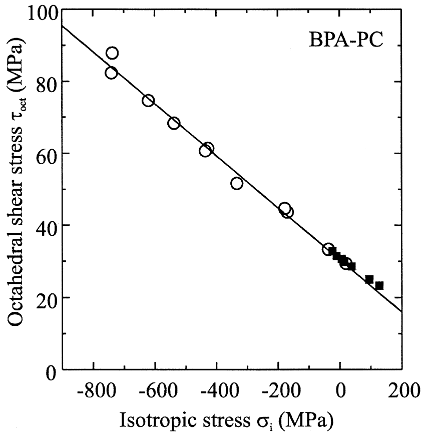

Fig. 10. Octahedral shear yield stress of BPA-PC plotted versus isotropic stress produced by $CO_2$ sorption $\sigma_{\mathrm{i}} = \sigma_{\mathrm{i}}^{\mathrm{def}} + \sigma_{\mathrm{i}}^{\mathrm{sor}}$ (■), and by a non-dissolving pressure environment $\sigma_{\mathrm{i}} = \sigma_{\mathrm{i}}^{\mathrm{def}} + \sigma_{\mathrm{i}}^{\mathrm{mech}}$ (○). The latter data were taken from measurements by Christiansen et al. [28]. The solid line represents a linear least square fit to the data of Christiansen et al.

Our data coincide reasonably well with the linear function fitted to Christiansen's et al. results [28]. That means that the internal isotropic stress $\sigma_i^{sor}$ produced by the $CO_2$ sorption influences the yield stress of BPA-PC just like an external mechanical isotropic stress $\sigma_i^{mech}$. A slight offset towards higher values of the octahedral shear stress may be due to the higher strain rate in our experiments: $\dot{\varepsilon}$ (this work) $= 8.33 \times 10^{-4}\ \mathrm{s}^{-1}$, whereas $\dot{\varepsilon}$ (Ref. [28]) $= 1.39 \times 10^{-4}\ \mathrm{s}^{-1}$.

The overlap of the two data sets around zero isotropic stress stems from the fact that Christiansen et al. conducted tensile tests, while we used deformation in compression. The uniaxial yield stresses $\sigma_{\mathrm{y}}$ that enter Eq. (13) have opposite signs.

## 5. Conclusions

Sorption induced softening of glassy polymers has been observed as a depression of the yield stress in uniaxial testing. At a given concentration, the amount of softening increases with the partial molar volume $V_{\mathrm{g}} - V_{\mathrm{h}}$, where $V_{\mathrm{g}}$ is the molar volume of the sorbent molecules and $V_{\mathrm{h}}$ is the molar volume of the occupied interchain sites in the polymer, as determined using the site distribution model (Eqs. (4)–(7)).

It has been suggested that the internal stress $\sigma_{\mathrm{i}}^{\mathrm{sor}}$ which is produced by the deformation of the polymer matrix when sorbent molecules occupy interchain sites, determines the softening. The octahedral shear yield stress $\tau_{\mathrm{oct}}$ depends on this sorption induced isotropic stress $\sigma_{\mathrm{i}}^{\mathrm{sor}}$ in the same manner as on an external mechanical stress $\sigma_{\mathrm{i}}^{\mathrm{mech}}$. For small molecules at moderate concentrations, the internal stress $\sigma_i^{sor}$ is related to the sorption induced volume dilatation $\Delta V/V$ via Hooke's law (eq. (12)). We find a unique and linear dependence of the yield stress on the volume dilatation for $H_2O$ and $CO_2$. The larger acetone molecule, however, leads to deformation of the polymer matrix beyond the elastic limits, and the internal stress $\sigma_i^{sor}$ is less than Eq. (12) would predict. Consequently, the softening at a fixed volume dilatation is comparably less.

The classical version of Eyring's theory (Eqs. (1) and (2)) can be modified by incorporating the sorption induced internal stress $\sigma_i^{sor}$ in the yield criterion:

$$\tau_0 = \tau_{oct} + \alpha\left(\sigma_i^0 + \sigma_i^{sor}\right) \tag{15}$$

where $\sigma_i^0$ is the isotropic stress from all other external sources. For small molecules, Hooke's law (Eq. (12)) and the site distribution model (Eqs. (4)–(7)) are valid, and the yield stress is fully determined as a function of molecular and polymer properties.

If one starts out with Eq. (15) as an assumption, the results of this present study may be considered as a support of the site distribution model. The yield stress $\tau_{oct}$ then serves as an indicator for sorption induced stress $\sigma_i^{sor}$. It shows in the expected way a dependence (i) on the molecular volume and (ii) on the concentration, where changes of the yield stress are less pronounced at low concentrations due to a preferrential occupancy of larger interchain sites and concomittantly smaller internal stresses $\sigma_i^{sor}$.

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