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Geochimica et Cosmochimica Acta 71 (2007) 691–702
Geochimica
www.elsevier.com/locate/gca

Influence of the sample history and the moisture status on the thermal behavior of soil organic matter

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Received 12 May 2006; accepted in revised form 25 September 2006

Abstract

Recent studies indicate that glassiness represents a characteristic feature of soil organic matter (SOM). It is however unknown, to which extent the transitions detected in humic substances and whole soil samples correspond to common models of synthetic polymers providing the theoretical basis for explaining their glass transition characteristics. Physical aging associated with structural relaxation of amorphous substances below their glass temperature is one fundamental basis for the glass transition behavior of synthetic polymers. According to the results of this study, aging processes also occur in SOM. In whole soil samples, this process can be observed by the shift of glass transition-like step transitions to higher temperatures within the time scale of years. Not only the structural relaxation of the macromolecular organic substances, but also interactions with water molecules, which may exhibit both plasticizing and antiplasticizing properties, influence the aging process of SOM. Especially under moistening or drying conditions, a differentiation between the effects of water and of alterations of the SOM structure in the course of time on the rigidity of the macromolecular network is difficult.

1. Introduction

Recently, glass transitions have been discovered in humic and fulvic acids (LeBoeuf and Weber Jr., 1997) as well as in whole soil samples, sediments, and peat (Schaumann and Antelmann, 2000; DeLapp and LeBoeuf, 2004; Hurrass and Schaumann, 2005; Schaumann and LeBoeuf, 2005). To date, it is however not known whether the properties of glassy and rubbery regions in soil organic matter (SOM) are comparable to those of synthetic polymers. The interpretation of sorption isotherms of organic compounds to humous substances by a polymer model, which is based on the coexistence of properties known for the glassy and rubbery states of synthetic polymers (LeBoeuf and Weber Jr., 1997; Xing and Pignatello, 1997), combined with the detection of glass transitions in SOM (Hurrass and Schaumann, 2005; Schaumann and LeBoeuf, 2005) supports the hypothesized comparability. However, due to the extremely heterogeneous structure of SOM, the macromolecular characteristics and processes possibly differ from synthetic polymers. The occurrence of two types of glass transitions in SOM also points to differences between the organic soil matrix and typical synthetic polymer systems, which only reveal one glass transition type.

In humous substances, in addition to a classical glass transition, which can be measured only in dried samples, an atypical glass transition type is observable in water-containing samples. Because of the only slowly reversing character of this transition, it does not agree with the classical definition of glass transitions (Seyler, 1994). To distinguish this transition type from the classical one, it is referred to as glass transition-like step transition with the transition temperature T_g^* (Hurrass and Schaumann, 2005). The glass transition-like step transitions occur at higher temperatures and reveal higher intensities than the classical glass transitions of SOM. They can only be observed in closed systems, which prevent an evaporation of water out of the samples, and due to their only slowly reversing character, they disappear in a second run of the measurement (Hur-

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doi:10.1016/j.gca.2006.09.022

rass and Schaumann, 2005; Schaumann, 2005; Schaumann and LeBoeuf, 2005). The two types of glass transition behavior in SOM can be explained by the hydrogen bond-based crosslinking (HBCL) model proposed by Schaumann and LeBoeuf (Schaumann, 2005; Schaumann and LeBoeuf, 2005). This model supposes hydrogen bond-based crosslinks by individual water molecules between the molecular chains of SOM, resulting in an antiplasticization of the SOM structure for low water contents. If these crosslinks are disrupted by the removal of water out of the system, the chain mobility increases, and consequently the glass transition-like step transition shifts to significantly lower temperatures and becomes a reversible classical glass transition (Hurrass and Schaumann, 2005; Schaumann, 2005; Schaumann and LeBoeuf, 2005).

Formally, glass transitions appear to be second order transitions (McKenna, 1989; Elias, 1997). One deciding feature of glassiness is the occurrence of time-dependent characteristics due to the non-equilibrium nature of the glassy state (McKenna, 1989; Höhne et al., 1996; Elias, 1997). Consequently, glass transition events can only be insufficiently characterized by thermodynamical approaches (McKenna, 1989; Höhne et al., 1996), but require kinetic models (Höhne et al., 1996). Below the glass transition temperature, amorphous polymers undergo a structural relaxation process, which also is called physical aging. During this process, physical properties of the amorphous phase change over time: these changes include reductions in segmental mobility, enthalpy, and free volume, causing an increase of density, yield stress, and elastic modulus (Struik, 1978). The kinetics of enthalpy relaxation correspond to the relationship, proposed by Cowie and Ferguson (1986):

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)\left[1 - \exp\left\{-\left(\frac{t_a}{\tau}\right)^{\beta}\right\}\right] \quad (1)$$

where ΔH_∞ represents the maximum equilibrium enthalpy of the glassy matrix. t_a and T_a are annealing time and annealing temperature of the aging process, and τ is the average relaxation time of the different compounds of the amorphous system undergoing the aging process. β is the non-exponentiality parameter ($0 \leqslant \beta \leqslant 1$), which is inversely correlated to the width of the distribution of relaxation times (Cortés and Montserrat, 1998; Hutchinson, 1998; Chung et al., 2004). The rate of the structural relaxation process increases with increasing annealing temperature, i.e., with decreasing difference $T_g - T_a$.

In well-annealed glasses, endothermic annealing peaks (enthalpic overshoots) can be observed in differential scanning calorimetry (DSC) thermograms. These annealing peaks reflect the aging process, which beforehand has occurred in the glassy matrix. With increasing annealing time or increasing annealing temperature during the aging process, the enthalpy loss and the peak temperature shift to higher values, on condition that T_a is distinctly below the glass temperature T_g (Illekova, 1994; Montserrat, 1994; Hutchinson, 1998; Chung et al., 2004). Additionally, the annealing peaks are influenced by the heterogeneity of the amorphous matrix. Chung et al. (2004) showed that a high structural heterogeneity in starches (small β values) yields a slow relaxation and with that small relaxation enthalpies, i.e., small annealing peak areas at a certain annealing time t_a. Generally, very wide distributions of relaxation times (small β values) result in broad glass transition regions with weakly pronounced or no annealing peaks (Cortés and Montserrat, 1998; Hutchinson, 1998).

On the basis of the detected glass transition behavior of SOM (DeLapp and LeBoeuf, 2004; Hurrass and Schaumann, 2005; Schaumann and LeBoeuf, 2005), the fundamental hypothesis of this study was that aging processes occur in soil samples, too. This hypothesis is supported by the observation that the transition temperature of a peat sample increased continually with time during at least 30–90 days of storage (Schaumann, 2005). To investigate the influence of annealing on the thermal behavior of SOM, we performed DSC measurements of unfractionated soil samples after different periods of storage at temperatures below their glass transition-like step transitions.

Due to the high heterogeneity of SOM, a wide distribution of relaxation times has to be expected for the structural relaxation process of SOM in the glassy state. This may explain that only weakly pronounced or no annealing peaks are observable in DSC thermograms of humous soil samples (Hurrass and Schaumann, 2005), so that the aging process cannot be studied by means of these peaks. Consequently, the transition temperatures of the glass transition-like step transitions were applied for examining possible effects of sample storage on the glassiness of the organic soil phase.

A further important objective of this study was to elucidate, if the aging process of organic substances in soil is affected by the moisture status, which frequently changes under natural conditions. For less heterogeneous polymer systems, as e.g., starch or epoxy resins, in which water acts as plasticizer, an influence of the water content on the aging process is known (Ellis and Karasz, 1986; Shogren, 1992). The decrease of the difference $T_g - T_a$ due to plasticization results in a faster relaxation process, so that the enthalpy of the annealing peak, measured after sample annealing at a constant temperature T_a, rises with moisture content. Only when the water content is so high that T_g is reduced below T_a, no annealing endotherm appears any more (Shogren, 1992).

Two processes which may alter the glass transition behavior of SOM in the course of time have to be taken into account: on the one hand, a structural relaxation process of the organic substances comparable to that of synthetic polymers may occur irrespective of the effects of water. On the other hand, we supposed that the pronounced influence of the water status on the glass transition behavior (Hurrass and Schaumann, 2005; Schaumann, 2005; Schaumann and LeBoeuf, 2005) is linked to slow changes of the glassy SOM matrix. Thus, for low moisture contents, increasing transition temperatures due to a gradual increase of the degree of SOM

crosslinking by hydrogen bond water molecules are to be assumed. Contrary to these antiplasticizing effects of water for low moisture contents (Schaumann, 2005; Schaumann and LeBoeuf, 2005), water has been found to act as plasticizing agent in humic substances (LeBoeuf and Weber Jr., 1997), in a soil sample (Schaumann and Antelmann, 2000), and in a peat sample (Schaumann, 2005; Schaumann and LeBoeuf, 2005) for moderate to high water contents due to swelling. Consequently, for high water contents, the transition temperatures of the glass transition-like step transitions are expected to decrease during the slow process of SOM swelling. Under field conditions, a differentiation between the effects of water and those of structural relaxation of the organic chain segments is impossible, because the moisture content as well as the way of water binding in the solid soil matrix usually change in the course of time.

As a result of possible plasticizing and antiplasticizing effects of water in SOM, the shifting of glass transition-like step transitions to higher temperatures due to possible structural relaxation processes can be either increased or reduced by water uptake or removal, depending on the moisture content in the system. By investigating the effect of time on the glass transition behavior of soil samples stored at different constant relative humidities, we attempted a differentiation between the effects of water and the aging effects which do not depend on the water status. The resulting water sorption isotherms were evaluated in order to get an insight into the mechanism of water binding, i.e., to obtain information, whether water acts as plasticizer or as antiplasticizer for the different relative humidities: antiplasticizing effects of water require specific sorption sites within the SOM for the water molecules. By contrast, swelling and with that plasticization of the SOM matrix only is possible for high water contents, if there are more water molecules than crosslinking sites (Schaumann, 2005; Schaumann and LeBoeuf, 2005). SOM plasticization by water consequently is linked with a sorption process which is not based on specific sorption sites, but presumably on a partitioning mechanism of water molecules in the organic soil phase.

2. Sorption models

Depending on the assumed sorption mechanisms, the sorption of water to humous soil samples can be described by different models. The Langmuir isotherm bases on specific sorption sites on a monomolecular adsorption layer (Atkins, 1994):

$$N = \frac{N_m\, p}{b + p} \tag{2}$$

where N and N_m are the number of adsorbed molecules and the maximal number of molecules in a monolayer. p is the partial pressure of the adsorbate in the gas phase. The sorption constant b is inversely correlated to the affinity of the sorbate to the sorbent. Assuming a specific adsorption area A_S of water molecules on the soil surface and a mass specific surface A_m of soil, with the Avogadro constant N_A and the molar mass of water M, Eq. (2) can be transformed to a form applicable to sorption data of water from the gas phase to soil:

$$\Theta = \frac{A_m}{A_S} N_A\, M \frac{N_m\, p_0 \mathrm{RH}}{b + p_0\ \mathrm{RH}} = \Theta_m\ \frac{p_0\ \mathrm{RH}}{b + p_0\ \mathrm{RH}} \tag{3}$$

where Θ_m is the maximal gravimetric monolayer water content. RH is the relative humidity, which represents the quotient of the partial pressure p of water and the respective saturation vapor pressure p_0.

Due to their dipole moments, several layers of water molecules, which are bound by hydrogen bonds among each other, may adsorb to porous soil surfaces. With the BET isotherm, this multilayer adsorption can be modeled. (Atkins, 1994):

$$\frac{\mathrm{RH}}{(1 - \mathrm{RH})V} = \frac{1}{c\ V_m} + \frac{(c-1)\mathrm{RH}}{c\ V_m} \tag{4}$$

where V and V_m are the sorbed volume and the volume corresponding to monolayer coverage. c represents a measure of the adsorption enthalpy. Transformation of Eq. (4) and the multiplication of V and V_m by the density of the sorbed water yields:

$$\Theta = \Theta_m \frac{c\mathrm{RH}}{(1 - \mathrm{RH})[1 - (1-c)\mathrm{RH}]} \tag{5}$$

with Θ_m as the maximal monolayer water content.

Additionally, the polymer-based dual-mode model (DMM) for NOM (Xing and Pignatello, 1997; Xia and Pignatello, 2001), which commonly is used for the sorption of organic molecules to SOM, was tested for our sorption data. The DMM model assumes the coexistence of glassy and rubbery domains in SOM. For the glassy regions, a hole-filling mechanism linked with the sorption to fixed sorption sites is proposed. In addition to the resulting Langmuir term, a partitioning term is added for the rubbery regions due to the fluid-like flexibility of their molecular chains:

$$\Theta = K_D\ p_0 \mathrm{RH} + \frac{\Theta_m\ p_0 \mathrm{RH}}{b + p_0\ \mathrm{RH}} \tag{6}$$

with K_D as the partition coefficient of the dissolution domain. Kamiya et al. (1986, 1998) extended the DMM and introduced a term that accounts for plasticization by the sorbate. For a high-organic soil, Xia and Pignatello (2001) have shown that the sorption of polar and apolar compounds agrees well with this extended DMM. However, an extensive data base over a wide concentration range is necessary for an evaluation of sorption isotherms with this model (Xia and Pignatello, 2001). Up to now, the DMM as well as the extended DMM were only applied for modeling sorption isotherms of organic compounds to NOM. It is unknown, if these models are appropriate for the sorption of water to humous substances. But, due to the supposed swelling and plasticizing effects of water in rubbery SOM at moderate to high water contents

(Schaumann, 2005; Schaumann and LeBoeuf, 2005), the applicability of these models may be assumed.

3. Experimental section

3.1. Soil samples

For this study, soil samples which are known to reveal glass transition behavior unambiguously originating from their organic phase (Hurrass and Schaumann, 2005) were used. In order to minimize the influence of the mineral soil matrix on thermal behavior and water sorption characteristics, only samples from O_h and A_h horizons were analyzed (Table 1). Due to its high OM content and the comparability to the fundamental study concerning the HBCL model of Schaumann and LeBoeuf (2005), a peat sample additionally was incorporated into the study (Table 1). The samples were used in air-dried, oven-dried, and vacuum-dried state. Before the measurements, the air-dried samples were equilibrated for at least three weeks in 0.31 RH at 20 °C. The oven-dried subsamples were obtained by heating the air-dried samples for 24 h at 105 °C. The vacuum-dried subsamples were obtained by exposing the air-dried samples for 24 h in a 3 mm thick layer to a pressure of 80 Pa in a Christ Alpha 1–4 freeze drying system (Christ, Germany).

To examine, if long-term storage of soil samples influences their glass transition behavior, DSC measurements of the Siberia samples were performed just after sampling and after three years of sample storage. Before the first measurements after sampling, reproducible moisture contents were achieved by an equilibration of the samples for two weeks over saturated NaCl solution (0.76 RH) at 20 °C. Then, the samples were stored for three years in polyethylene containers at 20 °C and measured for a second time.

In order to study the effect of the water content on the glass transition-like step transitions, the air-dried samples from Flossenbürg and Rothenkirchen as well as the air-dried and oven-dried samples from the Warnowtal were equilibrated at different relative humidities (RH) at 20 °C. Different RH were realized by means of dried $CaCl_2$, saturated salt solutions and over distilled water and were controlled with electronic thermohygrometers. After distinct periods of time, subsamples were taken out of the equilibration vessels for measuring their gravimetric water contents and for DSC analysis. Water contents were determined by weighting the samples before and after drying at 105 °C for 24 h and relating the weight loss to the dry sample mass.

3.2. DSC experiments

DSC analyses were performed with the Q1000 DSC (TA Instruments, Germany), as described in Hurrass and Schaumann (2005). For the standard measurements, the samples were heated in hermetically sealed aluminum pans from −50 to 110 °C with a heating rate of 10 K min^{-1}. In order to examine the reversibility of the transitions in air-dried samples, the pans with the Flossenbürg and Rothenkirchen samples were stored after the first DSC run and measured again after several periods of time. To study the effect of water evaporation, further DSC measurements were carried out in pans in which three holes were punched. In these punched pans, the samples were pretempered for 30 min at 110 °C before the heating cycle. The cooling between pretempering and heating cycle was conducted in two ways: method A involved an abrupt cooling from 110 to −50 °C within 6.5 min. In method B, the samples were cooled with a rate of −10 K min^{-1}.

Following a technique to determine the apparent activation energies of the structural relaxation process in the glassy state (Moynihan et al., 1996; Cortés and Montserrat, 1998), measurements with different heating rates were carried out for the air-dried samples from Flossenbürg, Rothenkirchen, and Siberia. Additionally to measurements with the heating rate of 10 K min^{-1}, measurements from −50 to 110 °C with heating rates of 1, 2.5, and 5 K min^{-1} were performed for these samples. But contrary to the method described by Moynihan et al. (1996), the samples

Table 1
Properties of the soil samples

Location	Soil type	Soil texture	Horizon	OM content (%)[a]	Θ (%) of air-dried samples[b]
Flossenbürg, Bavaria, Germany: spruce forest location (Level II monitoring plot under EU legislation)	Podzol	Sandy loam	O_h	37.1	3.3 ± 0.1
			A_h	14.3	1.5 ± 0.1
Rothenkirchen, Bavaria, Germany: spruce forest location (Level II monitoring plot under EU legislation)	Cambisol	Clay loam	O_{h1}	79.7	5.7 ± 0.1
			O_{h2}	71.2	6.2 ± 0.1
Plotnikovo, West Siberia: boreal forest in the southern taiga	Luvisol	Loam	O_h	60.4	4.1 ± 0.7
			A_{h1}	20.0	2.0 ± 0.2
			A_{h2}	12.7	2.3 ± 0.3
Warnowtal near Rostock, Germany: fen in glacial valley of Weichsel ice age	Histosol		H_v	63.9	13.6 ± 0.4

[a] Organic matter content on dry mass basis.
[b] Moisture content related to dry sample mass.

were not cooled prior to the heating cycle from above their glass transition region with a cooling rate which is equal to or proportional to the heating rate. Due to the atypical glass transition behavior of the air-dried soil samples, it was not possible to measure glass transition-like step transitions after such a cooling cycle. For the different samples, the apparent activation energies ΔH^* of the aging process of SOM were determined by the slope m of the function (Moynihan et al., 1996):

$$m = \frac{\mathrm{d}\ln q_\mathrm{h}}{\mathrm{d}(1/T_\mathrm{g})} = -\frac{\Delta H^*}{R} \tag{7}$$

where q_h is the heating rate, and R is the ideal gas constant.

DSC data analysis was performed with the Thermal Advantage V4.0 software (TA Instruments). In order to obtain horizontal thermograms in the glass transition regions, linear baselines were subtracted. For the evaluation of the classical glass transitions and the glass transition-like step transitions, tangent lines were applied to both limits of evaluation. The onset and the end point are defined as the intersections of these outer tangent lines with a central tangent line. The central tangent line is applied to the transition temperature T_g or $T_\mathrm{g}{}^*$, which is determined at half height between onset and end point. The associated change of specific heat capacity ΔC, which is a measure for the transition intensity, is calculated from the difference between end and onset tangent lines at T_g or $T_\mathrm{g}{}^*$ and is related to the total mass of the soil sample.

For each sample, all measurements were executed with three replications, which served to estimate the errors of the data on the basis of 95% confidence intervals.

4. Results and discussion

4.1. Effects of the sample history on thermal events in the DSC thermograms

In accordance with observations of Schaumann and LeBoeuf (2005) and Hurrass and Schaumann (2005), in hermetically sealed pans, glass transition-like step transitions of the studied air-dried soil samples only occur in the first DSC run (see curve 1 in Fig. 1 exemplarily for the O_{h1} horizon from Rothenkirchen). For the measurements in open pans, no glass transition region was detected after pretempering and abrupt cooling by method A (curve 2). In contrast, the heating cycle after cooling with the defined rate of $-10\ \mathrm{K\ min^{-1}}$ by method B shows a classical glass transition at (37 ± 1) °C with ΔC of $(0.02 \pm 0.01)\ \mathrm{J\ g^{-1}\ K^{-1}}$ (curve 3), which exhibits reversibility indicated by the reproducible transition temperature and intensity in subsequent heating cycles with cooling cycles of method B in between. The same behavior was observed for all samples from Flossenbürg, Rothenkirchen, and Siberia. After thermal pretreatment in open pans, they all showed reversible glass transitions at lower temperatures and with decreased intensities in comparison with the glass transition-like step transitions of the air-dried samples in closed pans. DSC measurements after the removal of SOM by different methods and of isolated humic fractions have shown that the organic soil phase is responsible for the observed glass transition behavior of the studied humous soil samples (Hurrass and Schaumann, 2005).

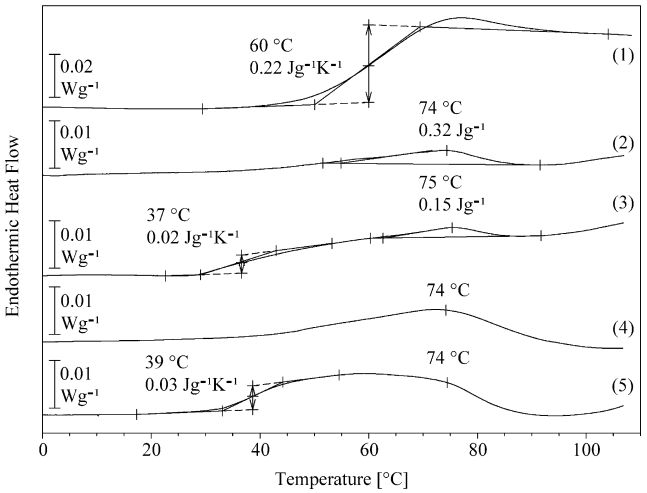

Fig. 1. DSC thermograms of air-dried (1), vacuum-dried (4), and oven-dried (5) samples of the O_{h1} horizon from Rothenkirchen in hermetically sealed pans. The air-dried sample was additionally measured in punched pans after water removal by pretempering and subsequent cooling by method A (2) and method B (3). Due to unknown limits of the endothermic process at (74 ± 2) °C, a quantitative evaluation of the peak area is not possible. The evaluation of this peak in the thermograms 2 and 3 only yields a rough estimation of the energy required for the process.

After oven-drying, a reversible transition at (39 ± 1) °C comparable to that after thermal pretreatment in the open pans was observed (curves 3 and 5 in Fig. 1). Both these transitions are expected to represent classical transitions most probably based on the same mechanism responsible for glassy matrix rigidity. In contrast to the oven-dried status, the forest soil samples from Flossenbürg and Rothenkirchen revealed no transition directly after vacuum-drying (curve 4 in Fig. 1). But, different from these samples, the thermograms of the oven-dried and the vacuum-dried peat sample from the Warnowtal (not shown) are comparable, as also described for another peat sample by Schaumann and LeBoeuf (2005). The oven- and the vacuum-dried peat samples from the Warnowtal both reveal a reversible step transition at (49 ± 2) °C with ΔC of $(0.04 \pm 0.01)\ \mathrm{J\ g^{-1}\ K^{-1}}$, whereas the air-dried peat sample shows a glass transition-like step transition at (62 ± 1) °C with ΔC of $(0.13 \pm 0.01)\ \mathrm{J\ g^{-1}\ K^{-1}}$.

These results of the different DSC measurement conditions (Fig. 1) are in accordance with the HBCL model (Schaumann, 2005; Schaumann and LeBoeuf, 2005). Thus, for water-containing air-dried soil samples in sealed pans, the disappearance of the glass transition-like step transition in a second DSC run conducted immediately after the first one can be explained by the disruption of water crosslinks during the first heating cycle (Hurrass and Schaumann,

2005; Schaumann, 2005; Schaumann and LeBoeuf, 2005). Based on the HBCL model, the lower temperatures and decreased intensities of the transitions after thermal pretreatment in open pans are due to a smaller degree of SOM crosslinking because of the absence of water molecules (Schaumann and LeBoeuf, 2005). But for some samples, the differences between the vacuum- and the oven-dried state indicate that besides the removal of water, a thermal pretreatment above 100 °C is necessary for the occurrence of this classical glass transition type directly after sample drying (Fig. 1). Supposing a kinetic control of the rearrangement of the SOM side chains and the formation of new crosslinks among themselves after destruction of the water crosslinks, this process is accelerated by higher temperatures. Consequently, there may be more crosslinks in SOM after oven-drying than after vacuum-drying, leading to a detectable glass transition in the studied temperature range. For the occurrence of the classical glass transition type in the peat sample and the absence of this transition type in the forest samples directly after vacuum-drying, differences in SOM quality may be responsible. For example, smaller distances between the molecular segments of SOM in peat than in the studied forest soils possibly cause smaller activation energies required to form crosslinks between the organic side chains of peat samples.

The differences between the cooling methods A and B show that slow cooling after the thermal pretreatment is also a deciding factor for the occurrence of a glass transition in the subsequent heating cycle. This supports the supposed kinetic control of the new formation of crosslinks after water removal out of the macromolecular SOM network.

Besides the glass transitions of the classical type, the DSC thermograms in Fig. 1 which were recorded after a thermal pretreatment and after water evaporation reveal an endothermic process at (74 ± 2) °C, which is most probably not interrelated to the glass transition behavior. A detailed study of this process will be published in a separate article.

4.2. Slow changes of the glass transition behavior of SOM in the course of time

The slowly reversing character of the glass transition-like step transition of the air-dried samples was studied by means of the pan storage experiment (Fig. 2): in hermetically sealed pans, this transition type disappears in a second DSC run performed directly after the first one (Fig. 2, curve 2). But, it reappears after storing the pans for one more week (curve 3). After further storage, the transition shifts to higher temperatures (from (47 ± 1) to (52 ± 1) °C after 7 months for the A_h sample from Flossenbürg; Fig. 2) and reveals a significantly higher intensity. It is uncertain, if the original T_g^* and ΔC values of the first run will be reached again at any time. Between one week and 7 months of sample storage, T_g^* increased by (4.5 ± 0.4) °C, and ΔC increased by (0.020 ± 0.008) J g^{-1} K^{-1} on average for the samples from Flossenbürg and Rothenkirchen. If a continuous increase of T_g^* and ΔC is assumed, it would take between one and two years to reach the original parameters of the glass transition-like step transition of the first runs. The reappearance of glass transition-like step transitions at decreased temperatures after one week of storing the pans and the increase of T_g^* and ΔC with proceeding time points to a slow rearrangement of the water molecules resulting in a new formation of water bridges within SOM. These results consequently reflect the pronounced influence of time after changes of the water status on the glass transition behavior of SOM.

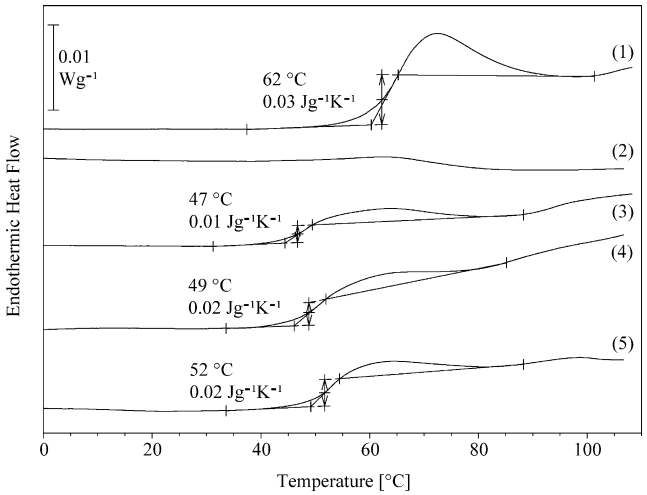

Fig. 2. DSC thermograms of the air-dried A_h sample from Flossenbürg in hermetically sealed pans. Directly after the first run (1), a second run (2) was performed with the same pan. Then, the pan was stored and measured again after one week (3), after further 8 weeks (4), and further 7 months (5).

Recent studies (Rudolph and Schaumann, 2006; Schaumann et al., 2006) indicate that besides the crosslinks by water molecules, crosslinks by metal cations also may effect the glass transition characteristics. But, we did not change the degree of crosslinking by metal cations during the experiments of this study, so that the role of this factor of influence can be neglected.

Changes of the glass transition behavior of SOM in the course of time also occur without preceded alterations of the water status by thermal pretreatment or drying of the samples. Thus, the three-year storage of the NaCl equilibrated Siberia samples in closed containers resulted in a significant increase of the transition temperatures T_g^* (Table 2).

For the three-year storage of the NaCl equilibrated samples, it can be assumed that effects of water on changes of the glass transition-like step transitions are smaller than after alterations of the water status (Fig. 2). Consequently, structural relaxation of the humous substances including reductions in segmental mobility and free volume (Tsereteli and Smirnova, 1992; Illekova, 1994; Cortés and Montserrat, 1998; Hutchinson, 1998) also may contribute to the

Table 2
T_g^* and ΔC of the NaCl equilibrated Siberia samples soon after sampling and after three years of storing them

Horizon	T_g^* (°C) after 2 weeks	ΔC (J g^{-1} K^{-1}) after 2 weeks	T_g^* (°C) after 3 years	ΔC (J g^{-1} K^{-1}) after 3 years
O_h	52 ± 2	0.05 ± 0.04	61 ± 2	0.13 ± 0.07
A_{h1}	56 ± 2	0.03 ± 0.01	61 ± 1	0.03 ± 0.01
A_{h2}	56 ± 2	0.04 ± 0.01	60 ± 1	0.02 ± 0.01

increase of T_g^* during this period of time. The aging studies described in the above mentioned publications were performed with synthetic organic polymers and gelatin as well as with metallic and chalcogenide glasses. In contrast to soil samples, already after annealing times of few hours, these glasses reveal endothermic annealing peaks which are distinctly higher than their glass transition steps. The minor annealing peaks of soil samples may result from a wide range of different relaxation times (small β values) due to SOM heterogeneity (Cortés and Montserrat, 1998; Hutchinson, 1998; Chung et al., 2004).

According to Moynihan et al. (1996), the slope of the fitted linear function in Fig. 3 yields an apparent activation energy of (200 ± 20) kJ mol^{-1} for the structural relaxation process of the air-dried O_{h1} sample from Rothenkirchen. For all other samples from Flossenbürg, Rothenkirchen, and Siberia, the activation energies range between 120 and 370 kJ mol^{-1} and show no correlation to the OM content, to the locations, or to the different soil horizons.

The determined apparent activation energies of the structural relaxation process of the air-dried soil samples are smaller than those quoted for synthetic organic polymers and inorganic glasses (Table 3). According to structural relaxation models for synthetic polymers (Cortés and Montserrat, 1998), the low activation energies would indicate small barriers to internal rotations of the backbone bonds of the SOM molecules and high relaxation rates. However, it is questionable, if these models for pure polymer systems can be transferred to soil samples, in which interrelations with the mineral matrix, ions, and water molecules may control the mobility of the organic substances.

Table 3
Activation energies ΔH^* of synthetic organic polymers and inorganic glasses

Polymers/glasses	ΔH^* (kJ mol^{-1})	Literature
Epoxy resin	1020 ± 60	Montserrat, 1994
Linear polyesters	650–1100	Cortés and Montserrat, 1998
Polymethyl(α-*n*-alkyl) acrylates	390–855	Hutchinson, 1998
Phthalates	650–1095	Hutchinson, 1998
Silicates	374–615	Moynihan et al., 1996
AgI–Ag_2MoO_4	360–640	Hutchinson, 1998
AgI–$AgPO_3$–Ag_2MoO_4	405–505	Hutchinson, 1998

4.3. Influence of the moisture status

After four weeks of equilibration in different RH, the water contents of the soil samples had reached equilibrium values. Later on, no significant changes of the water contents were observed. The water sorption isotherms show a sigmoidal shape (see Fig. 4 exemplarily for the oven-dried peat sample from the Warnowtal), as also observed by Miyamoto et al. (1972).

For RH ⩽ 0.8, water sorption data of the soil samples (Fig. 4) can be modeled by the Langmuir isotherm

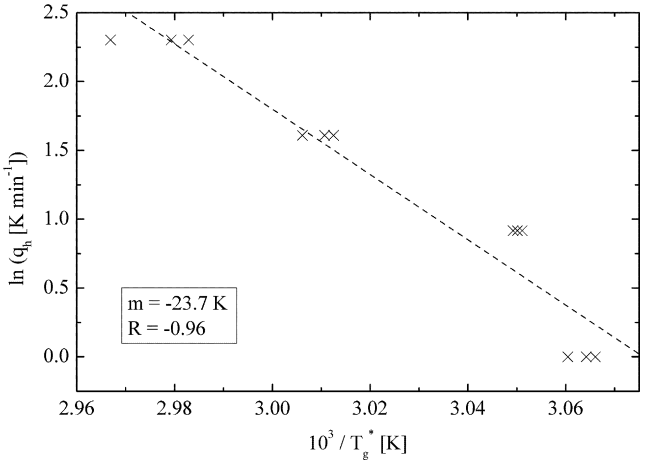

Fig. 3. Logarithm of the heating rate q_h versus reciprocal of transition temperature T_g^* for the air-dried O_{h1} sample from Rothenkirchen. The slope and the correlation coefficient of the linear regression are specified in the box.

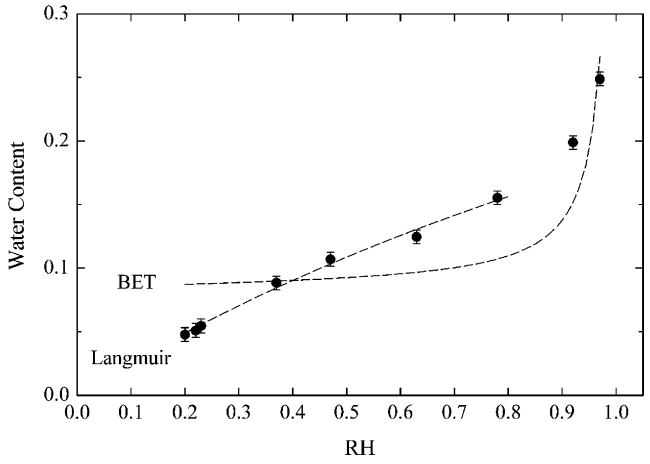

Fig. 4. Water content as a function of relative humidity for the oven-dried peat sample from the Warnowtal after 9 months conditioning time and BET sorption model fit as well as Langmuir fit for RH ⩽ 0.8.

Table 4
Parameters of the sorption models fitted to the water sorption isotherms of the oven- and air-dried peat samples from the Warnowtal and the air-dried forest soil samples from Flossenbürg and Rothenkirchen (Θ_0 in the BET model: axis intercept due to vertical shifting of the whole isotherm; see Section 2 for all other parameters)

	Warnow., oven-dried	Warnow., air-dried	Floss., O_h air-dried	Floss., A_h air-dried	Roth., O_{h1} air-dried	Roth., O_{h2} air-dried
Langmuir (RH $\leqslant$ 0.8)						
Θ_m	0.6 ± 0.1	0.3 ± 0.1	0.06 ± 0.01	0.02 ± 0.01	0.12 ± 0.01	0.11 ± 0.01
b (Pa)	5000 ± 1000	1800 ± 500	270 ± 90	500 ± 200	370 ± 90	400 ± 200
χ^2	$2 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-6}$	$8 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
DMM (RH $\leqslant$ 0.8)						
k_D (Pa^{-1})	$0 \pm 3 \cdot 10^{-4}$	$0 \pm 2 \cdot 10^{-4}$	$0 \pm 1 \cdot 10^{-5}$	$0 \pm 6 \cdot 10^{-6}$	$0 \pm 2 \cdot 10^{-5}$	$0 \pm 3 \cdot 10^{-5}$
Θ_m	0.6 ± 4	0.3 ± 1	0.06 ± 0.03	0.02 ± 0.02	0.12 ± 0.1	0.10 ± 0.1
b (Pa)	5000 ± 20000	1800 ± 4000	330 ± 200	400 ± 400	370 ± 200	400 ± 400
χ^2	$2 \cdot 10^{-5}$	$9 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$9 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
BET						
Θ_m	0 ± 0.001	0 ± 0.001	0 ± 0.009	0 ± 0.001	0 ± 0.01	0 ± 0.006
c	3 ± 400	7 ± 80	7 ± 800	4 ± 300	6 ± 700	4 ± 200
Θ_0	0.24 ± 0.01	0 ± 0.001	0.15 ± 0.01	0.04 ± 0.01	0.30 ± 0.01	0.15 ± 0.01
χ^2	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$7 \cdot 10^{-3}$	$5 \cdot 10^{-3}$

($\chi^2 < 0.0001$). The fitting results of the Langmuir model for RH $\leqslant$ 0.8 yield higher maximal water contents Θ_m for the peat sample than for the samples from the forest locations Flossenbürg and Rothenkirchen (Table 4). For the forest samples, they are correlated to the SOM content (Table 1). The higher maximal water content Θ_m of the oven-dried peat sample than that of the air-dried peat sample in combination with the comparable Langmuir constants b of both samples (Table 4) indicates that the sample alterations caused by oven-drying (Davies et al., 1997) are linked to higher amounts of water uptake. The fitting was not improved by application of the DMM instead of the simple Langmuir isotherm. Both models yield almost identical curve progressions with $\chi^2 < 0.0001$ for all samples (Table 4). The high errors of the DMM parameters (Table 4) however indicate that the low number of data points is over-interpreted by this model. The DMM model also was inappropriate to describe the water sorption for the whole RH range ($\chi^2 > 0.0001$). Neither the data for RH $\leqslant$ 0.8 nor the whole data set of water sorption do agree with the BET model. By a vertical shifting of the BET function, the fitting results slightly improved, but nevertheless are insufficient to describe the data (Fig. 4), as also indicated by χ^2 and the high errors of the BET constant c (Table 4).

The water sorption isotherms for RH $\leqslant$ 0.8 point to specific sorption sites, whereas for RH > 0.8, partitioning of the water molecules linked to swelling of SOM may become relevant. The mineral soil matrix also may account for specific sorption sites in low RH and the resulting non-linearity of the isotherms. Due to the high SOM content in the studied samples and its high water sorption capacity (Hurrass and Schaumann, 2006), the organic soil matrix is, however, expected to control the water sorption process. The fact that the fitting results cannot be improved by applying the DMM instead of the Langmuir model also is in accordance with fixed adsorption sites without partitioning-like behavior. However, the differentiation between these sorption models is difficult because of the small number of data points. The unsuitability of the BET isotherm, which is based on a fixed surface for adsorption, most probably is caused by SOM swelling for RH > 0.8. The BET model characterizes multilayer sorption, but it does not include the severe increase of the water contents for RH > 0.8 presumably caused by the development of additional pore volume and surface areas due to swelling. For a humic and a fulvic acid, Chen and Schnitzer (1976) also obtained poor fitting results by the BET model for RH > 0.5–0.6. They assumed that the condensation of water vapor into clusters around COOH groups of the humic substances caused this divergence from the BET model at high RH. Orchiston (1953) gave a range of only 0.05–0.35 RH for the applicability of the BET isotherm to soils.

The pronounced increase of water sorption for RH > 0.8 can only reasonably be explained by SOM swelling. Since this increase is comparable for all studied samples, which possess different amounts of mineral soil compounds partially containing very low clay contents, it most probably is not based on clay swelling. Moreover, swelling of the mineral soil matrix cannot explain the severe increase of the water contents starting only at high RH. In contrast to the predictions of the extended DMM by Kamiya et al. (1986), a linear or exponential function, fitted to the data points for RH > 0.8, does not intersect the origin, but intersects the abscissa at RH = (0.7 ± 0.2) for all samples. This points to a plasticizing effect of water only for RH > (0.7 ± 0.2), i.e., for water contents of above (15 ± 3)% for the peat sample and (7 ± 4)% for the forest soil samples. For lower water contents, the interactions between SOM and water are presumably dominated by crosslinks within the organic molecules by water molecules resulting in an antiplasticizing effect.

The transition temperatures T_g^* of the samples which were stored in the different RH slowly increased despite the constant water contents reached after four weeks. Figs. 5 and 6 show T_g^* as a function of time for

the oven-dried and air-dried peat samples from the Warnowtal. Only in 0.20 and 0.22 RH, no gradual increase of T_g^* was observed for the air-dried samples (Fig. 6). Interestingly, these two relative humidities are the only ones which caused a significant drying of this sample (to water contents of $(6 \pm 1)\%$ and $(7 \pm 1)\%$), while the other RH resulted in comparable or higher water contents with reference to the air-dried sample ($(13.6 \pm 0.4)\%$). Because of the low water contents of the air-dried samples from Flossenbürg and Rothenkirchen (Table 1) and the oven-dried peat sample from the Warnowtal, none of the relative humidities caused further drying of these samples. As for the oven-dried peat sample, but in contrast to the air-dried peat sample, the transition temperatures T_g^* of the air-dried samples from Flossenbürg and Rothenkirchen also increased during sample equilibration in 0.20 and 0.22 RH (not shown).

In summary, the equilibration of the soil samples in different RH has shown that sample drying does not necessarily show a significant trend of T_g^*, while constant or increasing water amounts in the samples cause a rise of T_g^*. Contrary to the results for the peat sample

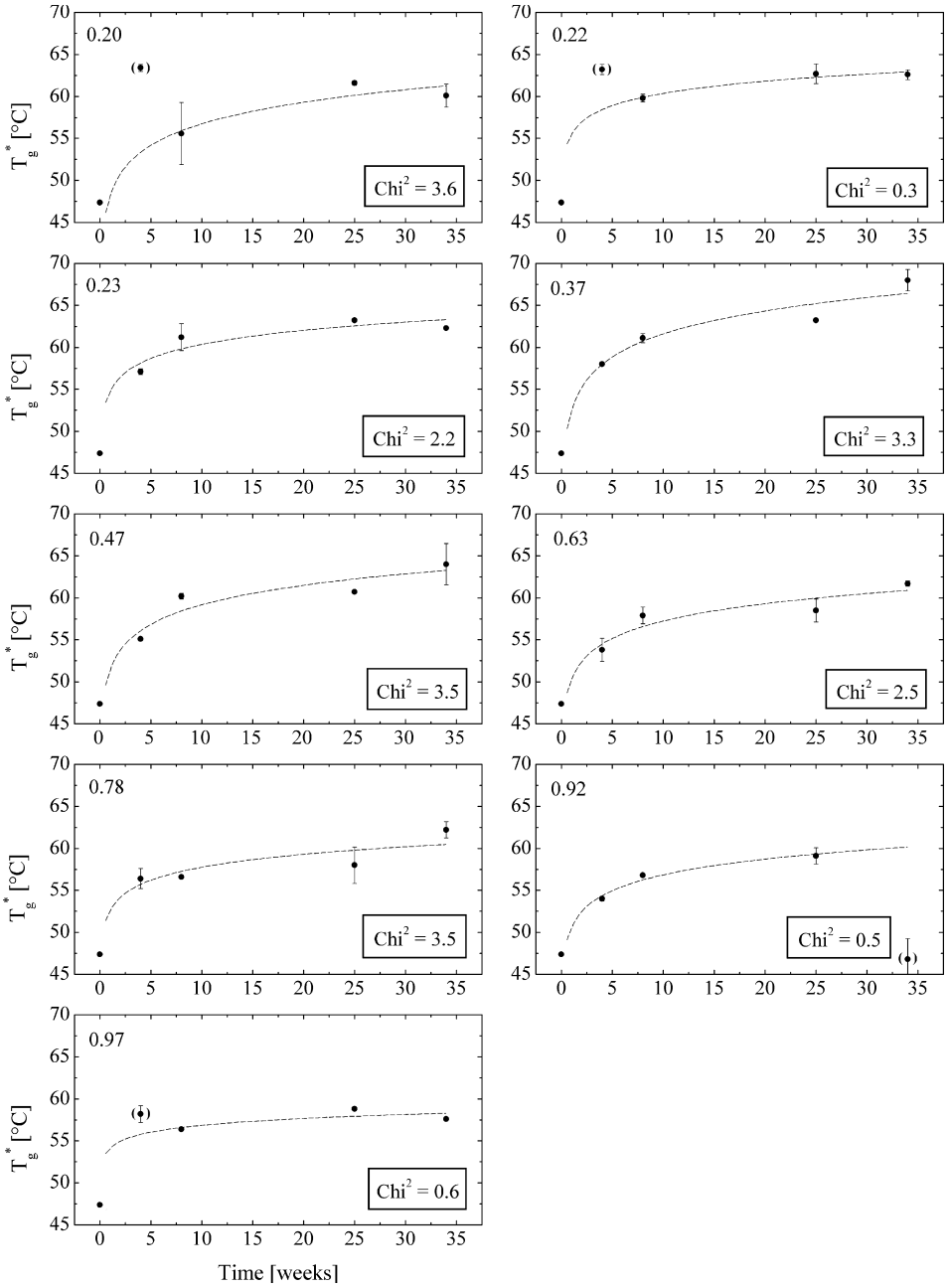

Fig. 5. Transition temperatures T_g^* of the oven-dried peat sample from the Warnowtal as a function of time for sample equilibration in RH of 0.20, 0.22, 0.23, 0.37, 0.47, 0.63, 0.78, 0.92, and 0.97. For each fitted logarithmic function, χ^2 is given in the plots. Data points in brackets were not included in the fitting procedure.

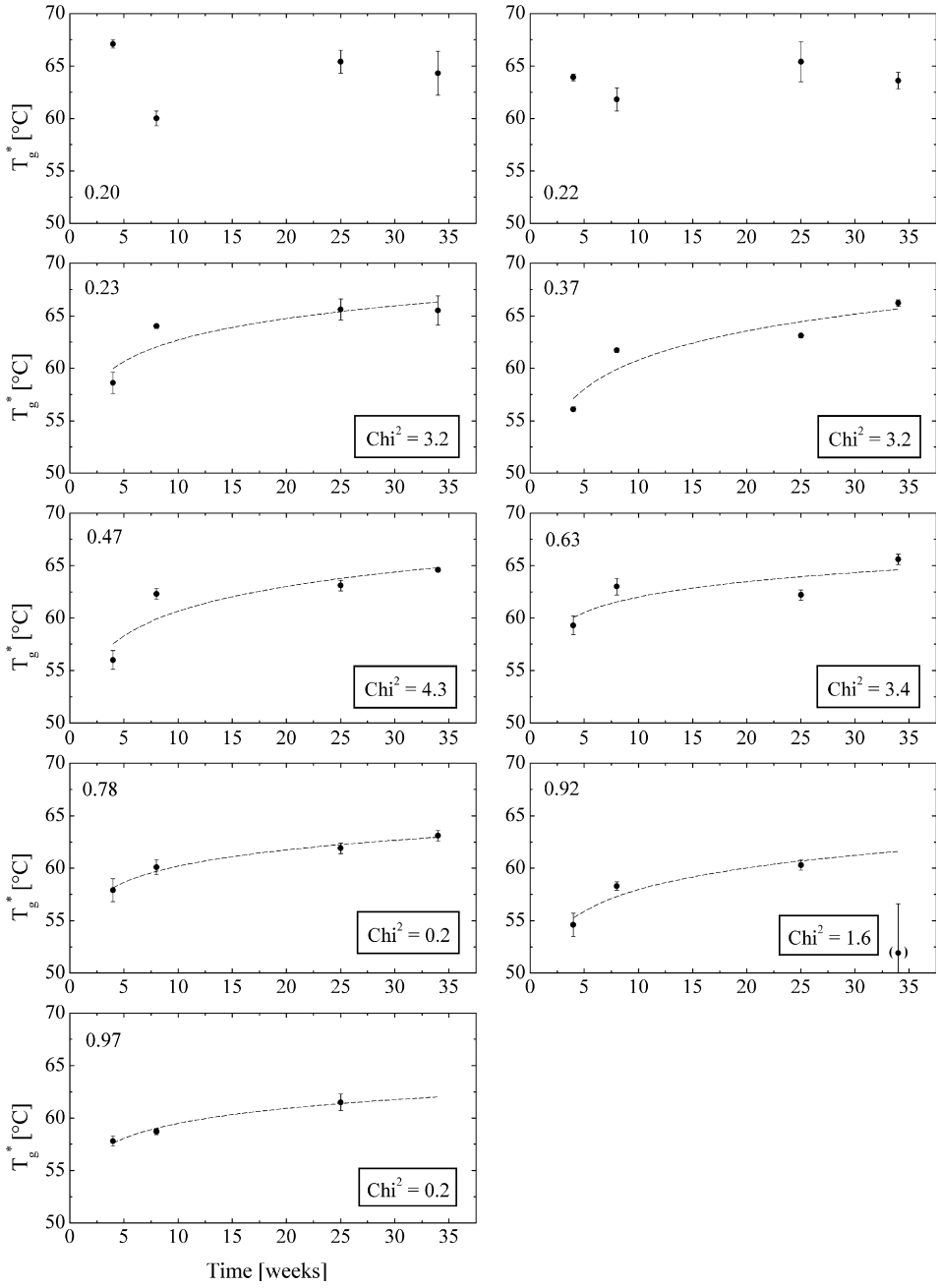

Fig. 6. Transition temperatures T_g^* of the air-dried peat sample from the Warnowtal as a function of time for sample equilibration in RH of 0.20, 0.22, 0.23, 0.37, 0.47, 0.63, 0.78, 0.92, and 0.97. For each fitted logarithmic function, χ^2 is given in the plots. Data points in brackets were not included in the fitting procedure.

from the Warnowtal, Schaumann (2005) observed for another peat sample a decrease of the transition temperatures in the first days after water attachment or water removal. This initial decrease was attributed to a fast disruption of water crosslinks occurring due to alterations of the water status (Schaumann, 2005). After the fast decrease, the transition temperatures slowly increased within a time scale of weeks under hydration as well as under dehydration conditions. Since for the peat sample investigated in this study, the transition temperatures were not recorded within days, but within months, a possible fast decrease of T_g^* occurring in the first days and subsequent slow T_g^* increases, which can only be identified in comparison to such an initial T_g^* decrease, could not be detected.

According to the HBCL model (Schaumann, 2005; Schaumann and LeBoeuf, 2005), the slow T_g^* increase for constant or increasing amounts of water within the SOM matrix can be explained by a strengthening of the degree of SOM crosslinking due to hydrogen bond bridges in the course of time. Following this model, an evaporation of water molecules out of the samples results in a decrease

of the amount of hydrogen bond-based crosslinks yielding a higher flexibility of the organic side chains and with that a lower transition temperature.

The transition temperatures T_g^* reached at the end of the sample equilibration experiment (Fig. 7) also reflect the influence of the different water contents caused by the different RH. If the moisture contents were reduced, T_g^* decreased probably due to the reduction of the number of hydrogen bond-based crosslinks. Especially, distinctly reduced water contents (below 6%), are linked to low transition temperatures T_g^*, which are more than 5 °C lower than the highest T_g^* values reached for water contents about 10% (Fig. 7). For further increase of moisture contents above 10%, the transition temperatures again show a decreasing trend, which may be a consequence of beginning swelling and with that plasticizing effects of the additional water molecules.

Besides the effects of water, structural relaxation of SOM may occur in the course of time. The increase of T_g^* for constant or increasing water contents (Figs. 5 and 6) presumably reflects the whole aging process of SOM, which includes both mechanisms. The absence of a T_g^* trend of the peat sample under drying conditions (0.20 and 0.22 RH in Fig. 6) may be due to the opposite effects of crosslink disruption and structural relaxation of the organic phase.

The slow increase of T_g^* under constant moisture status or hydration conditions is in accordance with physical aging studies, where the annealing peak temperatures of amorphous polymer materials increase linearly with $\log t_a$ (Shogren, 1992; Montserrat, 1994; Chung et al., 2004). For different starches, Chung et al. (2004) found that the annealing peak temperatures are positively correlated with the glass transition temperatures T_g, so that a logarithmic dependence of T_g or T_g^* on the aging time can be expected, too. The results of the sample conditioning in different RH indicate that the transition temperatures of SOM increase with a very slow rate: for the air-dried peat samples, T_g^* rose by (7 ± 2) °C within 30 weeks, and for the oven-dried peat samples, T_g^* rose by (13 ± 1) °C within 34 weeks. The slow increase of the transition temperatures T_g^* of soil samples may reflect the heterogeneous structure and high crosslinking density of SOM.

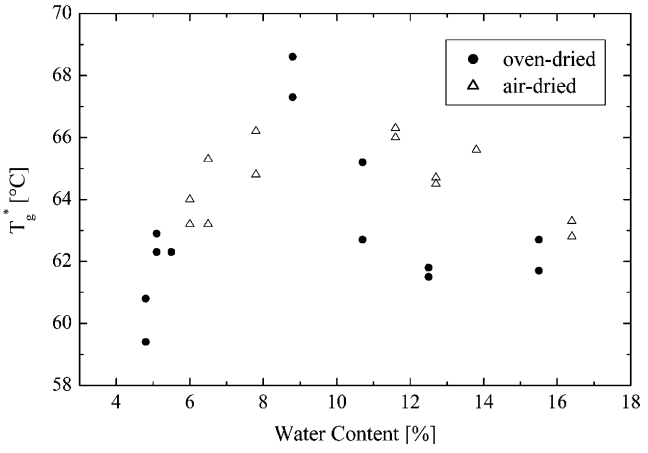

Fig. 7. Transition temperatures T_g^* of the oven-dried and the air-dried peat sample from the Warnowtal as a function of the water contents reached 9 months after starting the sample equilibration in different RH.

The increase of T_g^* during sample conditioning in different RH (Figs. 5 and 6) can be described by logarithmic or exponential functions. But, because of the low number of data points, it is not possible to assign specific functions to the development of the transition temperatures in the course of time. To obtain comparability with other glassy polymers (Shogren, 1992; Montserrat, 1994; Chung et al., 2004), Figs. 5 and 6 exemplarily show the fitting results for the function:

$$T_g^* = T_{g0}^* + k \log(t) \quad (8)$$

where T_{g0}^* represents the transition temperature T_g^* at the beginning of the sample conditioning. The constant k characterizes the extent of the T_g^* increase during sample equilibration time (in weeks). Due to the higher T_g^* of the air-dried samples compared with T_g of the oven-dried peat sample, the original air-dried samples ($t = 0$) could not be included into these functions (Fig. 6). For both the oven-dried and the air-dried peat sample, k amounts to values between 3 and 9 °C and shows no interrelation to the RH used for sample equilibration. The T_{g0}^* fitting results, which also show no correlation to RH, are (52 ± 3) °C for the oven-dried and (54 ± 2) °C for the air-dried sample. The fitting of the T_g^* development in the course of time by exponential functions (not shown), likewise yields no significant differences between the oven-dried and the air-dried sample and no interrelations between the fitting parameters and RH. The time constants of the exponential functions are between 2 and 8 weeks for all sample conditioning variants. Due to the low number of data, no further quantitative information on the aging process and its dependence on the water status can be obtained the by the fitting results. The possibility to describe the T_g^* development as a function of $\log t_a$ implies that the changes of the glassy SOM matrix may depend in a comparable way on time as physical aging processes in synthetic polymer systems.

The results of the conditioning experiments point to an aging process of SOM, which occurs irrespective of the water content of the soil samples. Both structural relaxation of the glassy SOM matrix and crosslinking of SOM by water molecules are supposed to contribute to this process, as indicated by the differences between sample storage under hydration or drying conditions. For a more detailed differentiation between the effects of aging associated with structural changes of the organic molecules and those due to a change of the water content, further studies of various samples with different water retention characteristics of their humous substances are required. Especially, solid-state NMR measurements may help to elucidate the role of water crosslinks within the organic soil matrix.

5. Conclusions

The sigmoidal form of the water sorption isotherms are in accordance with the HBCL model for SOM (Schaumann, 2005; Schaumann and LeBoeuf, 2005): they indicate antiplasticizing effects of water for low moisture contents, while SOM swelling and plasticizing govern the sorption process for high water contents.

The study has shown that the glass transition behavior of SOM in unfractionated soil samples is strongly influenced by time and thermal history. The shift of glass transition-like step transitions to higher temperatures during sample storage below T_g^* points to an aging process comparable to synthetic polymers. This process is distinctly affected by alterations of the moisture status of the soil samples. A comprehensive understanding of the aging process of SOM most probably represents an important key to predict the aging of contaminants in soil, so that further studies dealing with the influence of time and other factors of influence, as e.g., moisture status and temperature, on the glassy organic matrix are required.

Acknowledgments

We thank Katharina Knobel for the performance of many DSC analyses and Stephan Rosenkranz, who conducted a part of the experiments. The authors thank Prof. Rotard for the possibility to use the Environmental Chemistry laboratories at TU Berlin, where both authors were employed until recently. This study was funded by the DFG (research group INTERURBAN; project SCHA 849/4).

Associate editor: Donald L. Sparks

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