ELSEVIER

Thermomechanical analysis of air-dried whole soil samples

Gabriele E. Schaumann [a],[*], Eugene J. LeBoeuf [b], Rossanne DeLapp [b], Julia Hurraß [a]

[a] *University of Technology Berlin, Institute of Environmental Technology, Department of Environmental Chemistry,
KF3, Straße des 17. Juni 135, D-10623 Berlin, Germany*
[b] *Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN, USA*

Abstract

Macromolecular characteristics of organic matter in soil can greatly influence the sorption behavior of organic compounds. Previous investigations of the macromolecular nature of whole soil samples by differential scanning calorimetry (DSC) revealed step transitions in air-dried soil samples, which do not fully mimic typical glass transition behavior. This work further explores these step transitions through a second, independent method: thermomechanical analysis (TMA). TMA was validated with respect to detection, localization, and quantification of the step transitions in whole soil samples. TMA was found to sensitively detect the transitions, indicating sample softening near the step transition (T_g^*), while localization of T_g^* by TMA appears to be accurate in pellets only. Quantification via difference between coefficients of initial expansion and final compression, respectively, is favorable for weak transitions, where the sensitivity of DSC is too low to obtain reliable results.

Although the nonreversing nature of the step transition is atypical for glass transitions, the observed matrix softening suggests changes in matrix rigidity near T_g^*. This softening is hypothesized to be associated with water bridging individual soil structural units. The slow, nonreversing changes in soil rigidity are expected to affect the sorption behavior of organic contaminants, and the increase in compressibility further suggests relevance for soil mechanical properties.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Soil organic matter; Thermomechanical analysis; Differential scanning calorimetry; Glass transition; Physical aging

1. Introduction

Similar to synthetic organic macromolecules, natural organic matter (NOM) is suggested to consist of glassy and rubbery domains. Glassy domains, described as rigid, condensed organic matter, are considered responsible for slow desorption, non-Fickian diffusion, non-linear sorption, and sorption/desorption hysteresis, whereas rubbery domains may be responsible for increased diffusion rates, linear sorption, and partitioning-like processes [1]. The relevance of glassy domains in NOM for sorption of organic compounds has meanwhile been shown in a number of studies [2–4]. Glass transition behavior has been detected with differential scanning calorimetry (DSC) in several NOM fractions and in a small number of soil samples [3,5–7]. Complementary to

these findings, two types of step transitions have been identified in a peat soil [8,9]: a weak transition at 17–37 °C in dry and thermally pre-treated peat, which is comparable to the transitions found in NOM samples and corresponds to typical glass transitions [3,5–7], and a stronger transition at 60–70 °C, which is detectable only in water-containing peat. The latter resembles a glass transition, but shows atypical behavior: the transition mimics the form of a step transition in hermetic systems, but represents a rather continuous transition in open systems [9]. The transition occurs neither in a second, immediately subsequent DSC run nor following thermal pretreatment nor in the cooling cycle. It, however, reoccurs following a storage period [9]. The nature of this transition is discussed in detail in Refs. [8,9] and most probably is linked with a decrease in matrix rigidity near the transition temperature, which we refer to as T_g^* in this context to emphasize the irreversible nature of the transition. It was concluded that an additional mechanism besides temperature-induced decrease

in matrix rigidity may be responsible for the observed transition. Water bridges between individual structural units are believed responsible for the unexpected behavior, providing explanations to all unanticipated characteristics observed by DSC [8,9]. From the viewpoint of matrix rigidity, water may act in an antagonistic manner as a short-term plasticizer and long term antiplasticizer in the soil organic matrix [8,9]. The antiplasticizing function of water is unexpected, but has been observed also in starch [10], in a meat-starch extruded matrix [11], and in polypropylene oxide [12]. In the case of the peat sample employed in our work, water was hypothesized to bridge the soft segments and thus increase matrix rigidity [8,9]. For an improved understanding of the processes underlying the observed transitions and their dependence on water content and time, the hypothesized changes in matrix rigidity [8,9] requires verification by an additional, independent method.

Thermomechanical analysis (TMA) commonly serves as a complementary thermoanalytical method to gain further evidence of glass transition behavior [13,14]. While DSC possesses the advantage of great temperature accuracy, TMA is generally more sensitive to glass transitions than DSC [15]. It displays a wide range of useful application to the characterization of materials. The deformation or the dimension change of a sample (expansion, contraction) is measured under a defined load (static or dynamic) as a function of time or temperature [16]. From TMA, data can be obtained as diverse as transition temperatures, thermal expansion characteristics, modulus, viscoelastic properties, thermal stability, and liquid–solid interactions as functions of temperature and time [17]. The most common applications of TMA are expansion [18] and penetration [19] measurements. Glass transitions may be identified by a sudden increase in the linear expansion coefficient α [14,20], by a reduction of sample volume or increase of penetration [13,21,22], or by sample softening [16,23]. While the flow transition of polymers proceeds at temperatures above the main (glassy to rubbery) transition [24], sample softening is also observed above [25], at [26,27], or below [27] the glass transition temperature. Observations of softening below the T_g is observed especially with high loads [27]. TMA has only recently been applied to verify glass transition behavior in NOM fractions and organic whole soils and sediments [5,7,9].

One problematic aspect of the study of whole soils by TMA is sample consistency. Generally, samples need to be dimensionally stable. Granular or powdery samples need to be stabilized, which is usually accomplished by melt-pressing [18]. Pellets or tablets of whole soil samples can only be produced if the material is sufficiently homogeneous and possesses fine particle size. Mineral soil samples consisting of organic and mineral particles are often not amendable to investigation in the pellet form. To investigate such granular material, the material may be filled into a glass receiver and the dimension change may be recorded directly from the granular material ("powder form") in the instrument's dilatometer mode.

The goals of this study are to (i) further investigate the transition mechanism and to verify the decrease in matrix rigidity hypothesized from DSC results, and (ii) validate the powder form TMA method for detection, localization, and quantification of thermal transitions in air-dried whole soil samples. We therefore compared TMA traces of a sample in pellet and powder form, and compared the transition parameters derived from TMA and DSC for nine soil samples.

2. Experimental

2.1. Soil samples

The samples used in this study include the B8 soil described by DeLapp and LeBoeuf [7], the peat described by Schaumann and LeBoeuf [9], a sandy forest soil sample from Chorin near Berlin [28], sandy soil samples from Berlin Tiergarten and a former sewage farm in Berlin-Buch [29] as well as Ah and Oh samples from Siberia [29]. Selected sample characteristics are provided in Table 1; for a more detailed description please refer to the respective references. The samples were air-dried and then stored in a water atmosphere of 76% relative humidity (RH) at 20 °C to obtain a reproducible moisture content.

Table 1
Properties of the investigated soil samples

Sample	Soil type	Soil texture	Organic matter content (%)[a]	Water content (%)[b]
Peat [9]	Peat soil from Rhinluch fen	–	55.2	12
Chorin (Ah) [28]	Cambisol	Sand	10.4	0.6
Siberia (Oh) [29]	Luvisol	Loam	49.8	3.0
Siberia (Ah) [29]	Luvisol	Loam	21.1	2.0
Siberia (Ah) [29]	Chernozem	Loam	15.1	1.1
Tiergarten 1 (5–10 cm) [29]	Heterogeneous anthropogenic soil from inner-city park	Sand	7.6	1.6
Tiergarten 2 (5–10 cm) [29]	Heterogeneous anthropogenic soil from inner-city park	Sand	8.8	1.2
Buch 1 (5–10 cm) [29]	Anthropogenic soil from former sewage farm	Sand	5.8	1.6
Buch 2 (5–10 cm) [29]	Anthropogenic soil from former sewage farm	Sand	5.3	1.4

[a] Related to the sample dry mass.
[b] Of the air-dried sample related to the sample dry mass.

2.2. Thermomechanical analysis (TMA)

TMA involved use of a TA Instruments Model 2940 Thermomechanical Analyzer (TA Instruments, New Castle, DE, USA) using the instrument's dilatometer mode at 2.5 K min^{-1} with a force of 10 mN (probe diameter: 4 mm in the dilatometer mode for powdery samples, and a 6.25 mm diameter probe in the macroexpansion mode for pellets) and nitrogen purge gas (99.0% purity from A-L Compressed Gases, Inc., Nashville, TN, USA). Lower heating rates are typically employed in TMA versus DSC due to the relatively low heat capacity of the sample and the fact that the rate of heat conductivity is affected by the relatively larger sample sizes normally used in TMA. Temperature calibration was conducted with indium and water, and dimension calibration was conducted with aluminum. Samples were used either in pellet form or powder form. The pellets were produced as described in Ref. [7]. Fifty to 140 milligrams of the samples investigated in powder form were placed in a glass receiver containing a layer of silica. The height of the sample layer was 4–8 mm.

The first TMA run characterizes the current state of the sample without thermal pre-treatment, while the second run characterizes sample characteristics in a defined, thermally pre-treated state [7]. The second run is thus comparable to the DSC thermograms published in Refs. [5–7], while the first run is comparable to the DSC thermograms of the thermally non-pretreated samples described in Refs. [8,9,29]. TMA experiments were conducted in open conditions. The thermograms reflect the effect of heating on the sample volume, measured as dimension change. Glass transitions typically reflect a significant change in the thermal expansion coefficient, α, and thus are often identified by a change in the thermogram slope [7]. Data were analyzed using Universal Analysis 2000 software (V4.1; TA Instruments). The transition temperature, T_g^*, was determined either from the intersections of straight lines before and after the transition (see Fig. 1) or by application of three tangent lines to the step in the first derivative of the TMA trace, with T_g^* representing the temperature at the half height of the central tangent line (see Fig. 2). The thermal expansion coefficient before the transition, α, and the compression coefficient, κ, after the transition were calculated from the slopes of the TMA traces before and after the transition, respectively.

2.3. DSC experiments

TA Instruments Model Q1000 DSC (TA Instruments, Alzenau, Germany) using a heating rate of 10 K min^{-1} from -50 to 110 °C with nitrogen as purge gas (50 mL min^{-1}) was employed for DSC analysis. Heat flow and temperature calibration was conducted with indium. Two to 20 milligrams of air-dried samples were placed into sample pans, and the pans were sealed hermetically before the DSC experiment. The samples were investigated without pretempering in the first DSC run. The DSC transition data thus refer to the atyp-
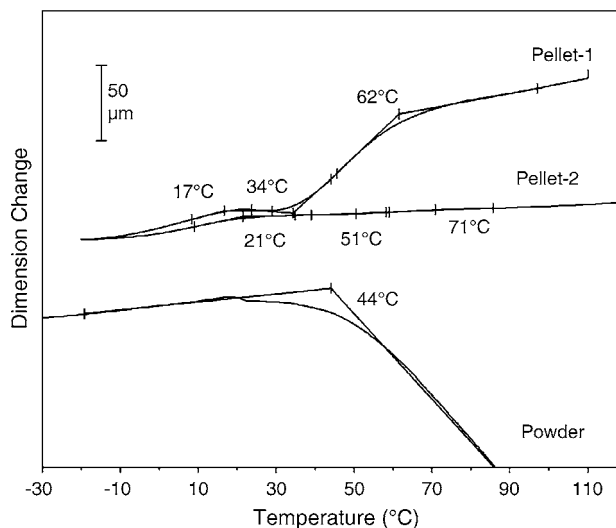

Fig. 1. TMA thermograms of the B8 soil described in Ref. [7] recorded in pellet form (first and second run) and in powder form (first run). The small step in the powder trace at 20 °C is not representative of other samples.
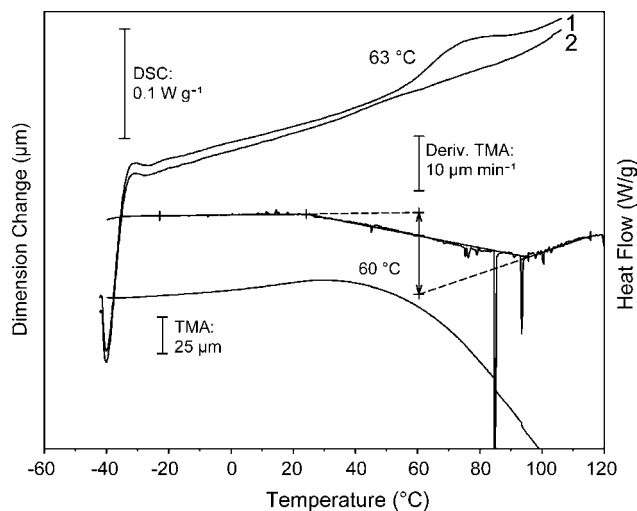

Fig. 2. Representative DSC (1: first heating; 2: second heating) and TMA thermograms (first heating) of an air-dried peat sample in powder form. The shape of the thermograms is representative for all investigated samples, and the respective T_g^* are summarized in Table 2.

ical transition described in Refs. [8,9,29]. DSC data were analyzed using Universal Analysis 2000 software (V4.1; TA Instruments). The change in the heat flow at T_g^* is indicated by an inflection in the thermogram. Operationally, three tangent lines are applied for evaluation (Fig. 2). T_g^* is defined as the temperature at the half height of the central tangent line. The change of heat capacity (ΔC_p) is calculated from the height of the central tangent line.

3. Interpretation of the TMA thermogram of the powdery sample

The soil sample is assumed to consist of organic matter showing thermal transitions in the investigated temperature

region and of (mainly mineral) particles without thermal transitions beside a continuous thermal expansion in the investigated temperature range. The latter samples are assumed to be thermally inert. TMA records the dimension change as function of temperature. The dimension change is associated with an overall sample volume change, dV, and the slope of the thermogram (dV/dT) represents the effective sample expansion or compression:

$$\frac{dV}{dT} = V_T\alpha \text{ (expansion)}, \qquad \frac{dV}{dT} = V_T\kappa \text{ (compression)} \tag{1}$$

V_T, α and κ represent the whole sample's total volume, effective expansion coefficient and compression coefficient, respectively. α (% K^{-1}) is positive, and κ (% K^{-1}) is negative. The TMA thermograms show quasilinear regions of different slopes (see Fig. 1), with a distinct change in slope at the transition temperature T_T. Below T_T (referred to as region I), an overall expansion is observed, which consists of the expansion of the thermally inert grains of the soil and the expansion of the organic matter:

$$\left(\frac{dV}{dT}\right)_I = \left(\frac{dV}{dT}\right)_{inert} + \left(\frac{dV}{dT}\right)_{OM,I},$$
$$\alpha_I V_{T,I} = \alpha_{inert} V_{inert,I} + \alpha_{OM,I} V_{OM,I} \tag{2}$$

α_{inert} and V_{inert} represent the expansion coefficient and the volume of the inert particles, respectively, and the index "OM,I" denotes the respective parameters of the organic matrix in temperature Region I. In Region II, i.e. above T_T, sample compression is observed in the powdery sample (Fig. 1), which is accounted for by an additional compression term:

$$\left(\frac{dV}{dT}\right)_{II} = \left(\frac{dV}{dT}\right)_{inert} + \left(\frac{dV}{dT}\right)_{OM,II} + \left(\frac{dV}{dT}\right)_{Se},$$
$$\kappa_{II} V_{T,II} = \alpha_{inert} V_{inert,II} + \alpha_{OM,II} V_{OM,II} + \kappa_{Se} V_{T,II} \tag{3}$$

The index "OM,II" denotes the parameters of the organic matrix in the temperature Region II, and κ_{Se} characterizes the compressibility of the whole sample due to sample settling ($\kappa_{Se} < 0$). The overall compression may be caused by the loss of intraparticle pore volume induced by a collapse of micropores in the softening organic matrix. The larger part of the compression is, however, likely caused by loss of interparticle pore volume, which is induced by deformation or relative movement of grains (sample settling) due to lubrication and particle softening. The compression is of irreversible character, i.e., it will induce changes in the sample which cannot reverse upon cooling. Therefore, the sample is in a different initial state in the second TMA run if κ_{Se} is not zero.

Although the expansion of the inert mineral matrix is unknown, it can be easily eliminated by subtracting Eq. (2) from Eq. (3). As all expansion and compression coefficients usually are considerably below 0.5% K^{-1}, the change of the absolute volumes of the individual compartments between

Region I and II can be neglected:

$$V_{i,I} \approx V_{i,II} \equiv V_i \tag{4}$$

with i = OM, T or inert, respectively. This results in

$$\kappa_{II} - \alpha_I = \Delta\alpha_{OM}\frac{V_{OM}}{V_T} + \kappa_{Se} \tag{5}$$

where $\Delta\alpha_{OM}$ represents the change in expansion coefficient of the organic matrix at the transition temperature T_T, e.g., due to glass transition. The difference $\kappa_{II} - \alpha_I$ can be calculated from the respective slopes of the TMA thermogram. If softening and lubrication are induced by the step transition observed with DSC, κ_{Se} as well as $\Delta\alpha_{OM}$ should be a function of the intensity of the step transition (I_G) and thus correlate with the apparent change of heat capacity, ΔC, determined by DSC. Additional effects are expected from the local pressure, which is a function of sample load and grain size and shape (e.g., edges). Based on these assumptions, both terms on the right handside of Eq. (5) are functions of I_G. Eq. (5) then transforms to:

$$\kappa_{II} - \alpha_I = (A + B(L))I_G \tag{6}$$

A and B represent constants of proportionality between I_G and α_{OM} or κ_{Se}, respectively. A correlation between ΔC and $\kappa_{II} - \alpha_I$ thus supports a connection between the TMA and DSC results. Eq. (3) also matches for the sample in the pellet form, where sample expansion as well as sample compression may be observed, depending on the sample load. In this case, κ_{Se} stands for the sample compression due to collapse of intraparticle micropores [5]. As long as such a collapse cannot be excluded, the TMA thermogram of a soil sample in the pellet form is expected to show irreversible characteristics, i.e., differences between the first and subsequent TMA runs. If the sample load is high, the compression term $\kappa_{Se}V_t$ may overbalance the expansion terms, and an overall compression will also be observed in the pellet (e.g., [5]).

4. Results and discussion

4.1. Pellet versus powder form

Fig. 1 shows two subsequent TMA thermograms of a pellet of the B8 soil described by Delapp and LeBoeuf [7]. The TMA traces reveal an increase in volume in the whole temperature range, and four regions with different slopes can be distinguished with transition temperatures of 15, 34 and 62 °C. The trace of the second run is qualitatively comparable to the first run, with significantly lower slopes and higher transition temperatures (21, 51 and 71 °C, respectively). In contrast to the multiple transitions indicated by TMA, only one single transition was detected by DSC at 52 °C after thermal pre-treatment [7]. This transition corresponds well with the transition temperature of 51 °C in the second TMA run. The more detailed transition structure of the TMA thermogram as compared to the single DSC transition corresponds

to observations that TMA usually shows a more complicated thermogram structure than DSC [18,20]. The lower slope above 62 °C (region III) may be explained by a beginning flow transition, but further experiments are required for a final interpretation. For a more detailed discussion of the pellet TMA thermograms please refer to DeLapp and LeBoeuf [7].

In contrast to the TMA thermograms of the pellet, the TMA trace of the B8 soil in powder form reveals only one significant transition, which extends from 20 to 60 °C. This transition indicates a broad expansion to compression transition. The exact localization of the transition point depends on the evaluation limits and varies within 44 ± 10 °C. The compression region can be explained by a collapse of the powdery sample packing due to particle softening and deformation [7] and is in accordance with literature observations describing reduction in volume or increased penetration due to softening at T_g [13,21,22,30]. The thermograms additionally revealed jumps, which can be attributed to sudden changes in the highly heterogeneous sample packing. In the second run, the dimension changes are less pronounced, and the jumps are then in the same size of order as the dimension changes, making quantitative evaluation difficult (data not shown). The above-mentioned collapse is partly irreversible, as indicated by the distinctly less pronounced traces in the second TMA run.

Commonly for pellet and powder forms, first and second thermal cycles show comparable behavior, but to a much less pronounced extent in the second run. This indicates irreversible changes for both sample forms, which may be caused by the high temperature, by water evaporation, or by irreversible changes in the inter- and intraparticle pore volume. There are, however, two basic differences between the TMA traces of the pellet and the powder sample.

(i) Expansion in the powder sample is observed only below the transition temperature, while the pellet form reveals expansion regions throughout the thermogram. The lack of expansion regions above the transition temperature indicates that the sample compression in the first run is not complete and leaves behind a number of interparticle pore spaces for subsequent runs. It would indeed be improbable that the overall sample compression in the powder sample during the TMA run (sample load pressure: 800 Pa) attains the same magnitude as pellets pressed at 200 MPa.

(ii) The powder sample reveals only one transition as compared to three transitions in the pellet form, and the transition in the powder sample is significantly broader than in the pellet form. The broadness of the transition may be explained by the overlay of the three transitions observed in the pellet, but it may also be caused by additional fuzziness due to the antagonistic effects of particle expansion on the one hand and sample settling on the other hand. It is, however, improbable that these effects account for the total broadening of the transition as compared to the DSC and the TMA (pellet) thermograms. The broadening suggests a rather continuous transition in the powder form extending over a significantly wider temperature range than in the pellet. This suggests that particle softening and particle expansion represent two different expressions of the transition with different thermal profiles, and their overlay leads to an overall broad transition.

We conclude that transitions can be identified in the same temperature range as for the pellet form. The exact localization of the transition temperature is, however, difficult, and quantification of α_{II} after the transition is impossible due to the overlay with the sample settling. Interpretation of the underlying processes remains difficult due to the overlay of a number of unknown processes.

Evaluation of this information provides reason to suggest additional questions. (1) Is the expansion to compression transition in the TMA traces of air-dried powder whole soil samples supportive of glass-like transition behavior in the respective samples despite its nonreversing characteristics? (2) To which extent do quantification of T_g and intensity in change in TMA lead to comparable results in TMA and DSC? To answer these questions, TMA thermograms of nine air-dried soil samples, which can only be investigated in powder form, are compared to the results obtained from the respective DSC thermograms, and parameters of quantification are compared between TMA and DSC.

4.2. Detection and localization of transitions

Fig. 2 illustrates well representative DSC and TMA (powder form) thermograms of the air-dried peat sample described in Ref. [9]. The DSC thermograms illustrate an initial (1) and an immediately subsequent second (2) run. The significant transition at $T_g = 63$ °C disappears in the second run as described and discussed in Refs. [8,9]. Thermogram evaluation was conducted in two manners: (A) interpretation of the transition as a pure step transition (right tangent line starts at 95 °C), and (B) the evaluation of the transition as a step transition with enthalpic overshoot peak (right tangent line starts at 105 °C). From the shape of this individual thermogram, both interpretations are possible; the evaluation of a larger number of high organic soil samples, however, suggests that the step transition is accompanied by a more or less significant overshoot peak [29]. Peak position and T_g increase with storage time under constant external conditions [8] and thus indicate processes comparable to physical aging in the organic matrix, although the annealing peak is not as strongly pronounced as expected for synthetic organic polymers.

The DSC step transition corresponds well to the expansion to compression transition at 60 °C in the TMA trace. The jumps in the TMA trace between 80 and 90 °C likely indicate unavoidable re-arrangements of the highly heterogeneous sample packing. While the transition in the DSC trace extends from above 40 °C to below 70 °C, TMA indi-

Table 2
Summary of transition temperatures (T_g^*) for the transitions determined by standard DSC and TMA measurements (powder form). α_I corresponds to the expansion coefficient below T_g^*, and κ_{II} corresponds to the apparent compression coefficient above T_g^*

Sample [reference]	T_g^* (TMA) (°C)	α_I (% K^{-1})	$-\kappa_{II}$ (% K^{-1})	T_g^* (DSC) (°C)	ΔC (J g^{-1} K^{-1})
Peat [9]	60 ± 10	0.0067 ± 0.0004	0.0518 ± 0.0036	65 ± 2	0.10 ± 0.02^b
Chorin (Ah) [28]	32 ± 10	0.0024 ± 0.0001	0.0062 ± 0.0004	64 ± 1^a	0.01 ± 0.01^a
Siberia (Oh) [29]	54 ± 10	0.0070 ± 0.0012	0.0492 ± 0.0034	63 ± 1	0.10 ± 0.03^b
Siberia (Ah) [29]	44 ± 10	0.0031 ± 0.0002	0.0130 ± 0.0009	59 ± 1	0.04 ± 0.01
Siberia (Ah) [29]	43 ± 10	0.0030 ± 0.0002	0.0123 ± 0.0009	47 ± 1	0.01 ± 0.01
Tiergarten 1 (5–10 cm) [29]	42 ± 10	0.0029 ± 0.0002	0.0105 ± 0.0007	64 ± 3^a	0.01 ± 0.01^a
Tiergarten 2 (5–10 cm) [29]	34 ± 10	0.0025 ± 0.0001	0.0137 ± 0.0010	n.d.	n.d.
Buch 1 (5–10 cm) [29]	31 ± 10	0.0026 ± 0.0002	0.0051 ± 0.0004	53 ± 3^a	0.01 ± 0.01^a
Buch 2 (5–10 cm) [29]	36 ± 10	0.0025 ± 0.0002	0.0052 ± 0.0004	n.d.	n.d.

The errors denote the estimated maximum error of evaluation. n.d. denotes not detected.
 [a] Weak transition.
 [b] With consideration of relaxation peak.

cates a broad continuous transition, ranging from 20 to 90 °C as illustrated by the first derivative of the TMA trace in Fig. 2. The broadness of the transition in the TMA thermogram is representative of all investigated samples.

Table 2 summarizes transition data derived from DSC and TMA thermograms for nine soil samples. The table compares transition temperatures (T_g^*) as well as ΔC for DSC, α_I and κ_{II}. While TMA reveals significant transitions in all samples, DSC identifies step transitions in seven out of nine samples, and all samples from Berlin-Buch and Tiergarten revealed only weak transitions in DSC. Transitions are thus identified in TMA even in cases where DSC reveals only weak transitions or no transition, which underscores the higher sensitivity of TMA than DSC [15].

The transition temperatures determined by TMA range from 31 to 60 °C with errors of ± 10 °C resulting from the broadness of the transition. The broadness indicates the lack of a distinct transition temperature and suggests a rather continuous process indicated by TMA. T_g^* (TMA) is lower than T_g^* (DSC) in all cases with differences of up to 35 °C. Considering the high error of T_g^* (TMA), however, the size of these differences is not significant. The lower transition temperatures can be explained by the lower heating rate in the TMA experiment [20,25,31] and by the mechanical stress applied in TMA, as T_g^* (*TMA*) is commonly reduced with increasing load [20,26]. No significant trend was found between T_g^* (DSC) and T_g^* (TMA). This may be due to different impacts of the load on the transition process in the samples, and further illustrates that the transition affects different material characteristics in a similar, but not exactly equal, manner. It is interesting to note that the TMA thermograms of the oven-dried B8 soil (Fig. 1) are comparable to the thermograms of the air-dried samples (Fig. 2). This may suggest that water was present in the oven-dried sample. The B8 sample may have absorbed low amounts of water between oven-drying and start of the TMA measurement due to the unavoidable open conditions of the TMA experiment and the relatively high relative humidity in the laboratory. Whether or not water was present in the B8 sample, the extent of expansion to compression appear comparable to the air-dried samples, which

contain larger amounts of water. This suggests that, if at all, the presence, rather than the amount of water, may lead to broadening of the TMA thermogram.

4.3. Quantification of the transition intensity

Common measures for the transition intensity (I_G) include the change in specific heat capacity (ΔC) from DSC, and the change in volume expansion coefficient ($\Delta \alpha$) from TMA. Due to the overlay of particle expansion, sample softening and settling of the sample packing, a determination of the expansion coefficient of individual particles is not possible from powder form TMA measurement. The apparent softening of the sample may, however, serve as an indirect tool to quantify the transition intensity as described in Section 3. The difference ($\alpha_I - \kappa_{II}$) between the initial expansion coefficient and the apparent compression coefficient after the transition could be taken as a measure for the transition intensity.

To test this hypothesis, ($\alpha_I - \kappa_{II}$) (TMA) was plotted as function of ΔC (DSC) in Fig. 3. The plot indicates a significant correlation between both parameters ($P = 0.01$) and thus
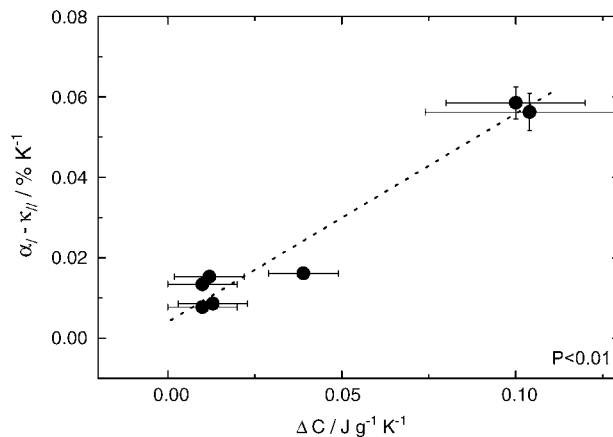

Fig. 3. Comparison of transition intensity parameters determined by DSC (ΔC) and TMA ($\alpha_I - \kappa_{II}$) for selected soil samples.

supports the use of $(\alpha_I - \kappa_{II})$ as a measure of transition intensity. The significance of the correlation is, however, determined mainly by the two datapoints at $\Delta C > 0.1\,\mathrm{J\,g^{-1}\,K^{-1}}$. The plot shows that $(\alpha_I - \kappa_{II})$ varies in the low ΔC range, where changes of ΔC were no longer significant due to the lower sensitivity of DSC. TMA may thus serve as a tool to estimate the transition intensity of weak transitions in powder samples, but a quantitative comparison between data of DSC and TMA remains difficult. The current scattering shows that calculation of ΔC from $(\alpha_I - \kappa_{II})$ may result in large errors for individual samples, even if the relation between ΔC and $(\alpha_I - \kappa_{II})$ is investigated for a larger sample set.

TMA thus represents a highly sensitive method to detect transitions in samples in pellet as well as powder form. Localization is accurate in pellets, but not in powder samples, where a broad transition range is observed. A source of error for the quantification of the transition intensity may be the mineral content of the samples, which is expected to additionally affect the apparent compressibility. This makes DSC more favorable for the quantification of stronger, more easily detected transitions. Quantification is more favorable from TMA measurements for weak transitions, where DSC is less sensitive.

While DSC points to changes in sample specific heat capacity, TMA indicates an apparent sample softening in the powder form and an increase in expansion in the pellet form. These characteristics are typical for glass transitions, and the observed softening supports the hypothesized decrease in matrix rigidity around T_g^*. The irreversibility of the transitions, however, underlines the atypical characteristics observed with DSC [8,9]. It supports the conclusion that an additional (physicochemical) process may be involved in the changes in matrix rigidity, which may be explained by the slow formation of water bridges between individual soft units of the matrix [8,9]. The TMA results further indicate that the transition proceeds continuously, i.e., not at a distinct transition temperature, in open systems. Changes in matrix rigidity – indicated here by changes in compressibility – thus also proceed at ambient temperatures. Results of this and other studies [8,9,28,29] show that changes in temperature as well as in water content or external humidity induce changes in the transition behavior of humous soil samples and may indicate slow matrix relaxation processes. The mechanisms involved in these processes are currently far from being understood or quantified. They illustrate, however, the need to address such processes while exploring sorption and transport phenomena in the upper soil layers. Thermomechanical analysis provides evidence that soil-relevant mechanical characteristics like soil compressibility may be directly affected by the glass transition behavior. The investigation of glass transitions thus may represent a means for further understanding soil compaction in agricultural soils.

Acknowledgements

References

[1] E.J. LeBoeuf, W.J. Weber Jr., Environ. Sci. Technol. 31 (1997) 1697–1702.
[2] B. Xing, J.J. Pignatello, Environ. Sci. Technol. 31 (1997) 792–799.
[3] E.J. LeBoeuf, W.J. Weber Jr., Environ. Sci. Technol. 34 (2000) 3623–3631.
[4] Y. Lu, J.J. Pignatello, J. Environ. Qual. 33 (2004) 1314–1321.
[5] K.D. Young, E.J. LeBoeuf, Environ. Sci. Technol. 34 (2000) 4549–4553.
[6] R.C. DeLapp, E.J. LeBoeuf, K.D. Bell, Chemosphere 54 (2004) 527–539.
[7] R.C. DeLapp, E.J. LeBoeuf, J. Environ. Qual. 33 (2004) 330–337.
[8] G.E. Schaumann, Colloids Surfaces A: Physicochem, Eng. Asp. 265 (2005) 163–170.
[9] G.E. Schaumann, E.J. LeBoeuf, Environ. Sci. Technol. 39 (2005) 800–806.
[10] Y.P. Chang, P.B. Cheah, C.C. Seow, J. Food Sci. 65 (2000) 445–451.
[11] C.I. Moraru, T.C. Lee, M.V. Karwe, J.L. Kokini, J. Food Sci. 67 (2002) 3396–3401.
[12] J.L. Illinger, Polym. Sci. Technol. (Plenum) 10 (1977) 313–325.
[13] S.E. Keinath, R.F. Boyer, J. Appl. Polym. Sci. 26 (1981) 2077–2085.
[14] J.B. Henderson, W.D. Emmerich, J. Thermal. Anal. 37 (1991) 1825–1831.
[15] H.R. O'Neal, S. Welch, J. Rogers, S. Guilford, G. Curran, K.P. Menard, J. Adv. Mater. 26 (1995) 49–54.
[16] J. Malek, R. Svejka, Scientific Papers Univ. Pardubice Ser. A: Faculty of Chem. Technol. 2 (1996) 211–222.
[17] J.M. Barton, Anal. Proc. 18 (1981) 421–424.
[18] D.N. Bikiaris, G.P. Karayannidis, J. Appl. Polym. Sci. 60 (1996) 55–61.
[19] P.E.M. Allen, C.H. Lai, D.R.G. Williams, Eur. Polym. J. 29 (1993) 1293–1303.
[20] E. Fukuoka, M. Makita, Y. Nakamura, Chem. Pharm. Bull. 37 (1989) 2782–2785.
[21] D.L. Miller, R.H. Wildnauer, J. Invest. Dermatol. 69 (1977) 287–289.
[22] A. Schwartz, J. Thermal. Anal. 13 (1978) 489–497.
[23] T.H. Ng, H.L. Williams, Makromol. Chem. 182 (1981) 3323–3330.
[24] E.-J. Donth, Relaxation and Thermodynamics in Polymers: Glass Transition, Akademie Verlag, Berlin, 1992.
[25] J.B. Barr, I.C. Lewis, Thermochim. Acta 52 (1982) 297–304.
[26] T.J. Maurice, Y.J. Asher, S. Thomson, Adv. Exp. Med. Biol. 302 (1991) 215–223.
[27] C.M. Earnest, ASTM Special Tech. Publ. STP 1249 (1994) 75–87.
[28] G.E. Schaumann, E. Hobley, J. Hurraß, W. Rotard, Plant Soil 275 (2005).
[29] J. Hurraß, G.E. Schaumann, Environ. Sci. Technol., submitted for publication.
[30] R. Domingo, K. Gan, T. McKay, E. Zahora, Proceedings of the 49th International Wire and Cable Symposium, 2000, pp. 646–649.
[31] R. Huggett, S.C. Brooks, J.F. Bates, Lab. Pract. 33 (1984) 76–78.