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THERMAL METHODS OF ORGANIC MATTER MATURATION MONITORING DURING A COMPOSTING PROCESS

M. T. Dell'Abate[*], *A. Benedetti and P. Sequi*

Istituto Sperimentale per la Nutrizione delle Piante, Via della Navicella 2, 00184 Roma, Italy

Abstract

The possibility to use thermal analysis for a quick characterisation of chemical changes in the organic matter of composted materials was tested. Nine samples were taken at progressive stages of maturation from the same trench of a fully automated composting plant. DSC and TG were simultaneously performed in static air conditions on whole ground composts. Progressive stages in the composting process yielded samples whose DSC traces revealed appreciable modifications in thermal patterns that agreed well with quantitative data obtained from TG measurements. The ratio between the mass losses associated with the two main exothermic reactions (R1) showed a good sensitivity in detecting the changes in the level of stabilisation during the composting process. Thermal methods seem to be a valid comparative method in evaluating the level of bio-transformation of materials during a composting process.

Keywords: compost, DSC, organic matter, TG, thermal stability

Introduction

The use of compost in agriculture as soil amendment is one of the practices for the sustainable management of soils and it also contributes to recycle organic residues. In order that it is correctly applied to the soil, these products are to be processed properly, so as they reach a sufficient level of organic matter stability. Thus, phytotoxicity, root system related oxygen deficiency and any possible excessive nutrient release in the soil and carbon and nitrogen loss can be avoided [1–2]. Composting can be defined as the solid state aerobic degradation of organic waste, mainly of plant origin, and resembles the natural humification processes in the soil. Lignocellulose is the main component of plant cell walls and thus it is the quantitatively most important raw material in the composting process. The complete or partial degradation of organic compounds, carried out by a consortium of microorganisms, results in a complex and stabilised network of macromolecules, whose varying degrees of degradation are a maturation level peculiarity reached at the end point of the process.

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[*] Author for correspondence: Tel.:+39-6-7008721, fax: +39-6-7005711, e-mail: mt.dellabate@isnp.it

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Several parameters, based on chemical, biochemical, and physical-chemical methods, were proposed in order to evaluate the level of maturation and stabilisation in the compost [3–4], since compost maturity is difficult to be defined with just a parameter.

A few methods applicable to the whole samples are available so far. In particular, most chemical parameters are based on the measurement of humic-like compound formation, and thus they require extracting and fractionating procedures, which are often time consuming. The possibility to use analytical techniques which are applicable to the whole sample, without pre-treatment, is therefore of great interest. In this context, thermal analysis of thermogravimetry (TG) and differential scanning calorimetry (DSC) were used for a maturity assessment in the compost [5–7], since naturally occurring lignocellulosic substrates analysed by thermal analysis, as well as pure bio-polymers, showed typical features [8–10].

The objectives of this study were as follows: (i) to study the changes of organic materials (agroindustrial residues) in thermal stability at progressive stages of bio-transformation and (ii) to verify the sensitivity of some parameters, deduced from both the TG and the DSC measurements, in monitoring organic material transformation during the composting process.

Materials and methods

Nine samples were taken at progressive stages of maturation from the CAVIRO composting plant in Faenza (Italy). In this fully automated plant, wastes coming from various agricultural products, such as wine, fruit, sugar and cereals, are mixed according to their chemical composition and are aerobically processed. Along the trenches, a machine turns up the mixing compounds: it first mills and mixes the matter, then turns the mixing matter over and displaces it towards the ripening area. A detailed description of this process was reported by Papi and co-workers [11].

Sample 0, taken before composting, was found to have the following composition of starting materials: 35% centrifuged fruit-sludge, 35% grape-wood, 10% wood-chips, 10% chestnut rind and 10% recycled compost. The presence of recycled compost insured an adequate microbial content to initiate the bio-transformation process. Compost samples were taken every 7 days from the same trench: they correspond respectively to 7, 14, 21, 28, 35, 42, 49, 56 days from the beginning of the composting process.

Each compost test sample (2000 g) was obtained by collecting the materials taken from four randomly located points. The samples were oven-dried at 40°C and pieces larger than 60 mm were eliminated. Finally, samples were ground with a knife-mill and crushed to pass at 1 mm.

For the total organic carbon (C_{org}) determination, mineralization of the organic matter to CO_2 was carried out as follows: 100 mg of compost was treated with 20 mL of 1/3 M $K_2Cr_2O_7$ and 26 mL of 96% H_2SO_4 for 10 min at 160°C [12]. The organic carbon content was determined by back-titration with a solution of 0.2 N $FeSO_4$.

The total nitrogen content (N) was determined by dry combustion (LECO FP 228), and the C/N ratio was calculated. The ash amount was determined by combustion at 650°C in a furnace until a constant mass of samples was reached.

DSC and TG experiments were carried out with a Netzsch Simultaneous Analyser STA 409 equipped with a TG/DSC sample carrier supporting a type S thermocouple of PtRh10-Pt. Samples were analysed without any pre-treatment, except for manual grinding in agate mortar. The following conditions were employed: heating rate of 10°C min^{-1} from 20 to 1000°C, static air atmosphere, alumina crucible, calcined kaolinite as reference, sample mass about 32 mg. Heat production in the 'heat-flux' DSC was calibrated under the same conditions by using a sapphire standard and subtracting a baseline obtained by an additional run for the empty crucibles. The Netzsch applied software SW/c_p/311.01 was used for data processing.

Both chemical analyses and thermal runs were repeated 3 times for each sample analysed. Mean values of measures are reported in the Tables.

Results and discussion

Total N and total organic C contents of samples at different composting time are reported in Table 1. The change in the C/N ratio showed a 30% total percentage decrease. This value reflects both the aerobic decomposition of organic matter, due to biological processes, and its stabilisation during composting. The optimum value of the C/N ratio in the mixture of starting organic materials should be within the range of 35 to 20, in order to obtain a good rate of microbial degradation, while at the end of the process it reaches a balancing value. The C/N ratio is the widest used index of the compost stability, since it is more sensitive to chemical changes in the organic matter than either N or C contents alone.

Table 1 Ash, total N and total organic C contents, and C to N ratio. Values are referred to dry matter at 105°C

Composting time/days	Ash/%	N/%	C_{org}/%	C/N
0	13.2	2.08	49.5	23.8
7	14.8	2.28	48.7	21.4
14	17.3	2.25	46.5	20.7
21	16.2	2.29	47.0	20.5
28	20.0	2.44	45.4	18.6
35	16.6	2.17	47.0	21.7
42	20.5	2.67	43.2	16.2
49	23.1	2.51	42.0	16.7
56	26.2	2.49	41.3	16.6

The DSC curves of all samples contained a peak system consisting of: (a) an endotherm with a maximum temperature at 85–89°C, generally representative of dehydration reactions, since it is unlikely that a large quantity of organic volatile groups were lost in such a temperature range, and (b) two distinct exotherms, the first one within the 295–307 range, while the second one within the 436–469°C range. Such behaviour, according to the kinetics of thermal oxidative decomposition, indicated a two-step process. This thermal pattern was similar to that reported for cellulose, the main plant material component [10], although other classes of organic compounds are expected to contribute [13]. According to previous authors, the first exotherm could be attributed to aliphatics and the second, at the higher temperature, to the thermal breakdown of more aromatic moieties, either naturally occurring in the sample or resulting from molecular rearrangements [14]. Pyrolysis studies showed the contribution of long chained hydrocarbons and nitrogen compounds to the reactions above 400°C [15].

TG and DSC traces for samples taken at 0, 28 and 56 days of composting time are reported in Fig. 1 (a, b and c, respectively).

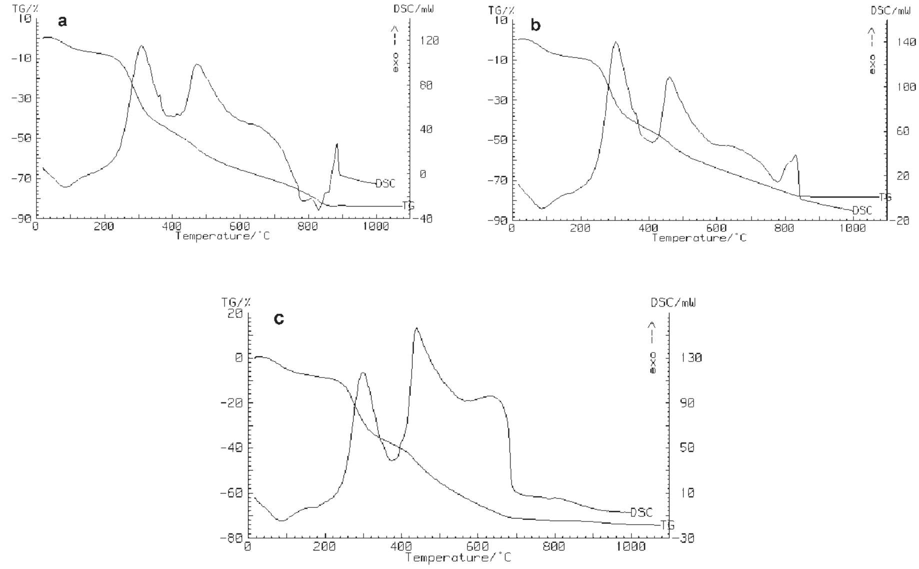

Fig. 1 DSC and TG traces related to the samples taken at 0, 28 and 56 days of composting time (a, b and c, respectively)

Progressive stages in the composting process yielded samples whose DSC traces revealed appreciable changes in thermal patterns. In particular, on the DSC curves corresponding to samples taken after 49 and 56 days of composting time, respectively, two dehydration process related endotherms were observed – the first one characterised by a temperature maxima at 87 and the second one at 167.8°C. This finding was confirmed by the two-step mass losses detected on both TG and its first derivative traces (DTG). The presence of different forms of hydration water in naturally occurring organic matrices, such as peat, was also previously demonstrated with the DSC and TG methods [16].

The combustion behaviour of samples coming from progressive stages of transformation revealed a temperature shift in both exotherm maxima: in particular, the peak temperature values of both the first and the second exotherms decreased with the composting time increasing (Table 2). These findings seem consistent with the change of sample composition during the composting process. Organic carbon content decreased because of microbial activity (CO_2 emission) and inorganic components increased, resulting in a progressive association with the organic matter that might changed the thermal stability of composted materials. Similar results were observed in derivative thermogravimetry (DTG) records of wheat straw composts [6], while the effect of metals on thermal behaviour of soil organic matter was found in podzol [17].

Table 2 Mean values of peak temperatures (°C). Mean standard deviations were 1.2, 3.3 and 2.5°C, respectively

Composting time/ days	1° endotherm	1° exotherm	2° exotherm
		T_p/°C	
0	85.4	306.5	468.5
7	86.1	301.1	464.6
14	84.9	304.1	464.6
21	85.5	298.6	463.7
28	87.3	302.2	459.6
35	86.1	306.0	451.2
42	87.4	309.8	448.8
49	87.5	294.8	437.3
56	87.6	294.7	436.2

A comparative inspection of the DSC traces revealed a decrease in the relative intensity of the first exotherm and a corresponding increase in the second one at progressive stages of the composting process. The presence of a more intense second exothermic peak is believed to be a distinctive character of humified organic matter [8] and was also been previously reported for both composts and soil organic matter extracts [7–18].

These exothermic reactions were associated with two distinct mass losses, due to organic matter combustion, on the TG and DTG records. Each decomposition step on the thermogravimetric trace was evaluated on the basis of the DTG characteristic parameters, such as both the onset and the end peak temperatures. Samples at more advanced stages of transformation gave different rates of mass loss on heating. In particular, the size of the first decomposition step decreased, while that of the second one increased with composting time (Table 3). Again, this provided an overall picture of the changes in chemical composition undergone by lignocellulosic materials during the mineralisation process, which was also demonstrated by the increased values of residue of combustion after the thermal run (Table 3). A similar trend was reported for organic soils with different degrees of humification [19].

Table 3 Mass losses (% of total sample) corresponding to the main exothermic reactions and content (%) of sample residue at 950°C. R1 refers to the 2° step mass loss to the 1° step mass loss ratio

Composting time/ days	Mass loss/% 1° step	Mass loss/% 2° step	R1	Residue/%
0	40.3	18.9	0.481	12.9
7	39.4	19.7	0.500	17.3
14	34.6	18.5	0.535	18.2
21	36.6	17.5	0.478	18.5
28	35.6	18.8	0.528	20.1
35	32.6	22.5	0.690	18.6
42	30.3	20.9	0.690	21.3
49	27.1	21.1	0.779	24.7
56	26.1	31.9	1.164	26.5

The ratio between the mass losses associated with the second and the first exothermic reactions (R1) was previously identified as a reliable parameter for evaluating the level of maturation of organic matter in composts [7]. This value indicates the relative amount of the thermally more stable fraction of organic matter with respect to the less stable one, without regard to either sample humidity or ash contents. During composting, the R1 ratio increased (Fig. 2), thus revealing a high sensitivity to the chemical changes induced by the bio-transformation of organic materials. In fact, the ratio was 2.5 times higher for the sample after 56 days of composting than in sample 0.

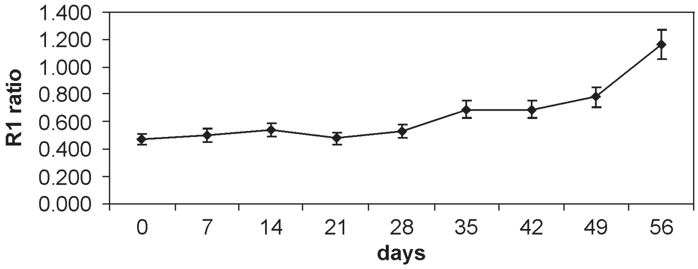

Fig. 2 Changes in the R1 parameter during the composting process. R1 refers to the 1° step mass loss to the 2° step mass loss ratio. Standard error bars are indicated

Conclusions

In this survey we have tested the possibility to use thermal analysis for a quick characterisation of the chemical changes in the organic matter of composted materials. Analysis of the results revealed the suitability of thermal methods to provide simple, quick and reliable information on organic matter stabilisation during the composting process of agroindustrial residua. The possibility to analyse the whole samples without any pretreatment, enables these methods can be used as routine tools in monitoring of composting process. In particular, quantitative data obtained from TG measurements agreed well with DSC patterns; the R1 ratio, which indicates the relative amount of the thermally more stable fraction of organic matter with respect to the less stable one, showed a good sensitivity in detecting the changes in the stabilisation level during the composting process. Nevertheless, further investigation needs to be carried out on a larger variety of products in order to define the influence of different raw starting materials on compost thermal patterns and, in particular, on the range of values of the proposed R1 ratio for the different materials. At the present stage of knowledge, however, thermal methods, and especially thermogravimetry, appear to be a valid comparative method in evaluating the bio-transformation level of the materials during a composting process.

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