Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 607–614

DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF COMPOSTED MATERIALS FROM DIFFERENT SOURCES

M. R. Provenzano[1], *A. Ouatmane*[2], *M. Hafidi*[2] *and N. Senesi*[1]

[1]Dip. di Biologia e Chimica Agroforestale ed Ambientale, Università di Bari, 70126 Bari, Italy
[2]Faculté des Science et Techniques, Beni Mellal, Morocco

Abstract

Differential scanning calorimetry (DSC) was applied to the study of material composted from sawdust, used coffee, farmyard manure and the organic fraction of domestic solid waste. Composting trials were carried out in Morocco and samples were collected after different periods of composting. The results obtained provided evidence that sawdust substrate is not a suitable source for composting due to the high content of lignin; samples from used coffee are characterized by a degree of aromaticity that is lower and a functional group heterogeneity that is higher than those of organic wastes from manure and the organic fraction of domestic wastes. The latter organic waste substrates appear to be easily degraded and humified and to give DSC curves that at the end of composting are vary close to those of native soil humic acids.

Keywords: composted materials, DSC, thermal characterization

Introduction

Composting is a process in which organic wastes of different origins and natures are transformed into relatively stable humic materials. This process involves various microorganisms, both aerobic and anaerobic. The main products of the process are CO_2, water, NH_4^+, a composite pool of microorganisms, minerals and stabilized organic matter, consisting mainly of humic-like materials. The composting process does not differ greatly from the natural transformation phenomena to which organic matter is subjected in soil, and consequently it is expected to have only a limited impact on the soil environment.

Composting products are of great interest in modern agriculture where agronomic practices cause substantial loss of soil organic matter; this loss should be rapidly replaced in order to restore the soil fertility functions relating to the quality and quantity of organic matter. The use of immature compost is well known to cause more adverse than beneficial effects on the soil environment and agricultural production. Evaluation of the maturity and the agrochemical properties of composted materials is important before composts can be used as soil amendments. However, there are currently no official or generally accepted regulatory standards for the evaluation

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

of organic amendment quality. A number of criteria and parameters have been proposed for testing the changes occurring in the organic material during its treatment. Evaluation of compost quality has been attempted by chemical methods, involving, for examples, the C/N ratio, the cation-exchange capacity, the degree of humification of organic matter, calculated as the percentage of humified compounds, humic acids and fulvic acids (HA+FA), with respect to the total extractable carbon, enzymatic and microbiological tests, biomass measurements, plant bioassays, etc. [1–11].

However, all these methods are indirect and often empirical. Thus, the use of rigorous and direct methods appears necessary. Spectroscopic methods including nuclear magnetic resonance, diffuse reflectance infrared Fourier transform infrared spectroscopy and fluorescence spectroscopy have been used directly on whole compost samples without any extraction [12]. Thermal analysis techniques such as thermogravimetry and differential scanning calorimetry (DSC) have been used to characterize soil organic matter and its humic fractions [13–18]. More recently, DSC analysis has been utilized to assess compost maturity, as a rapid, simple and reliable technique applied to whole compost samples [19–20].

The objective of the present work was to study the transformations of organic matter during the composting of different organic wastes, by using DSC in association with chemical analysis.

Material and methods

Composting trials

Four different organic wastes originating from Morocco were tested in this study: a) sawdust (Sc) of Cedrus spp., which is the main regional source of wood; b) used coffee grounds (Cf); c) freshly collected farmyard manure (Fm); and d) the organic fraction of domestic solid waste (Du). 5 kg of each sample was mixed and homogenized manually with 250 g of bird waste (C/N=2.5), used as a source of easy mineralizable nitrogen, and 500 g of local rock phosphate (Ca/P=2.8), used as a source of calcium and phosphorus. Composting trials were conducted in plastic boxes. Moisture was maintained at a level between 40 to 60% and was checked once a week with appropriate tensiometers. The temperature of the composting mass was controlled at a depth of 10 cm, daily for the first month, and then at 2 or 3-day intervals. The compost mass was occasionally turned and samples were collected after 20 (t1), 46 (t2), 76 (t3), 137 (t4), 197 (t5) and 302 (t6) days. Samples (about 200 g) were air-dried, ground manually in an agate mortar and stored at room temperature until analysis.

Chemical analysis

The pH was determined in a suspension of 2.5 g of compost in 50 ml of distilled water after stirring for 2 h. The ash content was determined by ignition of 1 g of sample at 550°C for 8 h. The total organic carbon (TOC) was calculated from the organic matter loss on ignition of each organic waste. Total nitrogen was determined by wet digestion (Kjeldahl method).

Humic substances (HS) were isolated by extracting 2 g of each compost with 200 ml of 0.1 N KOH for 2 h six times successively. The solution obtained from each extraction was centrifuged at 15 000 g for 15 min. The supernatant containing the dissolved HS was then collected and the residue was used for the next extraction. At the end of the six extraction steps, the supernatants were combined and filtered through Whatman paper. The filtrate was next acidified to pH ~2 with 3 N HCl. After flocculation for 24 h at room temperature, the precipitated HA were separated from the dissolved FA by centrifugation at 15 000 g for 15 min. The HA were re-suspended in 0.1 N KOH. The C content of the HA and FA were determined by wet oxidation with $KMnO_4$.

Thermal analysis

DSC was performed with a Perkin Elmer DSC 7 instrument equipped with an automatic thermal analysis program, on intact compost samples not subjected to any treatment or extraction. 5 mg samples were placed in an aluminum pan of 50 μl capacity and 0.1 mm thickness, and press-sealed with a not pierced aluminum 0.1 mm thick cover. An empty pan sealed in the same way was used as reference. DSC traces were recorded by heating the sample from 50 to 550°C at a rate of 20°C min^{-1} under a 20 cm^3 min^{-1} air flow. Indium was used as a standard for temperature calibration. Reproducibility was checked by running each sample in triplicate.

Results and discussion

Ash contents, N and C percentages, C/N percentage ratios and C_{HS}/C_{tot} ratios (i.e. the ratio of the carbon in the HS fractions to the TOC) are reported in Table 1. Evaluation of the C/N ratio is the traditional approach for the estimation of compost maturity. A decline from the initial value, which should not be >30 in the substrate, to a final value of <20, generally indicates an advanced degree of organic matter stabilization in the product. The C/N ratios exhibit different values, depending on the nature of the organic wastes. In particular, the N content is very low and the C/N values are very high for samples Sct1 to Sct6, and tend to decrease with increase of the duration of composting. These results can be ascribed to the high content of lignin, which is the component of soil organic matter most resistant to decomposition. Since lignin forms a three-dimensional polymer network of phenylpropane units with a complex and random structure, stringent conditions are necessary for their depolymerization and reversion to monomers. The N percentages in samples Cft1 to Cft6 are much higher than those for the Sc samples, and the C/N ratios are much lower. These results are related to the easily degradable organic components of the Cf substrate, which include fatty acids, heterocyclic compounds, carbohydrates, proteins, etc. For Dut1 to Dut6, the C percentage decreases, while the ash content and C_{HS}/C_{tot} ratio increase with increasing composting time. These results indicate a high rate of mineralization of organic matter, which is almost wholly mineralized at the end of composting, whereas only about half of the organic matter is humified. This behaviour can be ascribed to the nature of the Du substrates, which originated from the organic fraction of domestic wastes, and comprised mainly readily decomposable organic matter, mostly carbohydrates and proteins. For these materials, a shorter composting time (up to 137 days) is suggested, to limit the extended mineralization of the organic matter. The analytical results for the Fm composts are similar to those for the Du composts, although the original chemical compositions of the former are more complex than those of the latter.

Table 1 Ash content, N and C mass percentages, and C_{HS}/C_{tot} and C/N mass percentages ratios for the composts analysed

Sample	%Ash	%N	%C	C_{HS}/C_{tot}	C/N
Sct1	12.5	0.89	50.7	20.9	56.9
Sct2	13.3	0.51	50.1	17.5	98.2
Sct3	15.6	0.62	48.9	15.7	78.8
Sct4	16.6	0.58	48.3	14.4	83.3
Sct5	18.5	0.55	47.2	13.5	85.8
Sct6	20.5	0.51	46.1	13.0	90.4
Cft1	14.2	2.00	47.1	22.5	23.5
Cft2	16.5	2.19	45.8	27.5	20.9
Cft3	18.4	2.19	44.8	30.8	20.4
Cft4	23.1	2.37	42.2	36.7	17.8
Cft5	22.9	3.02	42.3	40.1	14.0
Cft6	25.1	3.55	41.2	40.7	11.6
Dut1	9.1	2.46	30.0	36.6	12.2
Dut2	13.5	2.55	28.5	34.7	11.2
Dut3	30.2	1.53	22.0	40.8	14.4
Dut4	49.6	1.81	16.6	51.8	9.2
Dut5	65.3	1.62	11.4	58.5	7.0
Dut6	71.1	1.44	9.4	47.8	6.5
Fmt1	32.6	1.65	30.3	36.3	18.4
Fmt2	36.1	1.51	28.7	36.5	19.0
Fmt3	41.3	1.44	26.3	33.8	18.3
Fmt4	47.2	1.44	23.7	40.4	16.4
Fmt5	48.1	1.68	23.5	39.8	13.9
Fmt6	52.5	1.82	26.1	32.5	14.3

The DSC technique has recently been applied to characterize HA and FA of various origins and natures, as well as humic-like materials derived from composts of different organic wastes [17–20]. A typical soil-HA DSC curve shows a strong endo-

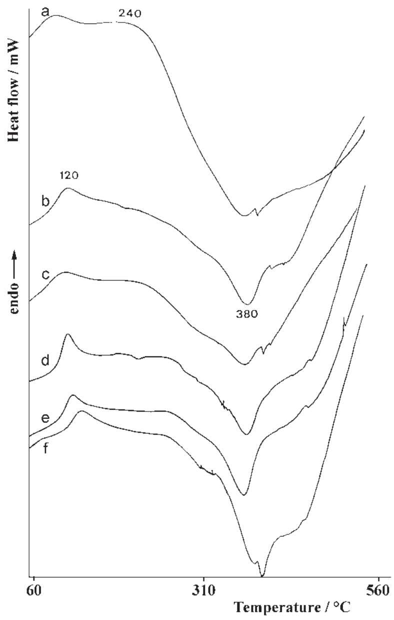

Fig. 1 DSC curves of composts from sawdust after different periods of composting:
a – 20 days; b – 46 days; c – 76 days; d – 137 days; e – 197 days and f – 302 days

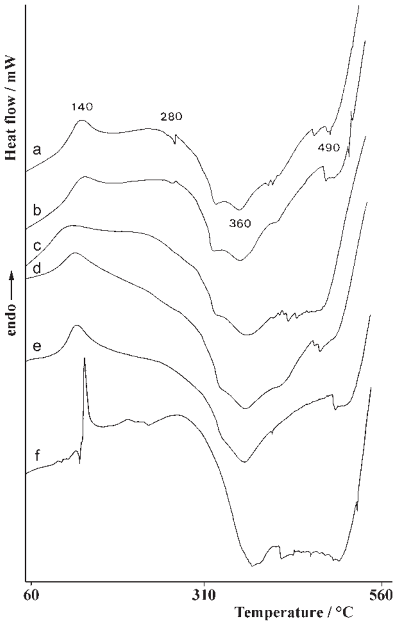

Fig. 2 DSC curves of composts from used coffee after different periods of composting:
a – 20 days; b – 46 days; c – 76 days; d – 137 days; e – 197 days and f – 302 days

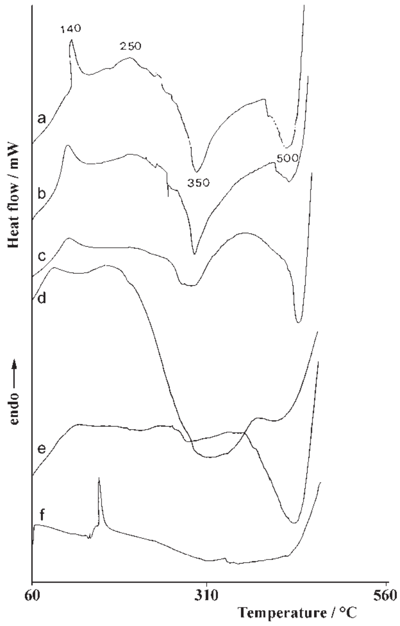

Fig. 3 DSC curves of composts from farmyard manure after different periods of composting: a – 20 days; b – 46 days; c – 76 days; d – 137 days; e – 197 days and f – 302 days

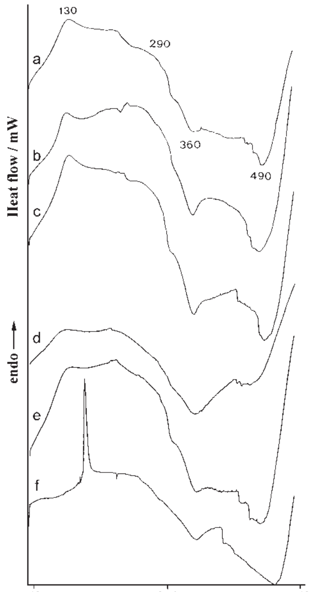

Fig. 4 DSC curves of composts from organic fraction of domestic solid waste after different periods of composting: a – 20 days; b – 46 days; c – 76 days; d – 137 days; e – 197 days and f – 302 days

therm in the low-temperature region (around 140°C), and an exotherm in the high-temperature region (around 500°C) [17]. These thermal effects have been assigned to dehydration and/or to the loss of peripheral polysaccharide chains and to oxidation and polycondensation of the aromatic nuclei of the molecule, respectively.

In addition to the previous effects, composted materials display a typical exotherm in the medium-temperature region (around 360°C), which is attributed to the loss of peptidic structures [19, 20]. The relative intensity of this exotherm seems to be related to the humification degree of the sample, and decreases with increasing composting time.

The DSC traces of the samples analyzed in this work depend on the nature of the substrate. The DSC curves of samples Sct1 to Sct6 (Fig. 1) present a very simple pattern, with only a broad endotherm at about 120°C and an exotherm at about 380°C, and no high-temperature exotherm. This result can be related to the predominant lignin structures and the consequent low aromatic character of the material. The minor differences exhibited by the DSC traces obtained for the materials after increasing composting time can be ascribed to the limited extent of transformation of these materials, which mainly contain chemically resistant components. The curves of samples Cft1 to Cft6 (Fig. 2) show several thermal effects due to the high heterogeneity of the substrate at the beginning of composting. With increasing composting time, the DSC shapes closely approach those of more homogeneous materials. Sample Sct6, collected at the end of the composting process, gives a sharp low-temperature endotherm at 140°C, similar to that of native soil HS.

The DSC curves of samples Dut1 and Dut6 and Fmt1 to Fmt6 (Figs 3 and 4) display similar trends with increasing composting time. In particular, samples collected at the beginning of the trial exhibit the typical exotherm in the medium-temperature region (350–360°C), previously observed for similar substrates. The intensity of this peak decreases with increasing composting time and it is not observed for the samples collected at the end of the trial, possibly because of the incorporation and stabilization of the peptidic structures in the humic macromolecules. Both samples Fmt6 and Dut6 exhibit a sharp low-temperature endotherm similar to that obtained for native HS. Thus, in addition to the medium-temperature exotherm, the latter endotherm can be utilized to evaluate the maturity of composted material derived from domestic wastes and manures.

Conclusions

Application of the DSC technique to the study of composted materials of different origins and natures has provided the following results:

a) The absence of the high-temperature exotherm from the DSC traces of the Sc samples, and the several thermal effects observed in the DSC traces of the Cf samples, suggest that they originate from wastes with a degree of aromaticity that is lower and a heterogeneity of the functional groups that is higher than those for the Du and Fm samples.

b) The Sc substrate does not appear to be a suitable source for composting, in consequence of the high content of lignin.

c) The Cf substrate can be readily degraded, becoming more homogeneous and humified by the end of the trial.

d) The Du and Fm substrates appear to be suitable sources for composting, as they are easily degraded and humified and give DSC that are very close to those of native soil HS by the end of composting.

In conclusion, DSC appears to be a suitable technique for evaluation of the maturity of composts obtained from different sources, and for the provision of useful information on organic matter evolution and stabilization during composting.

References

1 M. J. Blanco and G. Almendros, J. Agric. Food Chem., 42 (1994) 2454.
2 R. Barberis and P. Nappi, in The Science of Composting. M. De Bertoldi, P. Sequi, P. B. Lemmes and T. Papi, eds. Glasgow UK, Blackie Academic and Professional, 1996, Part 1, p. 175.
3 N. Senesi and G. Brunetti, in The Science of Composting. M. De Bertoldi, P. Sequi, P. B. Lemmes and T. Papi, eds. Glasgow UK, Blackie Academic and Professional, 1996, Part 1, p. 195.
4 J. L. Morel, F. Colin, J. C. Germon, P. Godin and C. Juste, in Composting of Agricultural and Other Wastes, J. K. Gasser, Ed., Elsevier, London 1985, p. 56.
5 E. I. Jimenez and V. P. Garcia, Agric. Ecosyst. Environ., 38 (1992) 331.
6 R. Jodice, Proc. International Symposium of Compost Production and Use, Instituto Agrario Provinciale, S. Michele all'Adige 1989, p. 363.
7 V. Chanyasak, A. Katayama, M. Hirai, S. Mori and H. Kubota, Soil Sci. Plant Nutr., 29 (1983) 251.
8 C. Ciavatta, M. Govi, L. Vittori Antisari and P. Sequi, J. Chromatogr., 509 (1990) 141.
9 C. Benny, P. G. Hatcher, Y. Hadar and Y. Chen, J. Environ. Qual., 25 (1996) 776.
10 A. Katayama and H. Kubota, Proceeding of the First Intern. Symposium on Composting (1995) p. 363.
11 C. Garcia, H. Teresa and F. Costa, Soil Sci. Plant Nutr., 37 (1991) 399.
12 N. Senesi, T. M. Miano and G. Brunetti, in Humic Substances in Terrestrial Ecosystem, A. Piccolo ed., Elsevier, Amsterdam 1996, p. 531.
13 P. Leinweber, H. R. Schulten and C. Horte, Thermochim. Acta, 194 (1992) 175.
14 H. Kodama and M. Schnitzer, Soil Sci., 5 (1970) 265.
15 M. B. Holder and S. M. Griffith, Can. J. Soil Sci., 63 (1983) 151.
16 U. Reh, W. Kratz, G. Kraepelin and C. Angehrn-Bettinazzi, Biol. Fertil. Soils, 9 (1990) 188.
17 M. R. Provenzano and N. Senesi, J. Therm. Anal. Cal., 57 (1999) 517.
18 M. R. Provenzano and N. Senesi, Fresenius Environ. Bull., 7 (1998) 423.
19 M. R. Provenzano, N. Senesi and G. Piccone, Compost, Sci and Utiliz., 6 (1988) 67.
20 M. R. Provenzano, N. Senesi and V. Miikki, J. Therm. Anal. Cal., 52 (1998) 1037.