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Federica Ruggero

FATE OF BIOPLASTICS IN COMPOSTING

Supervisor

Prof.ssa Ing. Maria Cristina Lavagnolo

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"Ogni scelta comporta una rinuncia e chi non sa rinunciare probabilmente non sceglierà mai niente, facendo scegliere gli altri al suo posto, o farà sempre scelte che non costano fatica. Le scelte che non costano fatica sono prive d'amore. L'amore senza le sue gambe resta nelle parole. Posso risparmiare sulla luce, ma mai sull'amore, perché non so spegnere tutte le stelle che ho dentro."

M. Bisotti, La luna blu

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1. INTRODUCTION

1.1 The beginning

The topic of bioplastics degradation in composting was proposed to me as a new research on which nobody had even worked before. The consequence of working on a new topic is that probably the most of problems met during the experimental part will be unexpected and they will not have a previously adopted solution. But I wanted to welcome this challenge for two reasons: on the one hand, driven by personal motivation to undertake a research path that would have shown me, with all its difficulties, if in this field I could make my plans for the future. On the other hand, I found that this research was significant of what an environmental engineer should do with his job. His task is to continuously wonder if the technologies, the materials, the processes, the innovations used in our world are compatible with a sustainable development: nowadays ever new products are immitted on the market, new industrial processes are elaborated to ensure a faster and more efficient production, new sources of energies are searched and so on, but it is not always proven that a better solution for the economy, is also a better solution for the environment, the human health and the sustainable development.

The question on the fate of bioplastics after waste management in the composting process, gave me the opportunity to enter in this world of environmental engineering, investigating the possible long-term impact on the environment of a recent material.

1.2 Introduction to the purpose of the research

Bioplastics now form part of the collective imagination, even though they have been in circulation since 1980s. Production of these materials have been growing; the numbers from European Bioplastics show that 1.13 million tons of bioplastics were produced in Europe in 2016, with an increase of 30% forecast by 2021.

The definition of bioplastics includes two features that can be present both simultaneously or one without the other: biodegradability and originating from renewable resources (European Bioplastics, 2016). The bioplastics with both characteristics, which are 23.2% of the total amount, fall into the field of this research.

It’s fair to say that the growing production and distribution of bioplastic products is related to the possibility to satisfy two societal needs: firstly, having a material with features and uses similar to plastic, which is so widely exploited in everyday life that in Europe it corresponds to 30.4% of the waste produced (Ispra, 2015). Secondly, the emergent need for sustainability. Bioplastics are an environmental responsible material (Karana, 2012), with a production chain cleaner than plastics: starting from the extraction of renewable resources to the return to earth trough waste disposal.

Some commonly used bioplastics are biodegradable and compostable, therefore the degradation time is much shorter than the hundreds of years required by plastics, and the certification EN 13432 allows their disposal of in composting plants. Composting is an aerobic biological treatment where organic waste can be broken down through the living activity of microorganisms, and it is divided into two phases: the thermophilic and the maturation phases (Bidlingmaier, 2016). In accordance with the above mentioned standard, the two characteristics required for bioplastics to be disposed of in a composting plant are described as follows: biodegradation is the breakdown of an organic chemical compound by microorganisms, while compostability is a property of a packaging material to be biodegraded in a composting process. To evaluate this property, the disintegration of the tested material has to be assessed and no more than 10% of the initial material should fail to pass a 2 mm sieve at the end of the process.

The fate of bioplastics at the end of the composting process may not be a complete disappearance but disintegration into microscopic pieces, and release on to cultivated fields through compost in the form of microplastics, which are less than 5 mm in size (Thompson et al., 2009).

Some research in recent years has been aimed at dealing with problems posed by microplastics, from identification, and enumeration, to extraction and cleaning of aquatic and terrestrial environments (Horton et al., 2016, Qiu et al., 2016). Microplastics due to their small size, abundance, attractive colours and similarity with food, are easily bioavailable for the species of the lowest trophic levels and consequently acccumulable in the food chain (Wright et al., 2013). Furthermore, bioplastics after composting are sticky; they start to melt due to the high temperatures during the process and to the increase in moisture after having been in contact with putrescible waste. Sticky microplastics deriving from disintegration can stay attached to crop foods, soil grains and vegetation.

The possible release into the environment of bioplastic fragments after composting raises an issue: bioplastics can be dispersed in soil through the fertilization of fields and reach waterways with run off during rainfall events, thus being in a new environmental condition that affects their potential to conclude degradation. The result and the timing will vary depending upon the environment, and in accordance with the varying outside temperature and humidity (Mehdi et al., 2016).

The object of the research is to investigate the fate of bioplastics during the composting process, in order to follow their biodegradation and disintegration up to release into the environment. With the growing use of bioplastics, the research has also developed to evaluate their effective potential for biodegradability; the analyses carried out mainly at lab scale demonstrated that bioplastics have different potential according to the polymers of which they are composed (Tabasi e Ajji, 2015): starch, PLA, PHB, PCL, PBAT. The temperature also has a significant influence; constant room temperature causes a low degradation (Mohee et al., 2008), while maintaining the process at the thermophilic phase for a long period can lead to a higher degradation (Balaguer et al., 2015, Javierre et al., 2015). Since the aim of this research is to obtain results that reflect the real world, the tests have been carried out on a small scale with the inclusion of some typical variables of a composting process, such as outside temperature and humidity changes, waste mixture, waste and bioplastics size.

1.3 Legend of the acronyms for samples

To simplify the names of the components within the tests, some acronyms will be adopted from now to the end of the research, and each of them identifies the moment of the test, the starting point and the end, and the matrix with or without bioplastics.

OFi = organic matrix to composting, without bioplastics, at the beginning of the test

BioPi = initial bioplastics

BioPOFi = matrix composed of organic waste and bioplastics

OFf = matrix obtained at the end of composting, without bioplastics. Or simply compost without bioplastics

BioPf = final bioplastics

BioPOFf = matrix obtained at the end of composting, with final bioplastics. Or simply compost with bioplastics.

MicroBioP = Micro-Bioplastics, bioplastics smaller than 5 mm

1.4 The research history

My master thesis work was composed on three parts: the first two months were dedicated to the research of methods available to the evaluation of biodegradability and compostability of bioplastics already applied in laboratory tests by other authors.

The bibliographic study was followed by a personal elaboration of the methods used in the experimental part of the thesis to reach the purpose of the study.

The next four months involved the preparation of the experimental part and the actuation of it (Figure 1.1 and 1.2), including the analyses to be carried out on the composting process and those on bioplastic material.

The last part was the elaboration of the obtained data and the writing of the thesis.

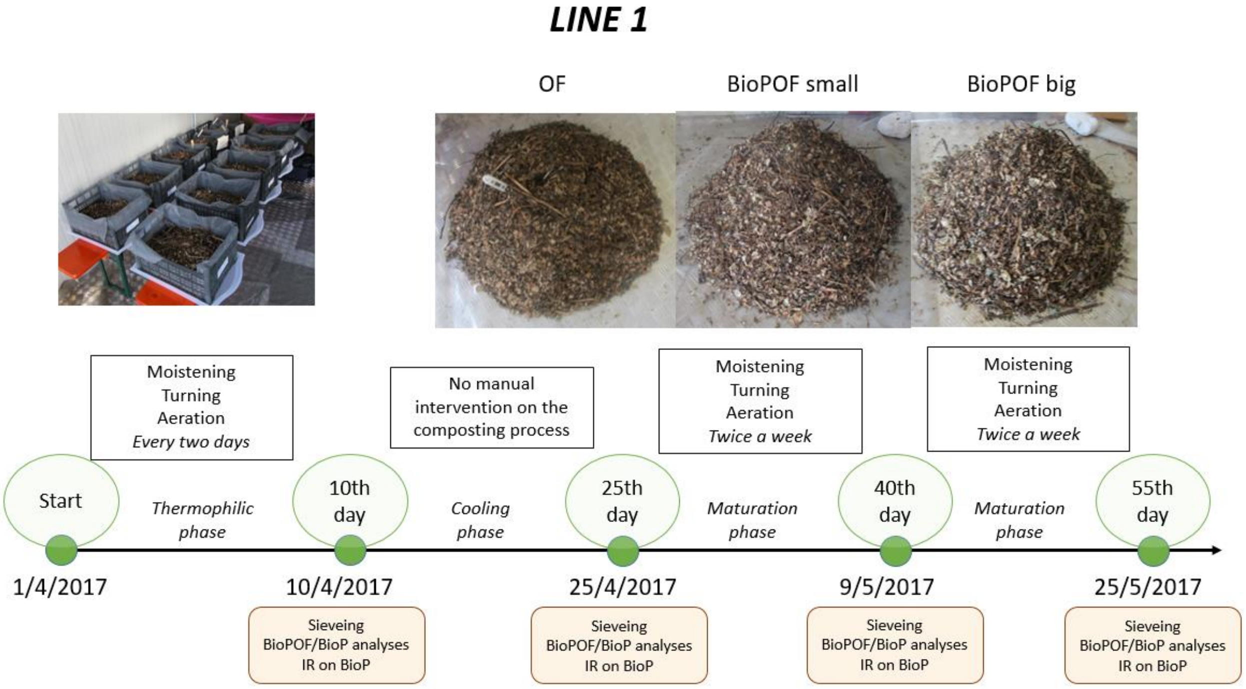


Figure 1.1-Experimental part of the thesis work - Line 1

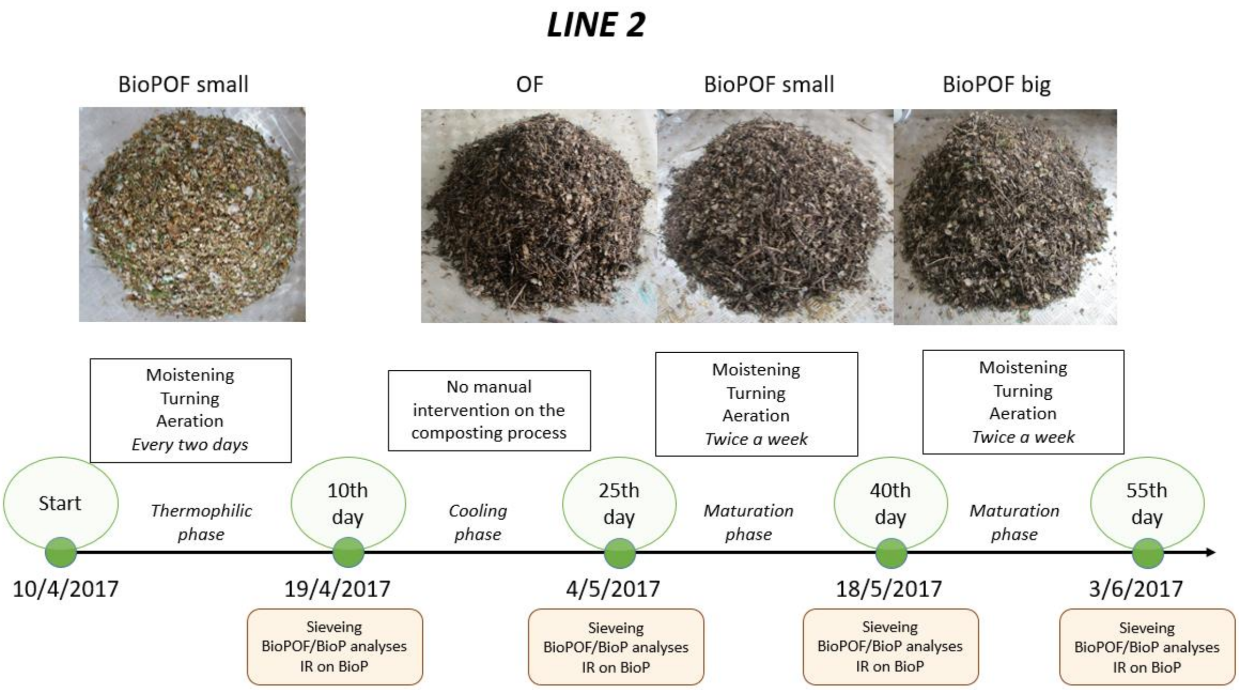


Figure 1.2-Experimental part of the thesis work - Line 2

2. PRELIMINARY STUDY TO THE RESEARCH

2.1 Bioplastic: the appearance of an environmentally responsible material

2.1.1 What are bioplastics?

Bioplastic materials appeared for the first time on the market at the turn of the years 1980s and 1990s, but the history of this new product is more in the future than in the past: in fact, in accordance with a study lead by the Hannover University, the production of bioplastics had been increasing until 2016 of 500%.

Bioplastics, or biopolymers, are an alternative for almost every conventional plastic material and corresponding application, having similar properties as conventional plastics.

The definition of bioplastic materials coming from the European Bioplastics includes the consideration of them as an eco-friendly alternative to petrochemical polymers due to the renewable feedstock used to produce them and to their biodegradability.

Considering both the source, which can be renewable resources or fossil resources, and the final degradation, made by bacteria or not, biopolymers are subdivided into three groups (Figure 2.1):

- Biobased or partially biobased non-biodegradable plastics such as biobased PE, PP, or PET;
- Plastics that are both biobased and biodegradable, such as PLA and PHA or PBS;
- Plastics that are based on fossil resources and are biodegradable, such as PBAT, PCL, PVA.

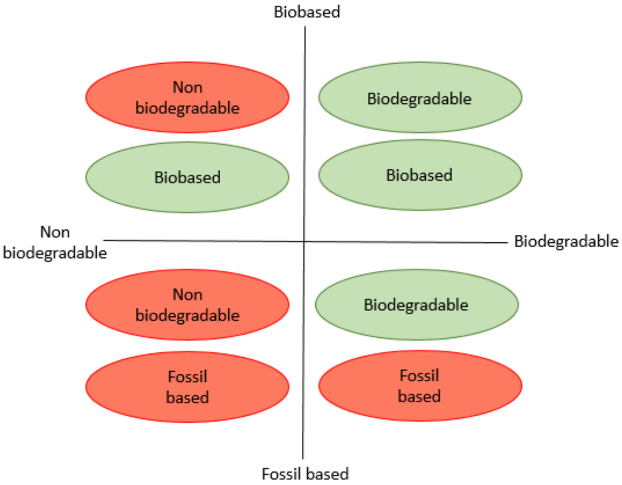


Figure 2.1-Subdivision of bioplastics according with European Bioplastics

2.1.2 Why bioplastics have been introduced on the market?

Plastic is a material with a widespread use all over the world; in accordance with ISPRA, the amount of plastic waste corresponds to 30,4 % of the total amount of waste produced by a person per year in Europe.

Data about waste production in 2013 resulted in a yearly production of 481 kg/ca, therefore plastic waste was about 150 kg/ca*y.

Due to environmental problems linked with plastic materials, in the last two decades the demand for solutions to move to a society that has its production based on environmentally responsible materials has rapidly increased.

Since the 1990s, many companies have moved from the pollution prevention, to the so called green chemistry as a more fundamental way to achieve sustainability. Green chemistry is a broad term which refers to a chemical production that aims to reduce environmental and health hazards to advance sustainability.

The major challenge, as discussed later, is to find ways to integrate sustainable innovations and new eco-friendly materials into the market.

In fact, industry's business models include that costumers are interested in buying the new product emitted on the market, and a central role in linking producers and customers is the awareness and the knowledge of benefits achieved with the use of bioplastics and environmental problems caused by plastic materials.

Bioplastics are a clean material which can be used for food packaging without risk of food contamination by additives, plasticizers or other potentially health hazardous substances present instead in non-biobased plastics.

Their production chain is cleaner than that of plastics from non-renewable resources: the main concerns with which plastic must face and that can in part be solved by new biobased materials, are, during the production phase, the use of non-renewable resources, and, during the disposal phase, waste generation and emissions into the environment.

Fossil fuel is the non-renewable resource employed for processes of plastic realization, and its availability is bound to end, so future generations will be obliged to find alternative solutions for energy production and for all the materials commonly used in everyday life coming from fossil fuel.

Furthermore, from an economic point of view, the price of this non-renewable resources has been fluctuating in the last years and, once the equilibrium point is overcome, it is bound to increase in accordance with the inverse relationship between the increasing demand and decreasing supply (Figure 2.2).

So, concerning the raw materials, the use of renewable resources is a strategy to reduce the dependency on fossil resources and to reduce CO_2 emissions.

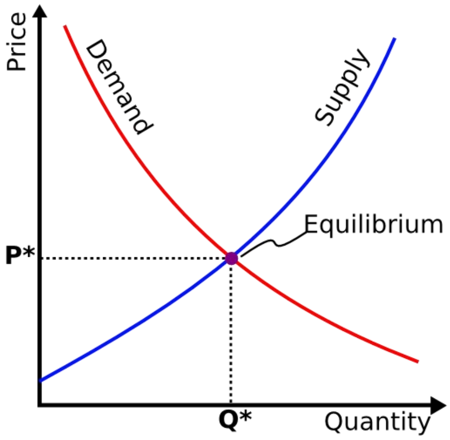


Figure 2.2-Graph of economic model linking demand and supply (www.khanacademy.org)

Finally, as concerns the use of energy for processes of material production, light-weight, resistance to corrosion and low temperature processing of bioplastics often result in energy savings.

Concerning plastic waste disposal, because of longevity and widespread use, managing plastic waste is actually a major problem. Unlike the materials they have replaced, such as glass and metal, the recycling of plastics has been less successful due to difficulties in identification and sorting and the presence of various other materials and additives, as fillers and plasticizers.

Plastics are organic materials so they can be potentially incinerated in order to reduce their volume and produce energy, but if this process is uncontrolled or poorly managed, it can result in hazardous emissions, such as dioxins from PVC.

So, even if the previously described processes are nowadays used for plastic waste management, a part of them is also disposed of in landfills, which, due to the increasing waste production, have a lowering capacity.

Bioplastic materials have much shorter degradation time than the one thousand years of plastics, and they offer different solutions for management of final waste: one possibility is recycling, but it is strictly regulated in accordance with some studies of European Bioplastics and CONAI.

In fact, the analyses carried out on bioplastics recycling together with virgin plastics showed that the they don’t negatively influence the recovery of plastics in an amount less than 10%. Moreover, bioplastics collected together with virgin plastics that will be led to a recycling plant must not be contaminated with food scraps.

The second option, widely discussed in this thesis, is composting bioplastics together with organic and green waste, in accordance with UNI EN 13432.

Using this way, the period necessary for waste disposal is only few months (in accordance with particularly well defined conditions), reducing both costs for management and time during which disposal plant is occupied by those waste. Composting leads also to the production of a fertilizer, so it can be considered as a form a recycling itself.

2.1.3 The main economic and environmental challenges of bioplastics

The question is if it is possible to introduce bioplastics in a new way, so that they will be perceived as natural and high quality product by society. This paragraph aims to analyse two doubts: people can like bioplastics as they like plastics? And are they effectively materials coming from nature and retuning back to nature in a short period?

Over the last decades, plastics have been fundamental for the progression of our man-made environment. But the appreciation of plastics and how they are received by costumers has changed over time in different societies; in fact, when they first emerged, they stood for cheapness, low quality and in-authenticity, and their tactile experience was generally unsatisfactory for people (Sparke, 1990). They were not brilliant, not heavy and not so hard as porcelain or iron.

However, with parallel improvements of their technical and sensorial qualities and with breakthrough applications, the value attributed to plastics has drastically increased.

After the establishment of the new status, critiques on environmental impacts and disposal management stimulated severe reactions on the use of plastics.

It’s also fair to say that, even if bioplastics are not very diffuse on the market and people are not sure about their properties and application, along the next decades they will supply to the needs of population, both social and environmental needs.

From the point of view of bioplastics mechanical properties, generally additives are used to improve resistance and hardness, because the most of these bioplastic materials alone, especially in the food packaging, have brittleness, stiffness, high sensitivity to moisture, high water sensitivity, poor impact resistance and thermal instability (Balaguer et al., 2015).

Additives used to improve these properties are not always biobased, because this type of market is nowadays not so developed, but some tests have been carried out to obtain new results in this field.

Obviously, companies have the heavy burden of integrating bioplastics and all biobased materials linked with bioplastics, as biobased additives, in their traditional boundaries.

It's not an easy question to face, because the emerging bioplastic sector poses new technical, business and infrastructure challenges that companies are still learning to address. To develop bioplastic product lines, chemical companies must attend to changing customer need, markets, and socio-political conditions together with the organizational, scientific, and marketing challenges of integrating industrial biotechnologies and agricultural resources into their supply chain in ways that can maximize existing manufacturing systems and demonstrate ecological value.

Companies need to develop the so called dynamic capabilities, which mean internal processes creating, replacing and adjusting a business model in response to changing business environments and new customer needs, in a way that doesn't imply a high failure risk (Iles and Martin, 2010).

Finally, it must be addressed the annoying question of environmental challenges presented by bioplastics.

Although biopolymers do not rely on fossil resources as a feedstock, the agricultural, milling, and production stages consume large amounts of energy, currently mainly derived from fossil fuel themselves.

There are additional environmental burdens associated with the agricultural stage, such as nitrogen and phosphorous emissions from fertilizers which result in eutrophication.

Other issues which may be raised concerning agriculture-derived biopolymers are finite land resources, the resulting competition with food crops, and their vulnerability to crop failure from flooding or drought. Crank et al. (2005) stated that if biopolymer consumption has a high growth rate, as forecast, there may be some conflict of interest with bioenergy crops around 2050.

Additionally, Colwill et al (2012) predicted that in the same year all crop and grazing land would not be sufficient to meet the demand for food, liquid fuels and plastics, resulting in the fact that if grass and forest land do require clearing to make space for biopolymer feedstock cultivation, the indirect greenhouse gas emissions associated with this need, may cancel out any carbon savings.

But the environmental problem with which this thesis faces, is the possible generation of microplastics and bioplastics litters after composting process. In fact, if they don't completely biodegrade during disposal process, they will be discharged in landscapes together with compost, resulting in their diffusion into the environment.

2.2 Knowing bioplastics

2.2.1 Actual and forecast bioplastics production in Europe and Italy

Data about production of bioplastics were found from three different sources: European Bioplastics documents, an article by Assobioplastiche and an article by MaTech.

There is a great difference between them, but a constant question is underlined by all the sources: the increasing trend in biodegradable bioplastics production, which makes difficulties in giving a precise prevision for the next years.

In fact, from 2011 to 2016 the production was quintupled, and actually more and more products usable not only for packaging but also for many different purposes are being launched on the market.

So, all the data given by the three sources had been considered and evaluated to set the quantity of bioplastics in the samples to carry out the analyses.

The first information is given by Assobioplastiche, not at European level but at national level: it is just a prevision. In fact, data are related to 2015, with an estimated production of 0.0545 million tonnes, increased of 25% with respect to 2014.

The value for 2018 production can be arranged around 0.11 million tonnes, basing this estimation basically on two points: firstly, the increasing trend of industries to create new and better biobased materials instead of plastic from non-renewable resources. Secondly, Italy with Mater-Bi produced by Novamont, is at the forefront in this sector and can be considered one of the major manufacturers of compostable bioplastics in Europe.

From European Bioplastics, in 2016 the global production of bioplastic was estimated to be about 4.16 million tonnes, distributed in the regions of the world in accordance with figure 2.3.

In particularly, the production in Europe was about 27.1 % of the total amount, corresponding to 1.13 million tonnes.

Figure 2.3-Global production of bioplastics in 2016 (www.european-bioplastics.org)

Furthermore, in the same document it is specified that not all the bioplastics produced are biodegradable and compostable: as the topic of this study are mainly compostable bioplastics, the graph with the percentages of biodegradable and non-biodegradable materials is shown in figure 2.4.

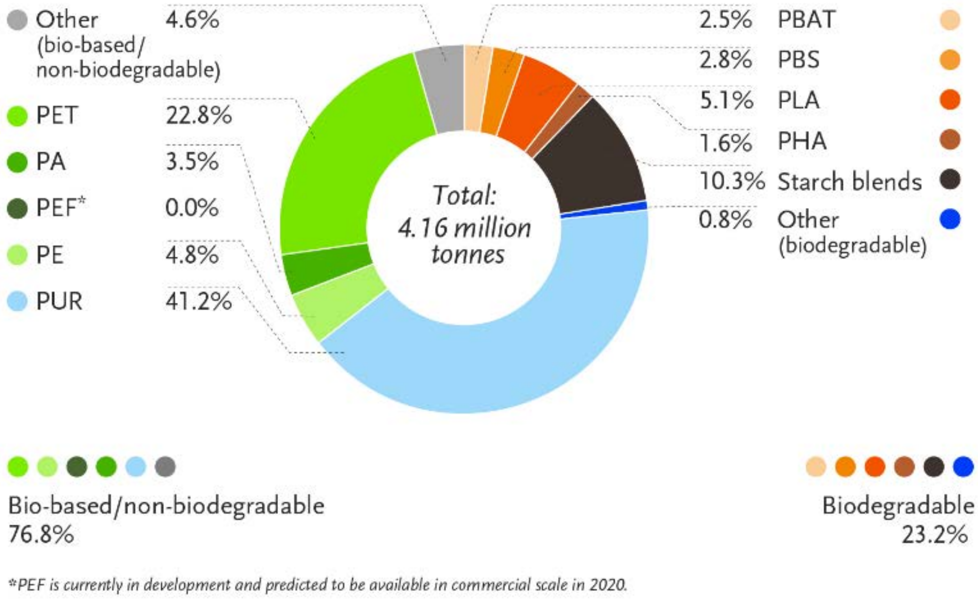


Figure 2.4-Biodegradable and non-biodegradable bioplastics production (www.european-bioplastics.org)

Among the 23.2% of biodegradable bioplastics, it's possible to underline the prevalent production of starch based materials (10.3%), which is in accordance with the recent appearance and development on the market of a new starch based bioplastic, called Mater-Bi.

To conclude, the quantity of biodegradable bioplastics produced in Europe in accordance with European Bioplastics agency, is equal to 0.26 million tonnes.

As the analyses on bioplastics are carried out considering Italian waste and bioplastics production, from the European production it's possible to reach the Italian production through a simple proportion.

In Europe, there are about 750 million inhabitants, while in Italy about 60 million: the bioplastic million tonnes produced in Italy in accordance with the proportion is 0.021.

But, considering also the two points already evaluated in the Assioplastiche previsions for what concerns Italian production, this quantity could be doubled, reaching 0.050 million tonnes.

Furthermore, another interesting question pointed out by European Bioplastics, is the potential increase in bioplastics production up to 30% into five years.

Data provided by MaTech are a prevision given in 2013 for 2016, for a production in Europe of about 5-6 million tonnes of bioplastic materials; considering 25% of them biodegradable, the quantity to consider for the study could be around 1.5 million tonnes.

With the same proportion use for European Bioplastics prevision, the Italian production can be arranged around 0.12 million tonnes.

Finally, in table 2.1 are summarized the quantities obtained considering the previsions provided by these three different bibliographic sources.

Table 2.1-Compostable bioplastics forecast production in Italy

References	**MaTech**	**Assobioplastiche**	**European Bioplastics**
Compostable bioplastics produced in Europe	5-6*10^6 ton * 0.25 = 1.5*10^6 ton.		1.23*10^6 ton * 0.232 = 0.26*10^6 ton
Compostable bioplastics produced in Italy	$\frac{1.5*60}{750}$ = 0.12*10^6 ton	0.11*10^6 ton	$\frac{1.5*60}{750}$ = 0.021*10^6 ton
Million tonnes of compostable bioplastics in Italy 2016-2018	0.12	0.11	0.050

2.2.2 New frontiers for the use of bioplastics

Bioplastics have been initially applied in the packaging sector: bags for the separate collection of the organic fraction, shopping bags especially in food stores, packaging for food products and gloves used in the supermarkets to take fruits and vegetables.

In figure 2.5 packaging bags taken from Novamont internet site, while in figure 2.6 some pictures about other bags made using Mater-Bi.

Figure 2.5-Novamont bioplastic bags and food packaging (www.materbi.com)

Figure 2.6-Shopping biobags and bags for the collection of the organic fraction (brand-finder-italy.info)

These products have spread very quickly on the market for the last five years; in Italy since 21 August 2014 it has been even banned the commercialization of shopping bags non-compliant with UNI EN 13432:2000.

Furthermore, industries of other different products are trying to adapt their production to this new trend of using bioplastics: innovation with disposable cutlery in PLA, plates and cups for ice cream made of cellulose of cardboard plus Mater-Bi, packaging for eggs, yogurt, ricotta cheese, capsules for coffee and finally packaging for soaps, drugs or personal care products (Figures 2.7-2.10).

Figure 2.7-Cutlery, ice cream cup and food packaging. From catalogue of Ecozema (www.ecozema.com)

Figure 2.8-Packaging for egg and packaging for ice cream (www.alcas.it)

Figure 2.9-Coffee capsules (corriereinnovazione.corriere.it) and packaging film and cups in Mater-Bi (www.materbi.com)

Figure 2.10-Packagings for drugs and personal care products (www.lameplastgroup.com, www.vib.be)

All these products are part of our everyday life, and if they can be thrown together with food waste in the organic bin, people will become used to do this. So, the amount of bioplastic intended to the composting plants will sensibly increase in a way directly proportional to the increase of the availability on the market of these new products.

For the last years, also industries of non-packaging products have been developed pieces of their commodities using bioplastics: some examples are stationary items, bottoms, glasses, shoes.

They are then applied in agriculture for mulching and in the automotive sector for car interiors (Figure 2.11).

Figure 2.11-Use of bioplastics for stationary items and mulching (www.novamont.com)

The disposal of this industrial products, especially car parts and interiors, is likely to be done in landfill, or in recycling sectors; so, it’s fair to say that the contribute of these commodities to the increase of bioplastics for composting will be less than which of domestic packaging products.

2.2.3 Characteristics and production of compostable bioplastics

Among the most diffuse biodegradable bioplastics, they are included: starch based materials, like Mater-Bi, polyactic acid or polyactide PLA, polyhydroxyalkanoates PHA, cellulose, polybutylene succinate PBS and polybutylene adipate terephthalate PBAT.

The products mainly present on the market for packaging are made of Mater-Bi, PLA, cellulose pulp and PHA, so these four types of bioplastics will be discussed in this paragraph to know their physical, chemical and mechanical properties.

Mater-Bi are a product made on corn-starch and biodegradable polyesters; so, it’s fair to give a piece of information on the way through which starch is used to produce bioplastics.

Starch is the most abundant and commonly used renewable raw material, its unique chemical and physical characteristics can be distinguished from all other carbohydrates (Figure 2.12).

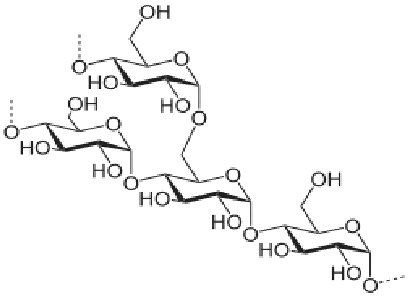


Figure 2.12-Starch chemical structure

It is obtained from seed, corn, wheat, potato, rice, sweet potato and cassava (Zhang et al., 2005). Starch is made up of repeating units of glucose and comprised of amylose and amylopectin. Amylose is a mostly linear glucan, while amylopectin is a very large, highly branched glucan with α,1-6 linkages at the branch points. The ratio of amylose and amylopectin depends on the source and age of the starch and can also be influenced by the extraction processes.

Starch for bioplastic materials is used as thermoplastic starch (TPS) and starch composites.

Thermoplastic starch can be produced after destructuration of starch in the presence of heat and plasticizers. Water and glycerol are the most common plasticizers, and water has a bigger effect than glycerol.

TPS has properties like those of common synthetic thermoplastics and can be processed as a traditional plastic: however, its sensitivity to moisture and poor mechanical properties limit packaging applications. Mechanical properties depend also on percentage of amylose and amylopectin; in fact, TPG with higher amylose content is more ductile.

Polymers derivate from starch are crystalline and can be used themselves or mixed with other polymers; for example, starch itself is added as a filler for other bioplastics to lower the cost production, and it has been reported that the addition of starch into biodegradable polymer like PLA, enhances the biodegradability of polymer composite (Liao and Wu, 2009).

If mixed with glycerol, polyesters and urea, intermolecular hydrogen bonds are reduced and properties of the product are stabilized.

Mechanical properties of starch are generally comparable to which of PE: they are ease to manipulate, but sensitive to thermal degradation and they tend to absorb humidity. In fact, starch interacts with water and degrades through hydrolysis.

Polymers from starch have a not high resistance to oils and solvents, but if mixed with other biopolymers, this capacity can be improved.

As said, Mater-Bi materials, made by Novamont, result from corn-starch and biodegradable polyesters. They are present on the market since 1990s, and it’s fair to say that its biodegradation rate is similar to that of cellulose and its mechanical properties close to those of traditional plastics like polyethylene PE and polystyrene PS, and it has a good resistance to heat, until 80-100°C.

It is also possible to submit these bioplastics to all the processes generally applied to traditional plastics, as filming to produce bioplastic films and sheets, extrusion to produce woven nets, thermoforming for rigid containers, vessels, pans, glasses, printing and injection to produce cutlery, toys, pens and finally expansion that generates loose fillers.

Five types of Mater-Bi are present on the market, four of them are classified as compostable.

Class A: biodegradable non-compostable material, with degradation in liquid medium of among 2 years. Products made from starch and vinylic ethylene alcohol copolymers.

Class Z: biodegradable compostable material, mainly used for manufaturing films and sheets. Biodegradation within 20-45 days in composting conditions.

The material is made from starch and polycaprolactone PCL in 50% ratio.

Class V: Biodegradable compostable and soluble materials, as sobstitutes for EPS material; it biodegrades faster than class Z, beacuase starch content is of 85%.

Class Y: biodegradable compostable material for injection molded, rigid and dimensinally stable product. Made of entirerly natural raw materials, such as starch with cellulose acetate.

Class N: Biodegradable compostable materials, it is made on starch and polybutylene adipate terephtalate PBAT.

The aspect of Mater-Bi is in granular form, as in figure 2.13.

Figure 2.13-Mater-Bi in granular form. They are made on corn-starch and biodegradable polyesters (www.novamont.com)

PLA is a family of biodegradable thermoplastic polyester made from renewable resources; it is propose for a commercial use as a substitute fro low density polyethylene LDPE and high density polyethylene HDPE, polystyrene PS and polyethyleneterephthalate PET.

It is produced by conversion of corn, or other carbohydrate sources, into dextrose, followed by fermentation into lactic acid. After this procedure, through direct polycondensation of lactic acid monomers or through ring opening polymerization of lactide, PLA pellets are obtained. Three different stereochemical compositions of lactide can be found and the composition determines the final properties of the polymer. It has a transparent granular aspect, as in figure 2.14.

The processing possibilities for this bioplastic ranging from injection molding and extrusion over cast film extrusion to blow molding and thermoforming.

Physical properties of PLA are comparable to PET, especially as for the tensile strength and elastic modulus; PLA however is a brittle material, with less than 10% elongation at break. Another major limitation is that it has poor gas barrier properties and low melt strength which creates limitations during melting processes with temperatures higher than 45-60°C in conditions of high humidity.

The low melting point of this product makes it difficult also the long-term storage.

On the contrary, it has a good resistance to welding and a high HDT, so it gives good performances for the junction between film and vessel, and for this reason it is widely applied in food packaging.

Figure 2.14-transparent granules of PLA (www.solostocks.it)

The PHAs family are a biodegradable thermoplastic polymers, produced by a wide range of microorganisms. The polymer is produced in the microbial cells through fermentation process and then harvested by using solvents such as chloroform, methylene chloride or propylene chloride. They are known more than one hundred PHA composites but polyhydroxybutyrate PHB is the most common, and it possesses chemical and physical properties comparable to those of poplypropylene PP except its brittleness.

The other PHAs are also similar to PP but also to PE while others are elastomeric: therefore, blending with members of the PHAs family can expand the potential range of applications.

Cellulose is the most widely spread natural polymer and is derived by delignification from wood pulp or cotton linters (Figure 2.15). It is a biodegradable polysaccharide which can be dissolved in a mixture of sodium hydroxide and carbon disulphide to obtain cellulose xanthate and then recast into acid solution, as sulfuric acid, to make a cellophane film. Alternatively, cellulose derivate can be produced by derivatization of cellulose from solvated state, via esterification or etherification of hydroxyl groups.

Figure 2.15-Cellulose after delignification (www.hempplastic.com)

Cellulose esters like cellulose di and triacetate need addition of additives to produce thermoplastic materials which can be submitted to injection molding or extrusion. Furthermore, most of cellulosic materials are water soluble and show excellent film-forming properties, but are too expensive for bulk use

2.3 Bioplastics in composting

2.3.1 The composting process: phases, parameters, waste to composting

With the D.Lgs 22/97 waste management underwent a turning point: the national and international legislation about waste are more and more facing toward the consideration of waste as a resource, a matter that can be recovered or recycled.

In this view the process of composting is a way of waste disposal through which it can be obtained a final product, compost, reached in humic acids, to be used as fertilizer.

Composting means the process of biological degradation and maturation of organic substances by a variety of living microorganisms, in aerobic conditions and solid state. At the end of the process products with a simpler molecular chain, more stable and hygenized, enriched in humus, are obtained, with the emission of CO_2 and water; the following is the basic reaction of aerobic degradation.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy (2870 KJ/mol)} + \text{Biomass}$$

Composting is a way of waste disposal suitable for three main reasons: from an environmental point of view, waste are transformed into a new product, useful in agriculture. Then, if temperatures during the thermophilic rise to 65-70°C there is an hygienization of the organic waste, and it is a process energetically autonomous.

It is interesting to specify that composting is one of the three possible aerobic stabilizations of organic waste: in fact, in aerobic conditions other two processes exist. Mechanical-biological pretreatment, MBT, and biodrying.

The processes are quite similar: two phases are well defined, the thermophilic phase, that lasts for about two weeks, and the curing or maturation phase, for a period of 2-3 months.

The preliminary step before starting the process is the shredding of waste to ensure the obtainment of a suitable size. What changes between composting, MBT and biodrying is mainly the aim for which the process is chosen and consequently the waste disposed of.

While biodrying and MBT are pretreatments, the first before incineration to increase the calorific power and the second before landfilling to stabilize organic waste and allow to reach the FSQ in one generation time, composting is done with purpose to recover a final product.

So, it’s important to pay attention to waste disposed of in a composting plant: they must come only from separated organic fraction, green waste, or waste water sludge not contaminated. Smaller powders as waste from street sweeping are not allow to be treat in this way, nor other organic contaminated waste, because they pollute the matrix and the compost.

The living organisms that carry out the process are bacteria, actinomycetes, fungi and also worms or beetles. Each microorganism is able to degrade a particular category of materials, and develops during the process in precise conditions.

Bacteria can be extremely fast-growing, they feel good at high temperature and moisture content, so they develop during the thermophilic phase, and they degrade the simpler substances as monosaccharides, starch and proteins.

Actinomycetes stay in the middle of the process, they are identifiable at a naked eye because of the white colour around the waste lump. Fungi are psychrophilic, can penetrate also the dry matter, are less sensitive to change of conditions and they degrade the most complex substances as lignin and cellulose, operating mainly during the maturation phase.

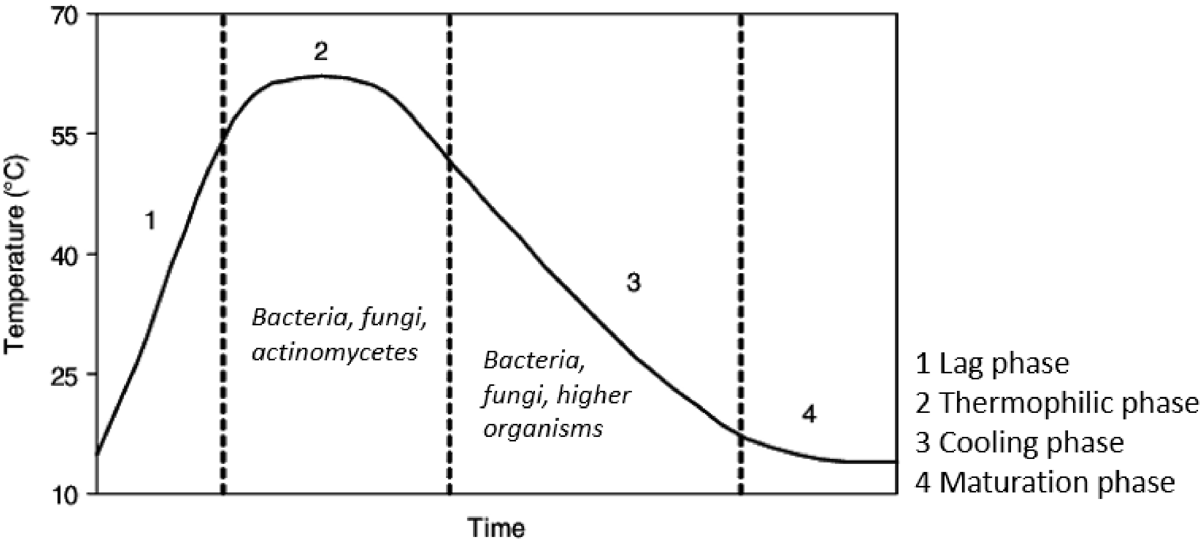


Figure 2.16-Phases of composting (www.researchgate.net)

There are some operational controlling parameters in the different moment of the composting process: before starting, water content, structure, substrate composition and nutrient content should be defined for waste matrix.

The treatment requires a good level of structure of the substrate, generally ensure by lignin and green waste. The nutrient content is given by C/N parameter, in accordance with the amount of carbon and nitrogen available for living organisms, that should be around 20-35 to guarantee the operativity of bacteria after the lag phase.

Finally the moisture content is fundamental to make the process start; a perfect value is of 50-60%. Water is necessary for bacteria to implement the hydrolysis, the first step in the biodegradation process, which breaks the more complex molecular bounds and leads to the production of simpler compounds.

During the process five parameters must be kept under control to ensure the effective activity of the living organisms: temperature, water content, oxygen content, the process is aerobic so a minimum of 20% of oxygen must granted for the aerobic bacteria to live, structure and pH values.

The operations to maintain these parameters suitable are aeration with turning, which allows to control the rise of temperatures and the fall of oxygen, and moistening.

At the end of the process, structure and compost properties are analysed: if the compost is sold it must respect the requirements of DM 5 February 1998 and in case of Veneto DGRV 766.

To evaluate if a composting process ran out, some parameters should be checked: C/N, self-heating and oxygen demand and their limit values are reported in table 2.2.

The values in table are a sum of more than one reference, www.venetoagricoltura.org then docenti.unicam.it for temperature, C/N and moisture, and from Cossu (2016) for respirometric index.

Table 2.2-Parameters to define compost maturity

Temperature	*RI_4*	*C/N*	*Moisture*
<25°C without high peaks	<5 mg O_2/g VS	< 10-15	< 40-50%

2.3.2 Bioplastics and composting in scientific papers

The behaviour of bioplastics after the composting process has already been studied, in particularly with the interest for their biodegradation timings and efficacy.

However, analysing the scientific papers about this topic, many different questions have been discussed, and from the consideration behind the experimental parts, the environmental conditions for the experiments, the purpose of the tests, some useful information were taken and applied to implement my personal research.

At this point it’s fair to specify that the most of the researches published in scientific literature are at a lab scale, just few on a full scale, but none of them were done on a small scale. Thus they generally referred to European standards, respectively EN 14806 for lab scale and EN 13432 and 14995 for full scale. While for a small scale it doesn’t exist a specific standard that gives information or improvements on how to carry out the experiments.

So, for the purposes of this research, some suggestions from standards and research methods of both lab and full scale were observed and considered in the view of a small scale test.

The lab scale experiments studied and analysed were mainly four. Starting from Javierre et al. (2015), a research which focuses on the different level of degradation for a painted and a normal bioplastic. In perfect accordance with the correspondent standard, the samples were kept at 58°C for 90 days, and CO_2 emissions were evaluated to define the biodegradation level. At the end of the process bioplastic pieces were dried at 40°C and finally sieved with a 2 mm sieves. A similar procedure was adopted by Balaguer et al. (2015) to assess the compostability of a nano-reinforced PLA film. The difficulties in copying these tests is that on a small scale test is not possible to keep the sample in an oven at 58°C for all the testing period. Furthermore, even if this technique allows the study of biodegradation in accordance with the standard, the condition of such high temperature for three months doesn't correspond to a real composting condition, which is instead the aim of my research. However from these two papers the two main techniques to evaluate the biodegradation level were learnt: CO_2 emissions and weight losses. To measure CO_2 emissions, it is necessary to operate in a closed environment, as the reactor proposed by the lab scale European standard, with an opening a tube through which gas is taken out and measured. On the contrary, weight losses can be simply calculated with the use of a balance, a method that is applicable to a condition of a small scale with baskets or heaps that can be put in a tank and weighted.

Furthermore, Balaguer observed that after 7 weeks of composting, bioplastics are assimilable to compost in their aspects and no distinctions can be made between normal and nono-rinforced bioplastics.

Considering this last observation, in my research a particular paragraph on bioplastic aspects was written, in order to follow the peculiarities of the tested material also from a visual inspection.

Another interesting research is which of Tabasi and Ajji (2015) on PLA film and PHB degradation: this was a short-term research, with a tested material size of 5 cm and a ratio between compost and material of 6:1. The most interesting point of this research was the study of bioplastics aspect changing in time, through a scanning electron microscope.

To conclude with the small lab scale tests, Mohee (2008) following EN 18455 analysed the degradation of a Mater-Bi bioplastic for 40 days; from this experiment, resulting in a degradation of 26.9%, it could be extrapolated an important suggestion. In fact the test was carried out at room temperature for all the time, on a sample of few kilos: as the degradation level was very low, it is possible to deduce that the main cause is linked with the low temperature, maybe a sign that the composting process had never started efficiently enough.

On the other hand, the most interesting scientific paper about a full scale research was Rawoteea et al. (2016), about co-composting of vegetable waste an carbon. At the end of the process, some sieves were used to define a granulometric curve for both the compostable matrix and the tested material, an idea which was used in my research to study the disintegration of bioplastics, not only at the end, but also during the composting process.

To conclude with the bibliography about researches on bioplastics, a considerable paper is Emadian et al. (2016) about the degradation of different types of bioplastics, from PLA, to PHB, to starch based materials, not only in composting but also in soil, sediments and water matrix.

The main and useful point of this article is that bioplastics degradation in greatly influenced by the surrounding environment, for example in water bioplastics have a degradability similar to which of plastics, it means very long, while in soil it depends on the type of soil, the microorganisms which live there, the climate. Thus, if at the end of the composting process bioplastics are still not completely degraded and they are released into the environment, external conditions of this new environment should be considered, accounting that they could be able to stop or slow down biodegradation.

2.4 Standards for definition of bioplastics compostability

To define if a plastic material is biodegradable and compostable, it must pass through the approval of European standards.

There is more than one standard on this topic, because one standard is general for plastic materials and each of the others is specific for the type of material under study, or the environment of degradation.

2.4.1 Full scale standards

EN 14995:2006

Plastics – Evaluation of compostability – Test scheme and specification.

This standard has not yet been implemented in the European Union or in Italy; in fact, this is the most general standard about plastic compostability, and it specifies requirements and procedures to determine the compostability or anaerobic treatability of plastic materials by addressing four characteristics: biodegradability, disintegration during biological treatment, effect on the biological treatment process and effect on the quality of the resulting compost.

The main points of interest for this study are biodegradability and disintegration under aerobic composting.

Aerobic biodegradation tests are discussed at point A.2.2.

A.2.2.1 “The period of application for the test specified in the test methods shall be a maximum of 6 months”.

A.2.2.2 “For plastic material the percentage of biodegradation shall be at least 90% in total or 90% of the maximum degradation of a suitable reference substance after a plateau has been reached for both plastic material and reference substance”.

Disintegration is discussed at point A.3.

A.3.1 Aerobic composting: “Following submission to the composting process for a maximum of 12 weeks, not more than 10% of the original dry weight of the plastic material shall fail to pass through a < 2 mm fraction sieve”.

Moreover, the ecotoxic effects of the resulting compost shall be analyse through OECD 208 test with the modifications describes in the Annex D of the standard.

EN 13432:2000

Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging.

This standard is specific for plastic packaging materials, and because of this, it is the standard to which all the compostable shopping bags, food packaging, cutlery and other bioplastics packaging refer.

It specifies requirements and procedures to determine the compostability or anaerobic treatability of plastic materials by addressing four characteristics: biodegradability, disintegration during biological treatment, effect on the biological treatment process and effect on the quality of the resulting compost. In case of a packaging formed by different components, some of which are compostable and some other not, the packaging itself as a whole is not compostable.

About this standard it’s fair to underline some interesting points: aerobic biodegradation and disintegration under aerobic composting are discussed in the same way of EN 14995:2006, at the same reference point A.2.2 and A.3.1.

Also for ecotoxicity tests the reference is OECD 208 modified.

To determine the other eventual negative effects on the resulting compost, its quality is evaluated through: volumetric weight, total dry solids, volatile solids, salt content, pH, the presence of total nitrogen, ammonium nitrogen, phosphorous, magnesium and potassium.

Chemical characteristics of compost are discussed at point A.1.

A.1.1 Volatile solids: “Packaging, packaging materials and packaging components shall contain a minimum of 50% of volatile solids which include largely inert materials”.

A.1.2 Heavy metals and other toxic and hazardous substances, listed in Table A.1 of the Annex. The element under evaluation are Zn, Cu, Ni, Cd, Pb, Hg, Cr, Mo, Se, As, F.

The last point to underlain is the granulometry of material before test starting, discussed in Annex D, point D.1.3: “The shredding of used packaging with machinery and procedures, commonly used in composting plants, shall not be disturbed and should lead to particle sizes of less than 10 cm in the longest dimension, suitable for the composting process”.

EN 14855:1999

Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide.

It exists a new version of this standard, EN 14855:2004, but the requirements and proposed tests are the same of the previous one. “This International Standard specifies a method for the determination of the ultimate aerobic biodegradability of plastics, based on organic compounds, under controlled composting conditions by measurement of the amount of carbon dioxide evolved and the degree of disintegration of the plastic at the end of the test. This method is designed to simulate typical aerobic composting conditions for the organic fraction of solid mixed municipal waste. The test material is exposed to an inoculum which is derived from compost. The composting takes place in an environment wherein temperature, aeration and humidity are closely monitored and controlled. The test method is designed to yield the percentage conversion of the carbon in the test material to evolved carbon dioxide as well as the rate of conversion”.

This standard is the first reference standard to evaluate the biodegradability of a test material: in fact, EN 19455 and EN 13432 are both based on it as for the procedure for biodegradability evaluation.

At point 8 of the standard, the procedure is exposed, starting from the preparation: the test is carried out with an inoculum, deionized water, test material and a reference material.

Well aerated compost from a properly operating aerobic composting plant shall be used as the inoculum; a mixture of 1 part of inoculum with 5 parts of deionized water is prepared, and finally tested material is added.

The evaluation of its biodegradation level is done by measuring carbon dioxide emissions, and the result must be compared with a reference material of which biodegradability was already ascertained.

This standard is no more use as reference by companies to define their product as compostable, and the main reason is linked with the affirmation at point 10 validity of test.

“The test is considered as valid if the degree of biodegradation of the reference material is more than 70 % after 45 days”.

Due to this definition, it seems that even if the material succeeds in this test, its compostability is in a level inferior with respect to a material succeeded in test of standard EN 13432:2000, which requires 90% biodegradation in 6 months.

2.4.2 Pilot scale standards

EN 14045:2003

Packaging – Evaluation of the disintegration of packaging materials in practical oriented tests under defining composting conditions.

“This European Standard is used to evaluate the disintegration of packaging materials in a pilot-scale aerobic composting test under defined conditions. Other methods should be used to measure the biodegradability of the packaging materials. Packaging materials are mixed with biowaste and spontaneously composted for 12 weeks in practical oriented composting conditions. At the end of the composting cycle the disintegration is measured by sieving of the compost and the calculation of a mass balance. The influence of the tested sample on the quality of the compost can be studied by using the compost obtained at the end of the composting process for further measurements such as chemical analyses and ecotoxicity tests.

Additionally, this method can be used for visual perception and photographic documentation of the disintegration of packaging materials and for evaluating the effect of their addition on the composting process”.

Since this is the specific standard used to demonstrate the compostability of packaging materials in the precise conditions analysed in this thesis, few worlds will be spent to describe the main points and requirements specified in the standard.

The principle of the standard is exposed at point 4: the test duration is established to be 12 weeks, with a continuous monitoring of temperature, pH, moisture content and gas composition.

At the end of the composting process, the mixture of compost and test material is sieved over 2 mm and 10 mm to evaluate disintegration of packaging material after sieving.

If possible, the standard requires a mass balance based on dry and wet weight. The compost obtained shall be used for further measurements such as chemical analyses and ecotoxicity tests.

The procedure of the test is specified at point 6: to simplify the discussion of this point, in table 2.3 are reported all the information exposed in the standard about the biowaste sample composition and physico-chemical characterization.

Table 2.3-Requirements of 14045:2003 for physico-chemical characterization of the biowaste sample

Physico-chemical characteristic	*Reference value from 14045:2003*
Sample wet weight	60 kg
Biowaste dimension	< 50 mm
C/N	20-30
Moisture content	>50%
Volatile solids	>50%
pH	>5
Temperature	<75° >60° for at least 1week >40° for at least 4 consecutive weeks

Some types of biowaste are suggested to be added to sample to reach a good structure: fresh mixed fruit and vegetable waste, rabbit feed, matured compost, urea, bulking agent as woodchips or bark.

At point 6.1.1.2 is specified that the dimensions of the test material shall be reduced to 10 x 10 cm.

At point 6.1.3.2 is defined the sieving procedure through which is finally defined the disintegration of the test material.

Table 2.4-Sieving Scheme from EN 14045:2003

Compost (at end of pilot scale test)	Analyses
Sieving > 10 mm	Particles > 10 mm: Segregation and determination of the dry mass of residual test material
Fraction < 10 mm	10 mm > Particles > 0 mm: Gently mixed: separation of a part of the compost for chemical analysis Option: Ecotoxicity testing
Sieving > 2 mm	10 mm > Particles > 2 mm: Segregation and determination of the dry mass of test material
Fraction < 2 mm	Use for optional analysis

At point 6.1.3.3 some visual observations are optionally proposed. In particularly: "A visual assessment of the criteria described below is carried out at the beginning of the test and also during the entire trial period whenever the test material is turned.

- Initially distribution of particle size of remaining packaging particles;
- signs of microbial colonisation of the packaging (fungal hyphae, bacterial growth) to be described and photographed.

At least 10 packaging particles shall be selected with the intention to provide an impression of all visible degradation phenomena, ranging from little decomposition to severe degradation of the packaging particles. The selected particles shall be carefully cleaned with water and evaluated visually for the following criteria:

- consistency and thickness of the material;
- discolouring;
- erosion of the material (holes, tunnels, etc.) and signs of local disintegration;
- ease of discovery".

At point 6.2.3.1 are discussed all the analyses to carry out on the resulting compost to evaluate its quality.

"The characteristics of the compost obtained in the presence of the test material shall be compared to the results for the biowaste control bins. The wet weight of the total compost before sieving shall be exactly determined.

A homogeneous sample of the < 10 mm fraction shall be analysed for dry matter, volatile solids, pH, NH4-N, NOx-N, Kj-N content, Volatile Fatty Acids (VFA) and maturity. The results of these analyses are used to describe the quality of the compost produced. If applicable the < 10 mm fraction shall also be used for further ecotoxicity testing".

To conclude, at point 7 it is presented the formula for the calculation of disintegration in %:

$$D = \frac{m1 * R * m2}{m2 * R} * 100 \qquad (1)$$

m1 = dry weight of test substance input

m2 = dry weight of retrievable test substance > 2 mm

R = $\frac{compost\ screened}{total\ compost}$ (w/ w)

2.4.3 Lab scale standards

EN 14806:2005

Packaging – Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test.

First, it is necessary to underline that even if a test on a plastic material succeeds in this test, it must also succeed in full scale tests to obtain the certification of compostable material.

"This laboratory scale test method using synthetic waste aims at simulating the environmental conditions found in industrial composting plants. Packaging materials exposed to this environment can be preliminary assessed for disintegrability. A negative result does not necessarily mean that the test material is not disintegrating under industrial composting conditions. This test does not replace the acceptance disintegration test as specified in EN 14045, in accordance with EN 13432".

So generally, this standard is used for demonstrative laboratory analyses.

Some information given in this standard will be reported, because a part of them will be used in the experimental part of this thesis work.

At point 5 there is a description of synthetic solid waste for the analysed sample, with its physico-chemical characteristics, summarized in table 2.5. Furthermore, synthetic waste suitable for the test and their percentages in the sample are suggested.

Table 2.5-Requirements of 14806:2005 for physico-chemical characterization of the waste sample

Physico-chemical characteristic	*Reference value from 14806:2005*
Sample wet weight	1 kg
C/N	20-30
Moisture content	>55%
pH	>5
Temperature	58°±2°, and after 30 days it can decrease until a 21°

Another important point of the standard is point 6, where the reactor suitable for the test is described: “The composting reactor is a box made with a suitable inert material which does not affect the composting process, having preferably the following dimensions: 30 cm × 20 cm × 10 cm (l, w, h). In the sequences the container chosen shall not vary more than 5 % in dimensions. The box shall be provided with a lid assuring a tight closing to avoid an excessive evaporation. Additionally, the closing between box and lid may be sealed with an adhesive tape. In the middle of the two 20 cm wide sides, a hole of 5 mm in diameter shall be applied at a height of about 6,5 cm from the bottom. The two holes provide gas exchange between the inner atmosphere and the outside environment”.

While at point 7 the dimensions for the test materials are specified: 25 x 25 mm if the thickness of the material is > 5 mm, and 15 x 15 mm if the thickness is < 5 mm.

The termination of the test and the final calculation of its degradation is described at point 10.

The compost is sieved through 2 mm sieve, and the smaller fraction is cleaned from the compost, washed by dipping in water and finally dried in an oven until a constant mass, as it was done initially before the test.

The disintegration in 100% is expressed through the formula:

$$D = \frac{Mi - Mr}{Mi} * 100 \qquad (2)$$

Mi = is the initial dry mass of the test material

Mr = is the mass of the dry residues recovered by sieving.

2.4.4 Certification of compostability

Once a plastic product has succeeded in the tests required by standards, producer company can ask for the certification of compostability.

It consists on a label which is drawn on the packaging material, near the name of the standard.

The commonly known labels of compostability can be released if the product meets the requirements of EN 13432:2003.

Label of CIC (Consorzio Italiano dei Compostatori) cerifies that a product is objectively eligible to composting, and when composted in an industrial facility no plastic residues will be left behind to destroy the value of the finished compost.

Label of Biodegradable Products Institute (BPI) certifies products as compostable, which means they will biodegrade quickly, completely and safely, when composted in well-run municipal and commercial facilities and that no plastic residues will be left behind to destroy the value of the finished compost. This certification does not guarantee the products will biodegrade completely in a backyard compost or that they will biodegrade in the ocean.

Then European Bioplastics offers the seedling label, which certifies that the product will biodegrade completely in a well-run industrial compost facility, but not necessarily in a backyard compost or in the environment.

DIN-Geprüft Biobased has a label which indicates a product is certified to contain a certain percentage of biobased material. The percentage is indicated on the label. This label does not tell you that the product is biodegradable.

In figure 2.17 the labels of CIC, BPI, European Bioplastics and DIN.

Figure 2.17-Labels certifying compostability (www.materbi.com)

Vinicotte has developed different labels, each of them specified a particular condition under which the bioplastic material can degraded in composting.

- OK compost certifies the product will biodegrade completely in an industrial compost facility. However, it does not guarantee that the product will break down in a home compost system;
- OK compost HOME certifies the product will biodegrade completely in a home compost system;
- OK biodegradable SOIL certifies the product will biodegrade completely in the soil without harming the environment. No composting system necessary.

Figure 2.18-Labels of Vinicotte certifying compostability (www.materbi.com)

3. MATERIALS AND METHODOLOGIES

The experimental part of thesis involved two parallel fields: the composting process, developed on a small scale, comprehensive of all the analyses carried out to study the evolution of the process, and the methods applied to follow the degradation and the disintegration of bioplastics within the composted matrix.

The decision to carry out the test on a small scale was linked with the necessity to have more than one replicate for a statistical definition of the results, in addition to the purpose to simulate a real composting plant, with the two main phases, the thermophilic and the maturation.

In particularly, as the aim was not to have the results only at the end of the process, but to follow the different steps and the evolution of bioplastics fate in composting, there were established five points of analysis, to study in parallel the composting process and the bioplastics degradation and disintegration.

The five timing of analysis were the 1st day, then the day correspondent to the end of the thermophilic phase, two points during the maturation phase and the last at the end of the process.

The test lasted for 55 days, in accordance with the purpose of simulating the period of activity of a composting plant, and with the effective possibility to do this in a small scale; it was observed that after two months the values typical of a good compost were obtained, and it was reached a size of the heap, consequently to the weight lost and the samples taken, no more useful to simulate a real process.

In this chapter the material and methodologies applied to the composting process and to the evolution of bioplastics in the process itself are explained; moreover, the preparation of the sample and the characterization of the waste matrix used are explicated.

3.1 Composting process

The composting process were studied during its different phases: in this paragraph the methods for the analyses of the process parameters, and the use of sieving analyses to follow the changing granulometry of the composted matrix are described in order to show the evolution of the process in time.

To carry out the analyses during the composting process, no more than 2 kg from the heaps were taken each time, to ensure the maintenance of a good mass of the heaps for the proceeding of the composting.

3.1.1 Analyses of the composting process parameters

The main parameters monitored from the beginning to the end of the process were: temperature, total and volatile solids, pH, moisture content, C/N, respirometric index.

It was established a program of research for the timing of the analyses, as show in table 2.1.

Table 3.1-Timing of the process parameters analyses

Parameter	**Daily**	**Weekly**	**Sampling days**	**Initial**
Temperature	x			x
Weight lost			x	
Moisture		x	x	x
Total solids		x	x	x
Volatile solids		x	x	x
pH			x	x
TOC			x	x
TKN			x	x
Nitrates			x	x
C/N			x	x
RI			x	x

The analyses carried out for these parameters are briefly exposed below.

- *Temperature*: the monitoring of the temperature was done through two thermometers able to provide a value between -50 °C and up to 200 °C, one thermometer with a probe of 10 cm, for the upper part and the sides of the heaps, and the other, to measure the bottom of the heaps, of 20 cm.

  Temperatures were taken at least daily, but during the thermophilic phase it was measured up to four times a day, because the heap was subjected to possible high increases, to which it followed an immediate mixing, and to a decrease due to the outside temperature. In this case it was provided a cover on the heap for the coldest hours of the day, to avoid a too great decrease of temperature. Furthermore, once the thermophilic phase was finished, the mixing of the heaps was done no more once a day, but twice a week, to supply also water to the heaps and maintain a god moisture content.

- *Outside temperature*: the monitoring of the temperature includes also the monitoring of the external climate, in order to find a possible connection between the changes within the heap. It was monitored through an outside probe, measuring also the humidity, positioned within the box in which the experiments were carried out.
- *Total weight*: the total weight was monitored through the use of a balance precise up to 30 kg. The heaps were dismantled, put within a basket and weight. Then they were recomposed in their original configuration.
- *Dry weight:* the dry weight, used especially to carry out the analyses that require a normalization on the total solids, was measured removing the water content from the total weight. Water content was previously analysed drying the sample in oven at 105 °C, in accordance with the procedure for the evaluation of the total solids, as described in the specific voice.
- *Total solids and moisture content:* the moisture content was daily monitored to a probe generally used in agriculture for the humidity of soil, but as the heap was small the measurements obtained with this simple probe was not precise, moreover they vary greatly in accordance with the materials of the composted heaps in which the probe was infixed.
  So the most suitable way to obtain a significant value for humidity and total solids was to take a sample of few grams generally one in the upper part of the heap and another on the bottom, and to dry it in the oven at 105 °C for 24h.

$$\frac{W105\,°C - Wcrucible}{Wraw} * 100 = TS\,(\%) \qquad (3)$$

- *Volatile solids*: they were calculated in accordance with the equation:

$$\frac{W105\,°C - W550\,°C}{W105\,°C - Wcrucible} * 100 = VS\,(\%) \qquad (4)$$

- *pH*: the evaluation of pH was done through a cession of the solid material in distilled water, with a proportion 1/10, and the measurement was done on the liquid sample.

- *TKN:* the analyses for the TKN, Total Kjeldhal Nitrogen, comprehensive of organic nitrogen and free and saline ammonia (FSA), were implemented by steam extraction at high pH (with the required dose of ammonia, 60 ml for all my samples) and condensation with boric acid (30 ml). Then there was a further titration by using H_2SO_4.

  The obtained results were in concentration of g TKN/ Kg TS, so to obtain the real trend of TKN decrease within the heaps, this value was multiplied by the dry weight.
- *Nitrates:* the nitrates were analysed with the UV analyser, after the cession of the solid samples in distilled water.
- *TOC:* the analyses of TOC were done through an oxidation by a combination of heat and oxygen, ultraviolet radiation and chemical oxidants. The inorganic carbon was also measured through this method, but with the CO_2 was then evaluated directly by an infrared analyser, allowing to obtain the results of the organic carbon.

  As for the TKN, the result directly obtained was a concentration, so multiplying by the dry weight it was obtained the bulk of organic carbon.
- *C/N:* this number represented the ratio between total carbon (organic and inorganic) and total nitrogen (TKN and nitrates), available for the bacteria active during the composting process. They required a minimum ratio of 20, up to a maximum of 35, in accordance with the Liebig law: in fact, bacteria require both nitrogen and carbon (also a small amount of phosphorous) to allow the internal metabolic processes active in feeding. If the value is less than 20, it means that carbon is not enough, while for a value higher than 35 there is an amount of carbon not compensated by the right amount of nitrogen so that bacteria cannot supply the energy required for survival.
- *Respirometric index*: the respirometric index is the parameter which identifies the consumption of oxygen by living organisms active in the composting process: the result of test is normalized for a moisture content of 50% so it is a potential respirometric index.

  This index can be done for four or seven days: in the analyses carried out for this research both the RI were developed.

3.1.2 Sieving analyses for the granulometric curve

The granulometric curve of the composted matrixes was drawn starting from the sieving analyses of a sample of less than 2 kg of each heap.

The purpose of this analysis is not directly related with the composting process monitoring, but with the necessity to divide the size of bioplastic pieces, and the only way to reach this result was previously to sieve the composted matrix and then to manually remove the bioplastics, as explained in details it the dedicated paragraph. Furthermore, the separation into different granulometries allows the evaluation of the main component of each withheld sample.

Six sieves were used to describe the granulometric curve of each sample during the composting process: The used sieves are, in accordance with ASTM: 3/4, 3/8, 5/16, 3.5, 8, 14, which corresponds to 20 mm, 10 mm, 8 mm, 5.60 mm, 2.38 mm, 1.40 mm.

This range of sieve highlights law limits, 10 mm and 2 mm, and it allows to comprehend different scales of values, from a sieve just smaller than the starting dimensions, up to much smaller sieves, under the limit posed for microplastics identification, which is 5 mm.

3.2 Evaluation of bioplastics disintegration and degradation in composting

The purpose of my thesis work consists, as said, in defining the behaviour of bioplastics in composting, because, as the most common and used way of bioplastics disposal, it must ensure the disappearance of potentially polluting materials before the use of compost in agriculture.

Compost in fact is mainly used as fertilizer, if it is a compost coming from waste of good quality, without heavy metals, powder from street sweeping, or toxicants, so all the components present in compost are discharged in field, soil and water due to run-off.

This is the reason why the research has the aim to evaluate the level of disintegration and degradation of bioplastics in composting process, providing an answer to the question of which is the fate of bioplastics during and at the end of this waste treatment process.

Disintegration and degradation were separately studied through a series of four analyses: sieving analyses on bioplastic pieces to differentiate them in accordance with the size, showing the trend of size along time. Then the concentration of each single fraction and on the total sample was calculated with the ratio between weight of bioplastics and the weight of the sample.

The study of the concentration involved not only the disintegration, it was just calculated using the data collected with the sieving and sorting analyses, but also the evolution of the influence of the bioplastics amount in the composted matrix.

Biodegradation of the tested material was analysed through the infrared, making a comparison between the spectra at the beginning of the process and during the timing of sampling, up to the last sampling at the of the process.

Through the changes in the bioplastic spectra it was observed the evolution of the material during the phases of the process, and knowing the type of bounds associated to the ranges of the wavelengths it was just possible to follow the passage from a polymer with high concentration of complex bounds to a polymer with a higher concentration of single and generally simpler bounds at the end of the composting process.

The last type of analyses, which showed directly the interventions of the process on the material surface and features, was the visual inspection of the removed bioplastic samples.

On these samples were also carried out TS analyses to define the moisture content of the bioplastics during the process in comparison with the beginning, and some of these pieces were accurately cleaned to measure the effect of dirt on the total weight of the pieces, used in the definition of the sieved fractions.

3.2.1 Sieving analyses of bioplastics disintegration

A crucial point of this research is to find if bioplastics effectively disappeared from composted matrix or if they are still present but in a smaller size than at the beginning of the composting process. Through the sieving of a sample the composted matrix during the phases of composting, it could be possible to divide also bioplastics in accordance with their different granulometries.

To obtain a subdivision of bioplastic samples in accordance with their size, a previous operation to separate the pieces of tested materials from the other components of the composted matrix was necessary.

The operation of the removal of bioplastics from the rest of the composted matrix was quite long due to the difficulties to find a solution different from a manual sorting.

In fact, as described well in the next paragraphs, there are more troubles that influence the removal of bioplastics; firstly their stickiness that keep them attached to wood chips and composted grains, and also they stick each other, secondly this lumps of bioplastics have a density similar to which of grains and wood chips so sedimentation is not always applicable.

When it occurred that bioplastics formed lumps with other components, they were manually taken off and divided from the lump.

It's also fair to say that with the manual sorting of bioplastics in the smaller fractions of the sieves the identification of them into the compost is unlikely on a naked eye.

So, the manual sorting was used until the fraction withheld by sieve 5.60 mm, while for last two fractions it was used firstly manual sorting and secondly sedimentation with water to ensure a total removal of the pieces.

Sedimentation was applied in a bowl with a proportion of 100 g of matrix /2 l of water, in a squared bowl. After the discharge of water within the bowl, a quickly mixing of the solution encouraged the separation of the components of the composted matrix in low and high dense; the solution was left in the bowl for 2 hours and at the end of the process the swimming pieces were removed with a strainer to recognize among them the bioplastics thanks to their aspect and colour.

At the end of the sorting, each bioplastic fraction was weighted with a precision balance and conserved for the further analyses on biodegradation.

In figures 3.1 and 3.2 there are some photographs taken during the manual sorting of bioplastics and the sedimentation.

Figure 3.1-Manual sorting of bioplastics (F. Ruggero, 2017)

Figure 3.2-Starting of sedimentation, mixing, BioPOF after 2 hours of sedimentation (F. Ruggero, 2017)

The manual sorting of bioplastic pieces from each sieve allowed then the subdivision of the tested material within six categories in accordance with their sizes; the smallest passing fraction, less than 1.40 mm, was too fine to allow the finding and the separation of bioplastic pieces, as they had an aspect and a density so similar to that of the compost that nor identification nor sedimentation were possible.

A direct comparison between the categories of size during the timing of sampling along the composting process would have shown the behaviour of disintegration and the consequent creation of the micro-fraction of bioplastics.

3.2.2 Bioplastics concentration

The second type of analyses carried out during the composting process was done exploiting the data collected with the sieving. It was possible through these data to calculate the concentration of bioplastics within the sample.

At the beginning, it was defined the initial concentration: it was determined from data of bioplastics quantity in the real composting processes, considering also a future increase in their production, as previously described, and it can be calculated through this formula:

$$BioP\ Concentration = \frac{BioPi\ (g)}{BioPOFi\ (g)} \tag{5}$$

Where BioP identified the bioplastics within the samples, and BioPOF the compostable matrix including bioplastics.

Then, with the data of the sieving analyses, the concentration was also calculated at the four chosen times during the composting process: it was calculated, using the following equations, the concentration of each withheld fraction, the concentration of the total sample, and of the microfractions smaller than 5.60 mm.

$$BioP\ Concentration = \frac{BioP\ (g)}{BioPOF\ (g)} \tag{6}$$

$$MicroBioP\ Concentration = \frac{BioP < 5.60\ mm(g)}{BioPOF < 5.60\ mm\ (g)} \tag{7}$$

The purpose of this second analysis was to follow the progression of the concentration trend during the process, underlining the differences between each phase and between the initial value and the value at the end of the 55th day.

Furthermore, from the experimental data of the concentration obtained from the collected samples, a more general development was elaborated: the aim was to define the final percentage of weight of bioplastics with respect to the initial weight in each kilo of compostable matrix.

To obtain this result, the following equation was applied:

$$BioP\ concentration\ \left(\frac{g\ BioP}{g\ BioPOF}\right) * BioPOF\ weight\ (g) = BioP\ weight\ (g) \tag{8}$$

Where BioP concentration is the value of the total concentration of BioP in each sample taken from the heaps at the times of analyses, obtained experimentally.

In this way, applying the concentration found for the samples to a general vision where the weight is no more that of the sample but that of the heap, it is possible to obtain the weight of BioP in the heap, or in 1 kg of matrix.

At this point, a further step consisted on defining all the possible variables involved in the weight of the BioP during the treatment, because it was observed that they had some features, so different from the initial ones, that they could contribute to weather the real weight of the plastic piece.

So, taking into account points, defined when the test had been already carried out, it was defined a ranging value of decrease with respect to the observed weight, to attest the real weight of bioplastics.

3.2.3 IR analyses of degrading bioplastics spectra

The study of biodegradability of bioplastics was done with the method of the infrared analyses: this method allowed to follow the changes in the spectrum of the tested material during the process, providing a new solution in the evaluation of the biodegradation, generally done through the monitoring of CO_2 emissions or of the weight losses.

Infrared analysis allows to know the spectrum of the tested material: in the spectrum, each of the peaks represent a bound, leading to the possibility to identify the main polymers of which the material is composed.

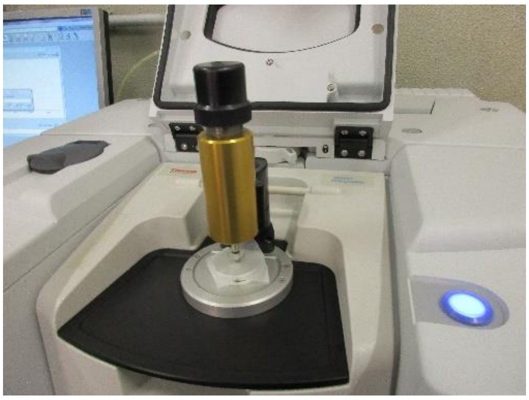


Figure 3.3-IR machinery (F. Ruggero, 2017)

Through this analysis the changes in the spectrum of bioplastics had been followed during the composting process, so that there could be identified those bounds which firstly were broken.

An important point of this method involves the fact that no literature of biodegraded bioplastics spectra was present before my analyses: as a consequence the analyses were not used to make a direct comparison between the spectra obtained and some reference spectra, but they were used to make a comparison among the obtained spectra in the times of sampling.

IR spectroscopy means the absorption of IR radiation, which is the part of the electromagnetic spectrum with wavelength between visible < 0.7 micron and microwaves > 1 mm. The wavelength used in organic chemistry is 2.5-25 micron, it corresponds to 4000-400 cm^{-1}.

The IR absorption bands have two characteristics: frequency and magnitude. The former is signed in the horizontal axis at it corresponds to the absorbed IR wave numbers. It depends on the constancy of the bound strength, coming from the bound order, and on the mass of the involved atoms. The latter corresponds simply to the amount of IR, and it is visible in the spectrum through the peaks. It depends on the variation of the dipolar momentum after a vibration.

The IR analysis was done as first step to identify if the spectrum of the different bioplastic bags was the same or not, in order to decide if keep the material as a variable or as a constant during the test.

The results, showed in figure 3.4, highlighted that all the four tested biobags were made of the same polymers. The main reason to which this result can be related is that the material used for bags come from the same industry and is then modelled by each agency for bags production.

The analysis was carried out also on the laces for bags closure, because they have a different colour form the rest of the material, but the resulted spectrum was the same.

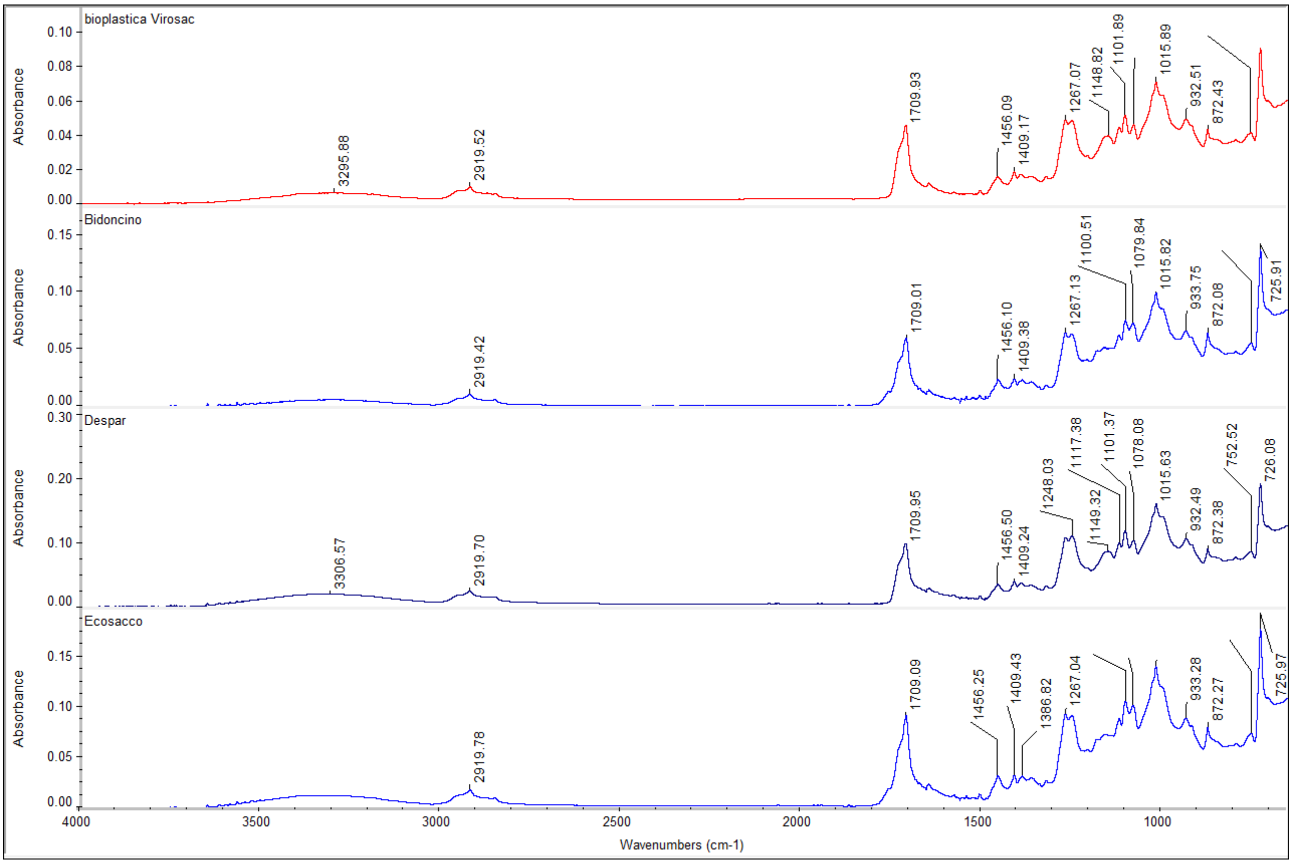


Figure 3.4-Comparison between spectra of four different bioplastic bags distributed in the Italian markets

Once this point was clarified, the identification of the polymers composing the material was done through a comparison with spectra already present in literature and in scientific registers of the laboratory.

Knowing first of all that these biobags are made on Mater-Bi, all the classes of Mater-Bi were studied and the spectra of the polymers used for their production were found in literature.

The most probable composition was a polymer with corn starch and PBAT, typical of Mater-Bi class N. In figure 3.5 the three spectra are compared: in the spectrum of BioP it's possible to identify the main peaks of the two polymers.

Between 4000-2500 cm^{-1} the peaks represent single bounds, as C-H and O-H, from 2500-2000 cm^{-1} the triple bounds, not present in this bioplastic, between 2500-2000 cm^{-1} the peaks are typical of the double bounds, then the smallest values of wavelenght correspond to other bounds, for example which of C=O with a glucosidic ring. It’s also fair to say that the same type of molecular bound can have different arrangements, in accordance with the different wavelenght.

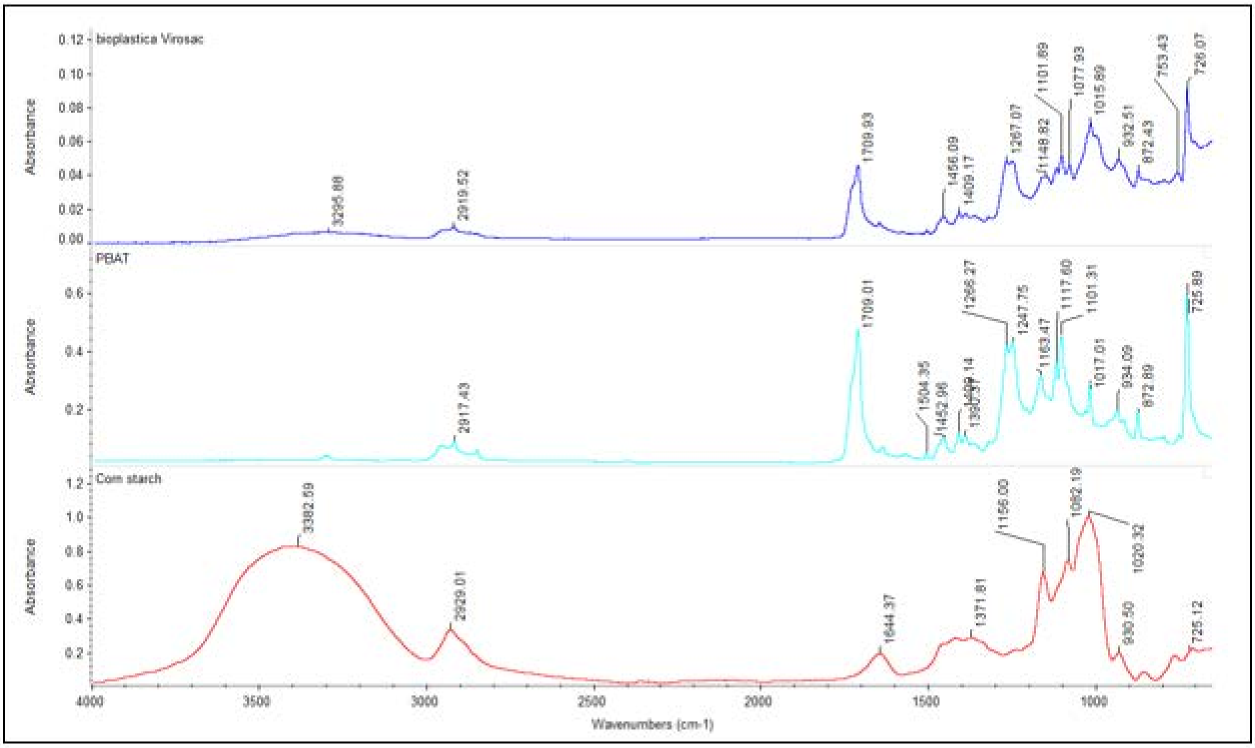


Figure 3.5-Spectra of polymers composing BioP

3.2.4 Visual analyses of bioplastics changing features

The visual analyses are proposed by the standards regulating the full scale tests on bioplastics: they allow the study of the surface aspect of bioplastic pieces during the phases of the composting process. In particularly, the visual inspection to evaluate the presence of holes, lateral erosion, dirty, and to show the differencies in pieces sizes in time.

Furthermore, observing the evolution of the aspect of bioplastics, it will be possible to define when is the turing point after which the pieces of the tested material become assimilable to compost for their size, colour, smell and features.

The second important analysis, linked with a visible and direct change of bioplastics features, involves the study of the physical and mechanical properties of the material, underlaing the differences between the beginning and the phases of the composting process.

An example of how this method will proceed in parallel with the other analyses is in figure 3.6, where, after the manual sorting of bioplastics, some photographs were taken to immortalize the changes of aspects.

Figure 3.6-Bioplastics aspect after the removal from composting (F. Ruggero, 2017)

3.3 Samples preparation and characterization

To start the research, the main decisions involved in the preparation of the samples, were: quantity of bioplastics inside tests, their initial sizes, quantity of waste matrix to be composted, numbers of replicated and the location.

3.3.1 Choice of the initial conditions

A relevant point to match in this small scale test, is the number of variables that could be involved in the disintegration and biodegradation of bioplastics: the initial quantity of bioplastics thrown away in the waste matrix, the size of bioplastic pieces, their thickness and composition, the different products made on bioplastics, the environmental conditions and the composition and quality of waste matrix.

Furthermore, before starting with the test, another consideration was done to choose the number of samples, and it concerns the management of the experiments. Analyses of weight, temperature, moisture content, acidity and oxygen are monitored once or twice a day, and mixing is done almost every day during the first phase, and twice a week during the maturation.

Considering all the possible variables, it was decided for this research to use as main variable the different sizes of bioplastics within the waste matrix, and the other as constants.

In fact, in the composting plants when bags with organic waste arrive, the first steps consist on bag opening and shredding, until dimensions from 1/2 cm to 7 cm.

In accordance with a not evenly performed shredding, two sizes were chosen: small size, from 1 to 3 cm, and big size from 4 to 7 cm.

The shredding was done manually with scissors, so the pieces are not homogeneous in length and width (Figure 3.7).

Figure 3.7-Small bioplastics size and big bioplastics size (F. Ruggero, 2017)

The pieces were accuratley divided because bioplastics have the tendency to remain attach each other when they stay in contact, but to start the test in a way as similar as possible to the real conditions of a composting plant they were separated, as the pieces of a biobag for waste collection.

This tendency to remain attach is called stickiness, and the evolution of this characteristics will be accurately followed during the composting process, as it could be an element involved in bioplastics degradation.

3.3.2 Choice of the constant values and variables of the tested material

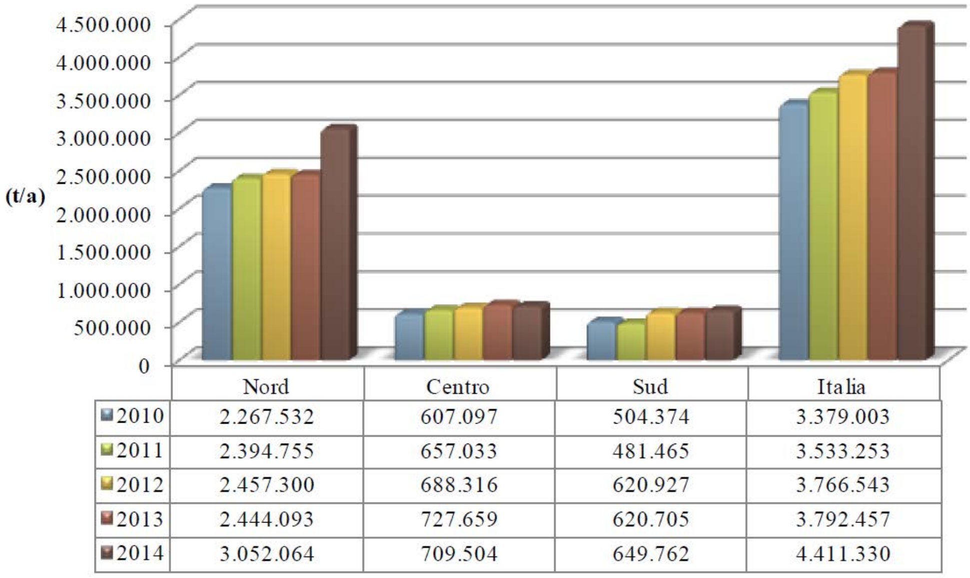
It’s fair to discuss also about the constants of the research: quantity of bioplastics in the sample, reference product, which is a bag for organic waste collection, and the typology of bag.

The first thing to underline is that the field of this research is a sector in continuous developments; consequently, the idea is not to focus on the actual situation, but to adjust it in the prospective of an expected increase of bioplastics use into the next five to ten years.

Made this clear, it’s possible to proceed with the explanation of the constant value chosen for quantity of bioplastics in the samples.

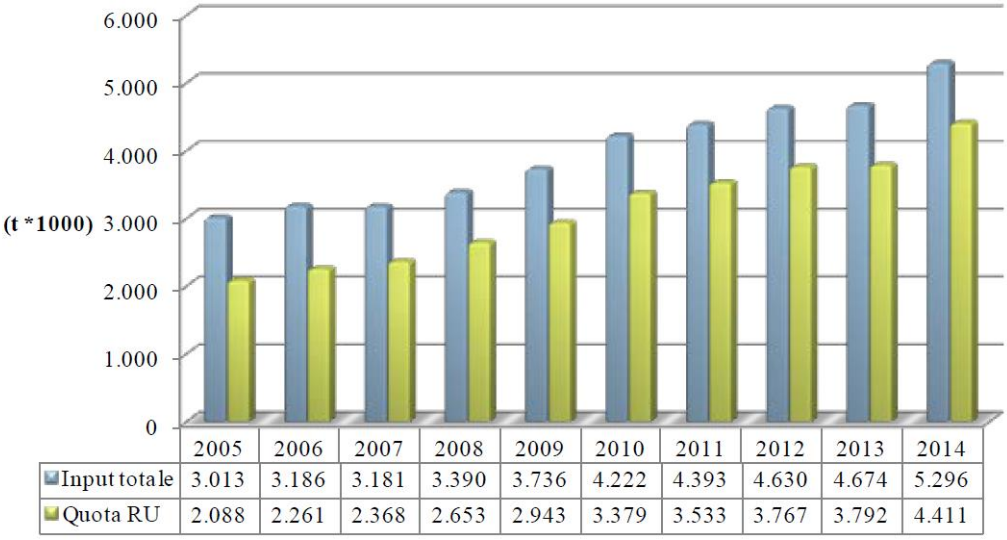
To evaluate the initial concentration of bioplastics inside the waste matrix to be composted, data from *Rapporto Rifiuti Urbani 2015*, ISPRA and from ARPAV were used.

Two representative graphs taken from ISPRA report are shown: the former in figure 3.8 with waste disposed of in composting plants, coming from separate collection of organic fraction, the latter in figure 3.9 with all the waste arriving at the composting plants, included green waste and sludges from waste water treatment plants.



	Nord	Centro	Sud	Italia
2010	2.267.532	607.097	504.374	3.379.003
2011	2.394.755	657.033	481.465	3.533.253
2012	2.457.300	688.316	620.927	3.766.543
2013	2.444.093	727.659	620.705	3.792.457
2014	3.052.064	709.504	649.762	4.411.330

Figure 3.8-Composting of organic fraction from separate collection in Italy. (ISPRA, 2015)



	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Input totale	3.013	3.186	3.181	3.390	3.736	4.222	4.393	4.630	4.674	5.296
Quota RU	2.088	2.261	2.368	2.653	2.943	3.379	3.533	3.767	3.792	4.411

Figure 3.9-Quantity of municipal solid waste disposed of in composting plants in Italy. (ISPRA, 2015)

In figure 3.10 it is represented the partition of the different fractions arriving at a composting plant on average in Italy.

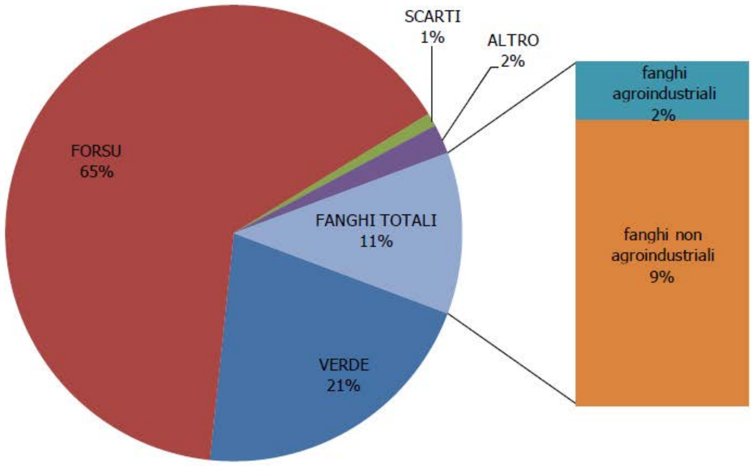


Figure 3.10-Fractions of waste to composting. (ARPAV 2015)

The waste mainly responsible of the discharge of bioplastics in composting plants are those coming from houses separate collection of the organic fraction, since putrescible waste are thrown in bins inside a bag, and this bag is made on bioplastics.

Furthermore, with the emerging use of bioplastic cutlery and packaging, also these products will be thrown away together with organic fraction.

Another important data available concerns the yearly organic waste production pro capite in Veneto; table 3.2 is built in accordance with ARPAV, 2015.

Table 3.2-Yearly production of organic waste pro capite in Veneto. ARPAV 2015

Year	*Kg/inh/y*	*Increase*
2015	140	-1.4 %
2014	142	+5.8 %
2013	134	+3 %
2012	130	+3.8 %
2011	126	-1.7%

Many biobags for organic waste collection are available on the market, with different dimensions: 10 litres, 15 litres or 30 litres. And different weights, variable between 6 grams and 14 grams depending on the bag size.

Some Italian composting plants provide bags for waste collection, so that all the waste conferred to the plant have the same bag, but generally people are free to use compostable bags bought in the supermarket.

So, it's not easy to give a statistical for the grams of bags per kilo of waste: to reach a final estimation, some considerations were met.

Firstly, it was made a proportion between the amount of waste disposed of in composting plants, from ISPRA data, and the production of compostable bioplastics from European Bioplastics data, as expressed in table 3.3.

The variables are on the one hand the bioplastic production in Italy, equal to 0,021 if the precise proportion between European population and Italian population is done, and equal to 0,050 in accordance with a little bit difference in bioplastics production all over the Europe, with Italy as a greater producer than other countries, as explained in paragraph 2.2.

On the other hand, it was taken into account also the forecast increase in bioplastic production and in waste collected and disposed in composting.

From European Bioplastics 30% was estimated as the increase in bioplastics production, shown in figure 3.11, while 3% is a mean value of increasing waste to composting over the last ten years present in the ISPRA report.

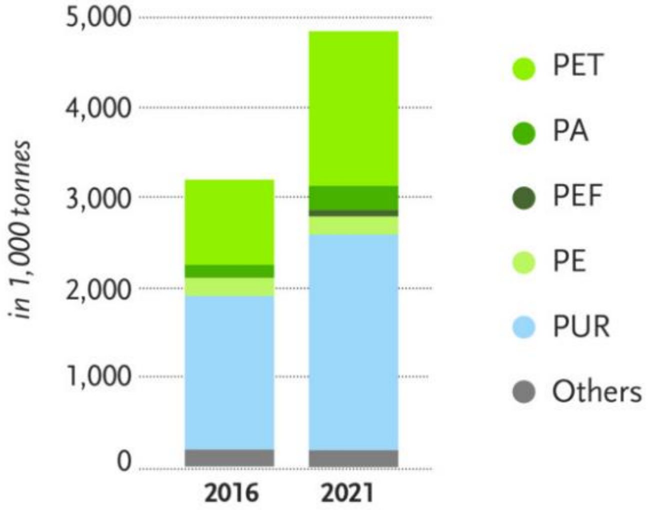


Figure 3.11-30% increase in bioplastics production all over the world. (www.european-bioplastics.org)

Table 3.3-Proportions between waste to composting and bioplastics produced

	Waste to composting (million tons)	*Bioplastics production (million tons)*	*Proportion: waste to composting/ bioplastics*
Data of 2015/2016	5,3	0,021	252/1
Data of 2015/2016	5,3	0,050	106/1
Data forecast for 2018	5,3 + 3 %	0,021 + 30 %	200/1
Data forecast for 2018	5,3 + 3 %	0,050 + 30 %	84/1

It's fair to consider that not all the bioplastics produced will be led to composting plants after their used, so the values in the proportions should be adjusted a little bit.

Secondly, knowing the capacity of a biobag and the amount of organic waste produced pro capite a day, an estimation of biobags grams per kilo of organic waste was done: few variables must be considered, as the number of householders, the fact that sometimes the bag are not completely filled before having thrown in the bins, the collection system, the period of the year, because in summer organic fraction is collected generally every days to avoid bad smells, and so for small families bags could be half full.

To conclude, the production of bioplastic waste is about 5,5 g every 1 kg of putrescible collected.

Adjusting this value with a future forecast increase of 30% in bioplastic products thrown away together with organic fraction, the amount is of 7 g per kilo.

The second constant consists on the bioplastic product to use as tested material: just because the main bioplastic product used is biobag for organic waste collection, a bag was taken as tested materials.

Bioplastics bags present on the market are almost all composed on Mater-Bi; the chosen bag is produced in Veneto, and has a high number of certifications: CIC, Vinicotte OK compost, Mater-Bi Novamont license and obviously, it is according with EN UNI 13432.

As explained in the paragraph 3.2.3, the decision to take constant the typology of tested material was supported by an infrared analysis of biobags spectrum. It defined that the analysed biobags, all bought in supermarkets, have the same spectrum, it means the same composition, so it was feasible to use only one type of bag.

3.3.3 Characterization of the compostable matrix

Waste used to simulate real matrix of composting plants are four, with the exclusion of waste representative of sludge from waste water treatment plants.

For the putrescible kitchen waste, without paper from handkerchiefs and napkins, were taken from university canteen: it was provided with a machinery which shreds the food scraps in pieces of about 1 cm with a moisture content varying from 60 to 80%.

Green waste was simulated using clipping grass and wood chips; the adding of grass adjusted the nutrients contents, while wood chips increased the structure of the composting matrix and decreased the moisture content until a suitable level.

Finally, a percentage of manure enriched in bacteria were added as inoculum (Figure 3.12).

Figure 3.12-Food waste, wood chips, clipping glass and inoculum to compose OFi (F. Ruggero, 2017)

To verify the initial mixture of waste composing OF complied with the requirements of waste to composting, the analyses of the main parameters were carried out on the single components of the matrix and a mean value of them was elaborated with a weighted average.

Table 3.4-Paramters of the single components of the waste matrix

OFi composition	*Percentages%*	*Quantity Kg*	*Moisture %*	*VS%*	*TKN g/kg TS*	*TOC g/kg*	*C/N*	*pH*
Kitchen waste	53	2,65	80	96,4	29,5	493	17	7,4
Clipping grass	3	0,15	50	46,9	11,7	311	27	5,5
Wood chips	33	1,65	25	96,9	7,2	511	71	6,4
Manure	11	0,55	18	63,8	34,5	348	10	5,6

The main requirements are the value of moisture, volatile solids and C/N, so their weighted average is elaborated in the following table, with the purpose to show that they are suitable for the composting process, in accordance with the standards. In fact moisture content and VS are higher than 50%, C/N is in the required range 20-35, and pH higher than 5.

Table 3.5-Weighted average of the parameters required by composting standards

OF Initial conditions				
Parameter	*Moisture %*	*VS%*	*C/N*	*pH*
OF weighted average	54	91	34	6
Required values (EN 13432)	> 40-50	> 50	20-35	> 5

When these values had been analysed in the initial matrix with all the components mixed together, they were found to be a little bit different, especially the C/N; the observation is linked with some considerations, as the points of sampling, the effect of the mixing, the predominance of a component on the others.

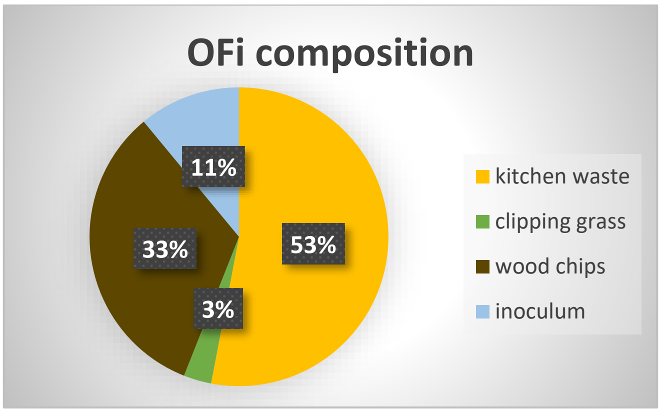


Figure 3.13-OFi composition in percentages

3.3.4 Location of the tests and their mounting

The location for the storage of the samples was a box, with internal temperature in accordance with the external one; for the hot climate in summer an air conditioner was installed inside the container to maintain the temperature around 25 -30 °C.

The initial idea for this research was to compose small baskets with 5 kg of waste each, in order to disassemble all of them in different established timings to carry out analyses on the composting process and on bioplastics.

Three blanks for the first line, five samples with small bioplastics size for the second and five samples with big bioplastics size for the third line.

The three blanks were useful to compare the final quality of compost without and with tested material, and to evaluate the differences in weight losses between them along the process.

It was considered that in number of three they can be representative of a statistical, and if along the process it was considered worthwhile to destroy one of them to carry out some deeper analyses on composting parameters and granulometry, other two blanks would be continued until the end of the experiments.

For the two lines with bioplastics, five replicates were prepared, in accordance with the necessity to have four samples to be analysed along the process (Figure 3.15).

To hold the composting waste, baskets with holes generally used for fruits and vegetables were kept; holes are necessary to allow exchange of oxygen and exit of water, but to avoid the passage of the smallest fractions of the matrix, the basket was internally lined with a mosquito net, firm seals with clips. At the bottom of the basket a tray was displaced in other to collect water and allow the weighting of water losses during the process (Figure 3.14)

Figure 3.14-Photographs of materials supplied for the experimentation (F. Ruggero, 2017)

Line: Blanks	Blank 1 5000 g OFi	Blank 2 5000 g OFi	Blank 3 5000 g OFi		
Line: Small size	Sample 1 Size 1-3 cm 5000 g OFi 35 g BioPi	Sample 2 Size 1-3 cm 5000 g OFi 35 g BioPi	Sample 3 Size 1-3 cm 5000 g OFi 35 g BioPi	Sample 4 Size 1-3 cm 5000 g OFi 35 g BioPi	Sample 5 Size 1-3 cm 5000 g OFi 35 g BioPi
Line: Big size	Sample 1 Size 4-7 cm 5000 g OFi 35 g BioPi	Sample 2 Size 4-7 cm 5000 g OFi 35 g BioPi	Sample 3 Size 4-7 cm 5000 g OFi 35 g BioPi	Sample 4 Size 4-7 cm 5000 g OFi 35 g BioPi	Sample 5 Size 4-7 cm 5000 g OFi 35 g BioPi

Figure 3.15-Scheme of the samples od line 1

To have the precise weight of waste along the process and daily weight of water, in table 3.6 the weights of basket and tray for each test are reported.

Table 3.6-Weight of basket and tray for test storage

Sample name	*Basket weight with nets and clips (kg)*	*Tray weight (kg)*
OF 1	0,478	0,509
OF 2	0,484	0,482
OF 3	0,582	0,508
BioPOF 1 small	0,475	0,506
BioPOF 2 small	0,681	0,509
BioPOF 3 small	0,652	0,480
BioPOF 4 small	0,553	0,483
BioPOF 5 small	0,492	0,484
BioPOF 1 big	0,660	0,509
BioPOF 2 big	0,477	0,482
BioPOF 3 big	0,531	0,483
BioPOF 4 big	0,761	0,481
BioPOF 5 big	0,701	0,509

The heaps of waste to be composted were prepared by mixing together the amount of the different components previously discussed in blanks, and adding the shredded bioplastics for the samples with tested material.

To be sure that the established proportions were perfectly respected in the samples, each matrix was individually prepared, mixed and disposed in the respective basket, after ensuring the total weight was equal to 5 kg for blanks and to 5,035 kg for the two lines of BioPOF (Figure 3.16).

Figure 3.16-Working on the sample building (F. Ruggero, 2017)

The resulting aspect of the heaps immediately after their building is shown in figure 3.17; each component is easily distinguishable from the others, and the shape of the sample can be maintained as a heap thanks to the presence of wood chips that ensure a good structure of the matrix.

For the first days, the baskets were partially covered with a bag; this was done only during the night, because the experiments began at the end of march and, with a minimum temperature in the night between 5 and 10 °C.

So, the coverage allows the temperature inside the heaps to increase and the process to start, avoiding a high influence coming from the external cold.

Air could enter from the sides of the basket, as the photograph shows, so that oxygen level remained suitable for the advancement of composting process.

To conclude, all the samples were aligned on tables inside the container, finally ready to start their composting process (Figure 3.18).

Figure 3.17-Heaps aspect immediately after their building, and coverage for the night (F. Ruggero, 2017)

Figure 3.18-Heaps on their baskets, on tables inside the container (F. Ruggero, 2017)

Having followed the composting process during the thermophilic phase, it was noticed that such small heaps of waste were not able to retain the heat; so, being in a period between winter and spring, during the night the temperatures decreased both in the box and in the heaps.

Problems like this are possible when it is carried out a research in a new field, without a bibliography to support the experimental part: the solution thought to overcome the problem was firstly to join the baskets of each sub-lines at the end of the thermophilic phase, creating three bigger heaps. Secondly to start with a new line directly with three heaps of 25 kg each, one for the blank, the other two with the tested material in the two defined different sizes. The same bioplastic material was used and the initial composition of waste compostable matrix was the same of the previous tests.

The heaps were located in the box, a nylon cloth was put on the floor in order to retain the leaching water, and edges were made with tubes to keep separate the heaps and avoid mixing of their materials during the operations of turning, weighting, sampling and water adding (Figure 3.19).

In figure 3.20, the photographs of the heaps just composed: bioplastics are visible even if their colour is similar to which of the waste.

Figure 3.19-The place for compostable heaps (F. Ruggero, 2017)

Figure 3.20-Line 2: OF, BioPOF small, BioPOF big (F. Ruggero, 2017)

From this point to end of the research, the two lines are called Line 1, started from the baskets jointed into three heaps after the thermophilic phase, and Line 2, started directly from the heaps of 25 kg.

In figure 3.21 is reported the scheme of the two lines with the respective blank (OF), matrix with small size bioplastics (BioPOF small) and matrix with big size bioplastics (BioPOF big), while in figure 3.22 the three just composed heaps of Line 2 on the right and the three heaps of Line 1 at the end of the thermophilic phase on the left.

It was already visible the difference in the process development even if the two lines had been started only with ten days of distance.

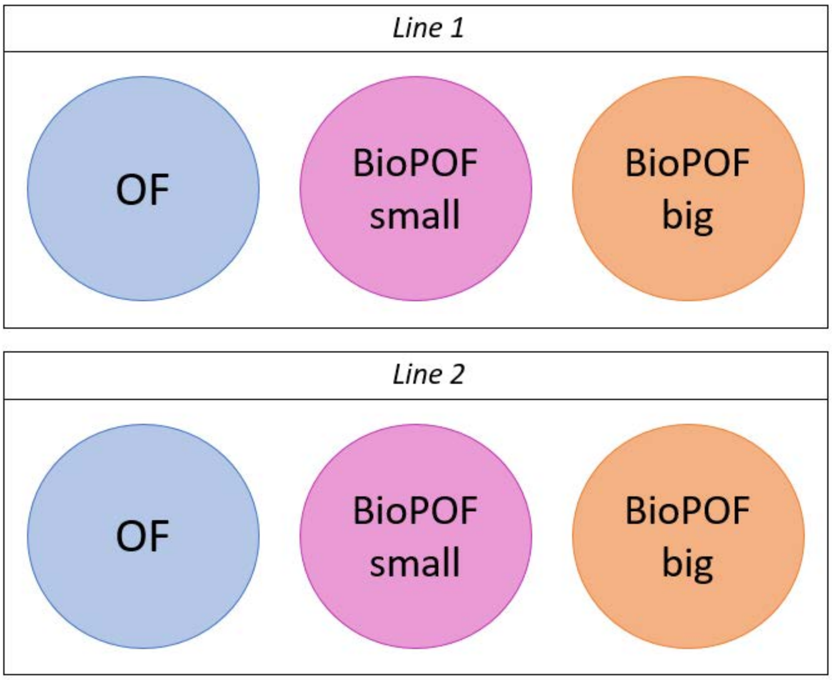


Figure 3.21-Scheme of the two lines with the respective heaps

Figure 3.22-Line 1 and Line 2 with blanks and heaps containing the tested material (F. Ruggero, 2017)

4. RESULTS AND DISCUSSION

4.1 Analyses of the composting process parameters

The parameters analysed during the composting process are reported in this paragraph to follow the evolution of the composted matrix in time, up to the results which defined the end of the process, in accordance with the required standard values.

The graphs and tables are in part reported in the Annex I: composting process parameters.

4.1.1 Temperature

During the period of experimentation, the outside temperature had a great variability, and the thermophilic phase of the two lines coincided with two different climatic conditions: for the Line 1 at the end of march the outside temperature was around 10 up to 20 °C, feeling the influence of night and rainy days, while for the Line 2 the external conditions were more favourable, with a higher constancy of temperature around 25 °C.

Figure 4.1 shows a comparison between the outside temperature and the heap temperatures for Line 1: in the Annex I the graphs with also the comparison between temperatures of the three heaps of each lines, even if their values are significantly similar one to the others.

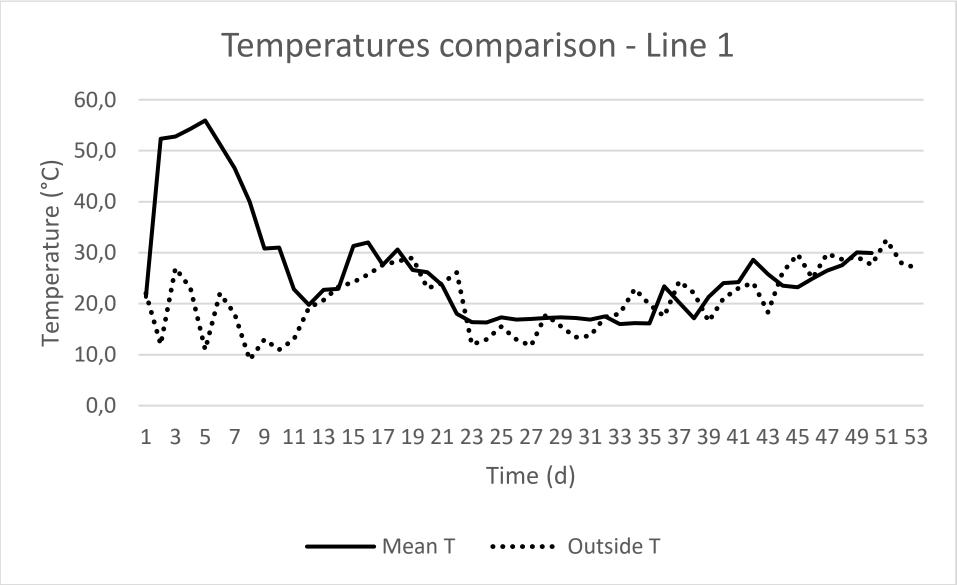


Figure 4.1-Comparison between outside temperature and heaps temperature - Line 1

It results then interesting the graph built in figure 4.2 which representing the different phases of the two lines with the respective changing temperatures; making an average between the main steps of temperature values during the process, four phases could be identified. Starting from the lag phase, very brief due to the small mass of the compostable heap, then the thermophilic phase of nine days, the cooling phase of eleven days, followed by the maturation phase of one month. This last phase presented an increase of temperature from the 47th day to the end, and it was clearly linked to the outside increase of temperature. In fact, as the lower temperature of thermophilic phase in Line 1 than in Line 2 was linked with the outside lower temperature, also the influence of a hot climate was able to influence in the opposite way the increase of temperature within the heap.

This influence from outside was mainly reliable with the small mass of the heap which was not a good buffer between inside conditions and outside climate.

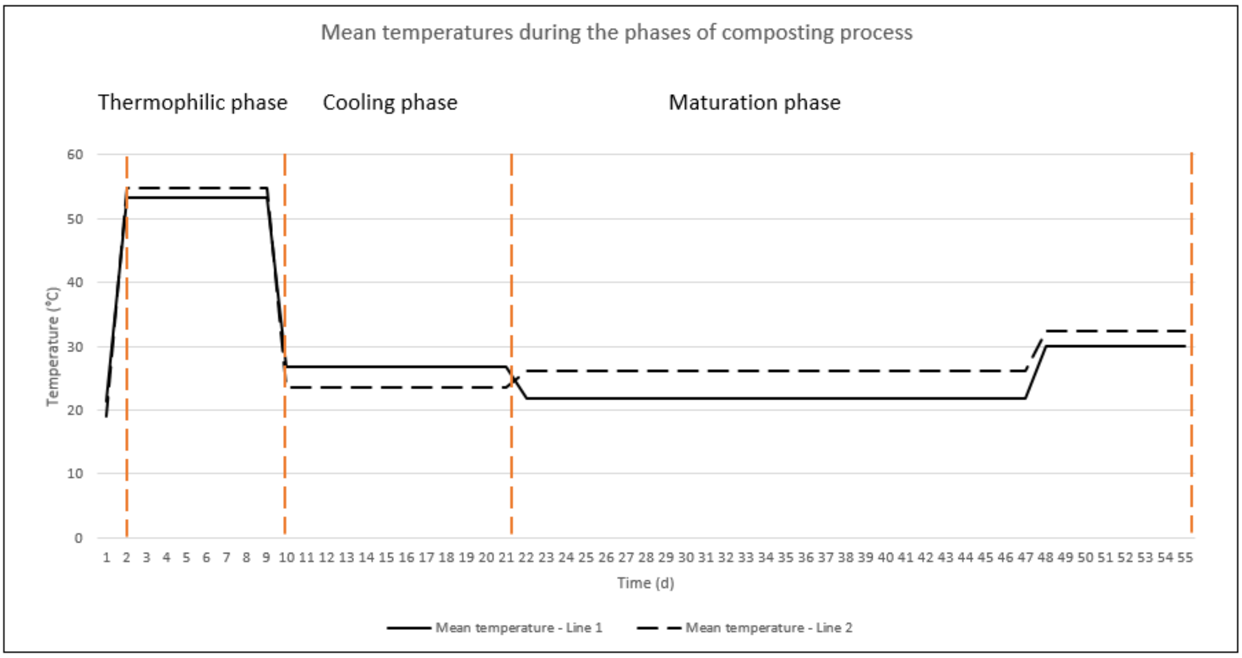


Figure 4.2-Mean temperatures during the phases of composting process

4.1.2 Weight

The weight losses were monitored every day during the thermophilic phase of the Line 1, when the samples were located in the baskets. Then, after the composition of the six heaps, the weight was monitored in the timings of sampling for the analyses.

In fact, to weight the heaps, they were dismantled and put within a big basket to be weighted in a balance precise up to the grams, able to weight no more than 30 kg.

Each heap was then rebuilt in the typical pyramidic shape.

The total weight of the heaps is shown in figures 4.3 and 4.4, for the two lines, and summarized in table 4.1.

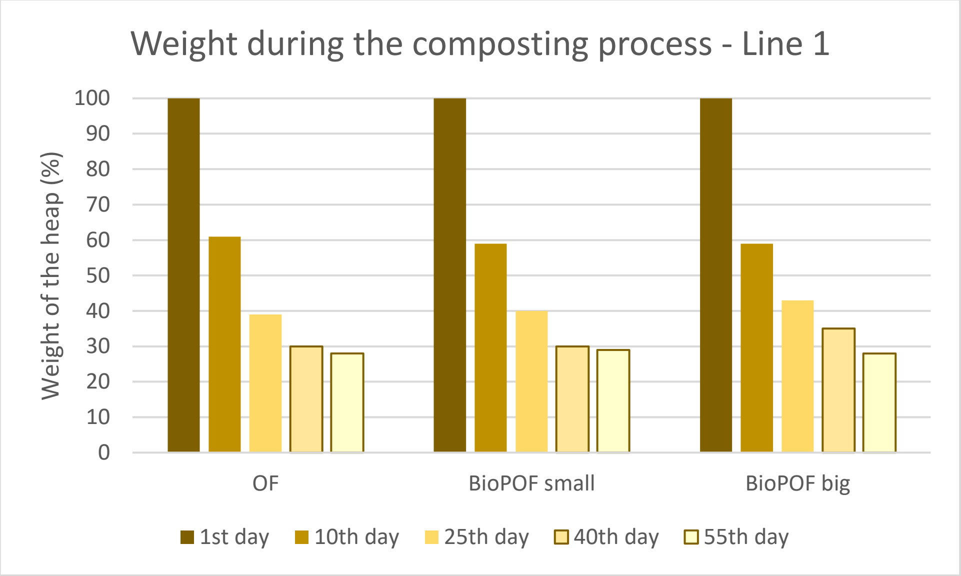


Figure 4.3-Total weight of composted heaps- Line 1

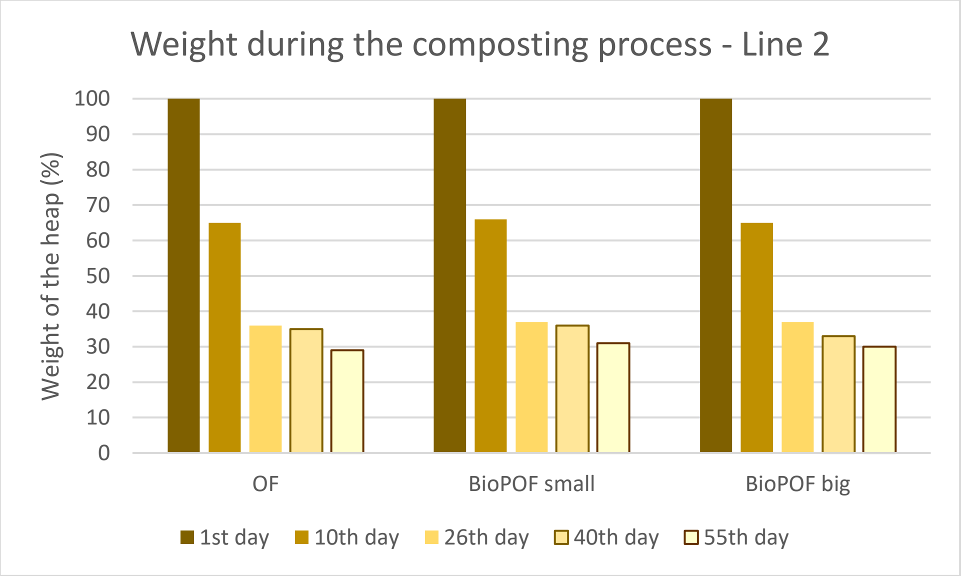


Figure 4.4-Total weight of composted heaps- Line 2

Table 4.1-Total weight of heaps during composting process

	Line 1 Weight %			**Line 2 Weight %**		
	OF	*BioPOF small*	*BioPOF big*	*OF*	*BioPOF small*	*BioPOF big*
1st	100	100	100	100	100	100
10th	61	59	59	65	66	65
25th	39	40	43	36	37	37
40th	30	30	35	35	36	33
55th	28	29	28	29	31	30

As the histograms elaborated for each phase of the process show, the weight decreased in fifty-five days from 100% to 30%, in accordance with the general values reliable to a real composting process.

In particularly it is fair to observe that the main weight losses were between the 1st and the 10th day, so during the thermophilic phase, and between 10th and 25th, the cooling phase.

During the maturation phase there was a weight stabilization, consequently also to the stabilization of the moisture content.

In the monitoring of the weight, the sampling and the water adding were taken into account for the elaboration of the mass balance.

In table 4.2 and in figures 4.5 and 4.6 it is represented the dry weight during the days of the sampling.

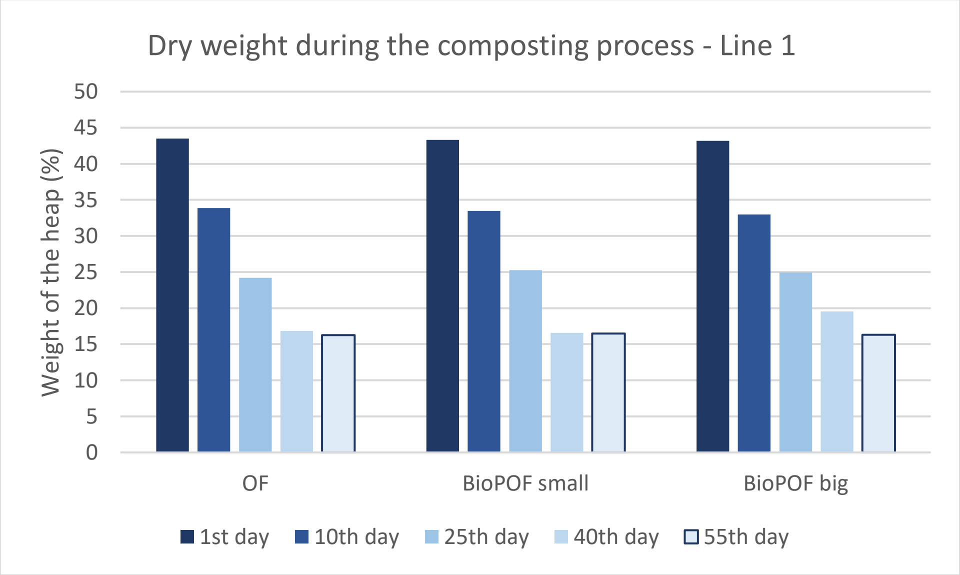


Figure 4.5-Dry weight of composted heaps- Line 1

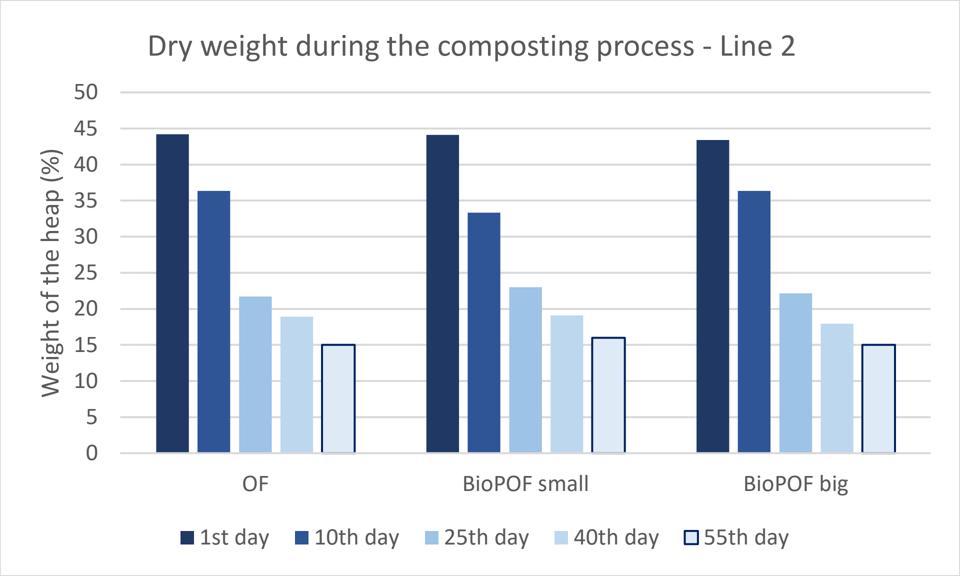


Figure 4.6-Dry weight of composted heaps- Line 2

Table 4.2-Dry weight of heaps during composting process

	Line 1 Dry weight %			**Line 2 Dry weight %**		
	OF	*BioPOF small*	*BioPOF big*	*OF*	*BioPOF small*	*BioPOF big*
1	43,5	43,3	43,2	44	44	43
10	34	33	33	36	33	36
25	24	25	25	22	23	22
40	17	17	20	19	19	18
55	16	17	16	15	16	15

4.1.3 Total and volatile solids

Since to apply this procedure a sampling was necessary, it was done during the thermophilic phase once every two days and during the maturation once a week, in order to keep under control the water content within the heap and to maintain it constant up to 55%, adding water, when it decreased.

The water was added with a watering can for flowers, to distribute the water in all the points of the heap, and then mixed to ensure an equalization of the moisture content.

The graph here reported is the moisture for Line 2, but the tables and the graph of total solids and moisture for Line 1 are reported in Annex I.

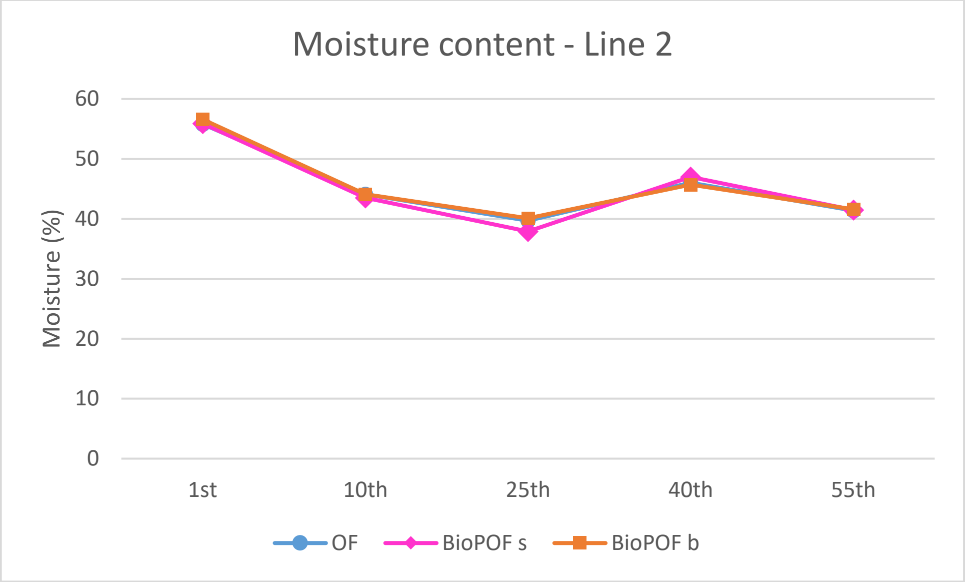


Figure 4.7-Moisture content - Line 2

The decreasing peak from the 10th to the 25th day was linked with the initial try to not supply a manual intervention on the heaps, to leave them making their own pathway during the cooling phase and observe if the degradation activity was still intense or not.

Because the water content had fallen down to 40%, it was necessary to supply water: at this point the process showed an increase also in temperature, it meant that the activity of degradation of the organic substance was not finished at all and the conditions suitable for the living organisms should be maintained for all the process.

Furthermore, it was noticed that the degradation of bioplastics still proceeded even when water was not supplied, so the try to leave the process without manual intervention gave the information that bioplastics are degraded by those microorganisms, as fungi, which are less sensitive to internal conditions of the heap.

The results of the volatile solids are reported in Annex I, even if they didn't show a great variation in time, especially due to the presence of wood chips which need more time to be degraded and it is so reach in carbon content that it contributed to increase the value of all the samples taken along time.

4.1.4 pH

In accordance with the composting process, the pH of the samples taken never went under 5, it meant that no anaerobic processes of fermentation had happened and the process remained aerobic at all.

In fact, through the mixing, the supply of oxygen above 20% was ensured: it's possible to observe that around the 40th day there was an increase of the values around 8, but at the end of the process the pH was stabilizing around the neutral value of 7,5 as required for a mature compost.

Table 4.3-pH

pH					
	Line 1				
	1st	10th	25th	40th	55th
OF	5,48	7,17	7,45	7,86	7,61
BioPOF s	5,23	6,32	7,56	7,92	7,71
BioPOF b	5,51	6,44	7,23	7,91	7,54
Mean	5,4	6,6	7,4	7,9	7,6
	Line 2				
	1st	10th	25th	40th	55th
OF	5,53	7,07	7,42	7,97	7,5
BioPOF s	5,22	7,13	7,31	7,92	7,77
BioPOF b	5,37	7,03	7,42	7,78	7,75
Mean	5,4	7,1	7,4	7,9	7,7

4.1.5 TKN and nitrates

The results of TKN analyses drew a behaviour which was not uniform nor constant at all, but it's important to keep in mind that the experiment, even if was done on a small scale, could have some differences in the results due to the different points of sampling, so it was possible that for OF it existed a decrease instead of a constant increase between 25th and 40th days.

However, having started from values of about 250 g per heap, the losses were of 100 g, showing a consumption of nitrogen by microorganisms that mainly needed it, in accordance with the Liebig law, for their metabolic processes.

The results are reported in table 4.4 and graph 4.8 for Line 2.

Table 4.4-TKN in grams

TKN g					
	Line 1				
	1st	10th	25th	40th	55th
OF	116	112	120	64	77
BioPOF s	219	207	158	84	134
BioPOF b	235	205	163	122	138
Mean	190	175	147	90	116
	Line 2				
	1st	10th	25th	40th	55th
OF	222	230	140	130	120
BioPOF s	247	223	186	156	136
BioPOF b	170	228	173	141	130
Mean	213	227	167	142	129

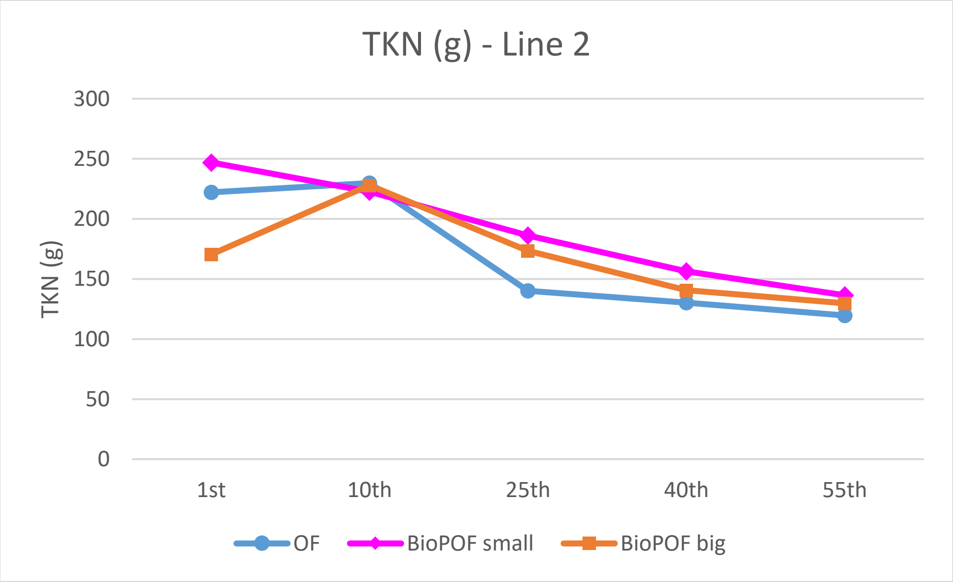


Figure 4.8-TKN behaviour during the composting process – Line 2

As for the nitrates, in all the analysed samples they were less than 10 mg/Kg TS, with the exception for:

- OF Line 2 55th = 23,6 mg/Kg TS
- BioPOF Line 1 55th = 15,4 mg/Kg TS

It means that there contribute to C/N is negligible.

4.1.6 TOC and inorganic carbon

The graph 4.9, reported here only for Line 2, shows the decrease of total organic carbon, linked with the consumption of the organic substance by the microorganisms: the final amount of carbon present in the heaps was still high because, as valid for the volatile solids, it corresponded to the presence of wood chips which require a longer time to be attacked and degraded by fungi, during the maturation phase.

Table 4.5-TOC in grams

TOC g					
	Line 1				
	1st	10th	25th	40th	55th
OF	3334	2346	1566	1093	1022
BioPOF s	5553	3839	2682	1858	1613
BioPOF b	5594	3818	2590	2182	1669
Mean	4827	3334	2279	1711	1435
	Line 2				
	1st	10th	25th	40th	55th
OF	5658	4260	2562	2159	1967
BioPOF s	5689	3867	2660	2156	1571
BioPOF b	5436	4133	2477	1967	1560
Mean	5594	4087	2566	2094	1699

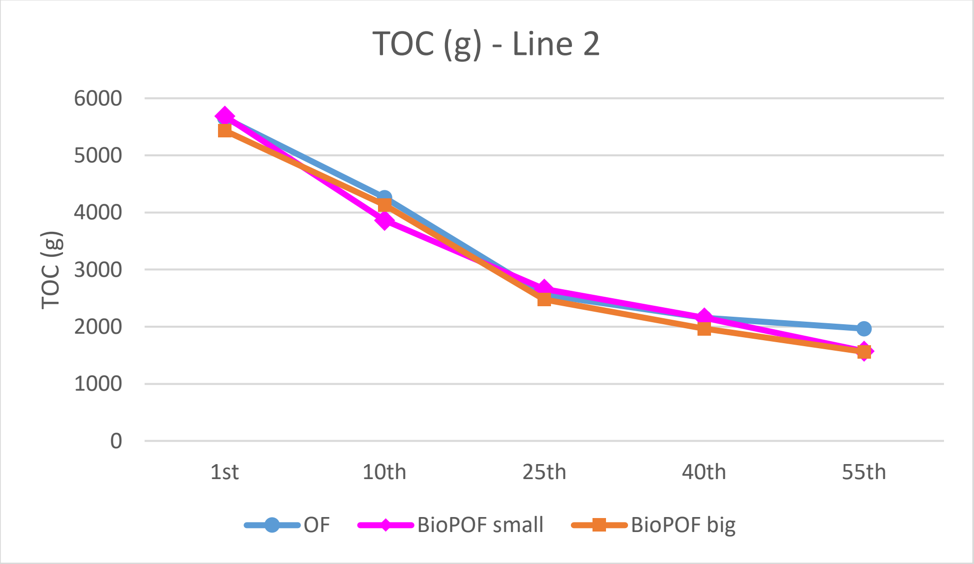


Figure 4.9-TOC behaviour during the composting process - Line 2

Moreover, the analyses on the inorganic carbon resulted less than 1 g/kg TS, it means that the parameter is negligible with respect to TOC.

4.1.7 C/N

In table 4.6 they are reported all the values of C/N along the process of composting: as specified in the previous paragraphs, inorganic carbon and nitrates have a negligible contribute in the total amount.

Table 4.6-C/N (TOC on TKN)

C/N					
	Line 1				
	1st	10th	25th	40th	55th
OF	29	21	13	17	13
BioPOF s	25	19	17	22	12
BioPOF b	24	19	16	18	12
Mean	26	19	15	19	13
	Line 2				
	1st	10th	25th	40th	55th
OF	25	19	18	17	13
BioPOF s	23	17	14	14	11
BioPOF b	32	18	14	14	12
Mean	26,8	18,0	15,6	14,8	12

The initial experimental values enter in the range required by the Liebig law, allowing the process to start: they were less than the C/N equal to 34 found with the weighted average of the single fractions of the waste matrix, but they still remained in the necessary range.

Finally, the values obtained at the 55th day of the process, respected the standards for a mature compost, being in a range 11-13, suggesting a positive result for the process with the consumption of the organic matter by microorganisms.

4.1.8 Respirometric Index (RI)

In table 4.7 there are reported the values for all the days of sampling, including the 1st, to show the evolution of the respiration within the composted matrix.

It is generally valid that for a fresh waste the RI_4 = 70-80 mg O_2/g VS, while for a mature compost RI_4 < 5 mg O_2/g VS (Cossu, 2016). In the case of these samples the RI was done not only for 4 days but also for 7 days; all the numbers are exposed in the Annex I.

The graph and the table with the results of RI_4 show that the final values, even if a little bit higher for the Line 2 than the Line 1, are below the required value for a mature compost, defining that the phase of activity of the microorganisms is almost finished.

Table 4.7-RI 4 normalized on volatile solids

RI4 mgO2/g VS					
	Line 1				
	1st	10th	25th	40th	55th
OF	52,3	38,7	38,2	26,4	1,3
BioPOF s	51,9	39,1	41,0	33,3	3,4
BioPOF b	49,8	36,5	43,7	30,2	5,3
Mean	51,3	38,1	41,0	30,0	3,4
	Line 2				
	1st	10th	25th	40th	55th
OF	49,5	33,9	27,1	13,1	8,6
BioPOF s	50,0	34,8	35,4	22,1	6,6
BioPOF b	53,2	27,9	32,1	16,2	8,4
Mean	50,9	32,2	31,5	17,1	7,9

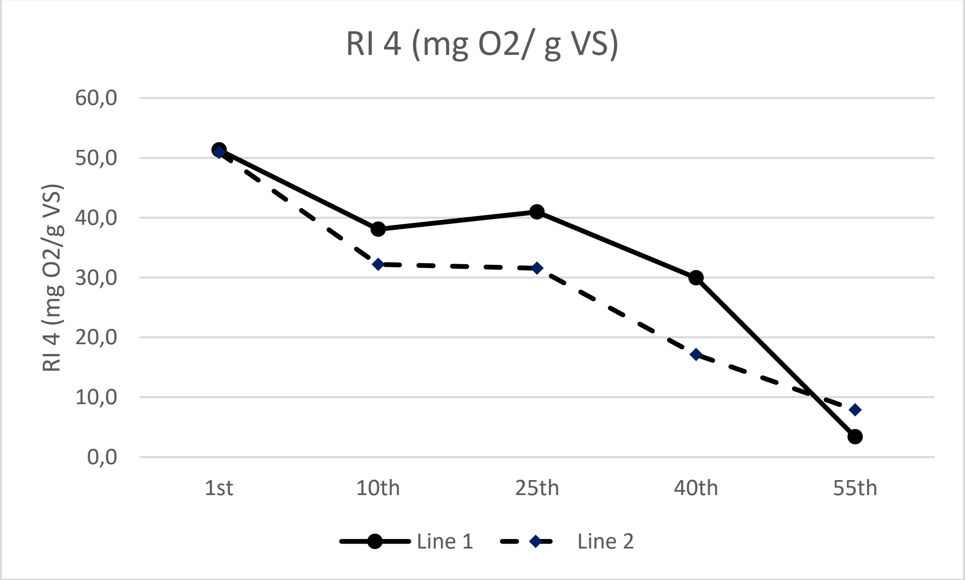


Figure 4.10-RI 4 normalized on volatile solids

4.2 Sieving analyses for the granulometric curve

After each sieving, the passing fractions and the withheld fractions were weighted, and from the withheld the further sieving could start. In figures 4.11 and 4.12 are shown the seven bowls with the withheld (except for the last one which contains the passing at 14 sieve) fractions, respectively for a blank and for a BioPOF small.

Figure 4.11-Sieved fractions 10th day, OF (F. Ruggero, 2017)

Figure 4.12-Ssieved fractions 25th day, BioPOF small (F. Ruggero, 2017)

In figure 4.13 the manual sieving operation is captured, with also a focus on one of a single witheld fraction.

Figure 4.13 Sieving operation (F. Ruggero, 2017)

After sieving the samples through the six sieves, a granulometric curve was drawn with the passing fractions.

In this way it was possible to have a clear vision of the changing in time of the fractions, making a comparison between the analysed points.

The graph and the table with weight and percentages are reported in Annex II, while in figure 4.14 it is drawn the granulometric curve of BioPOF small, Line 1, to show the difference among the composting phases.

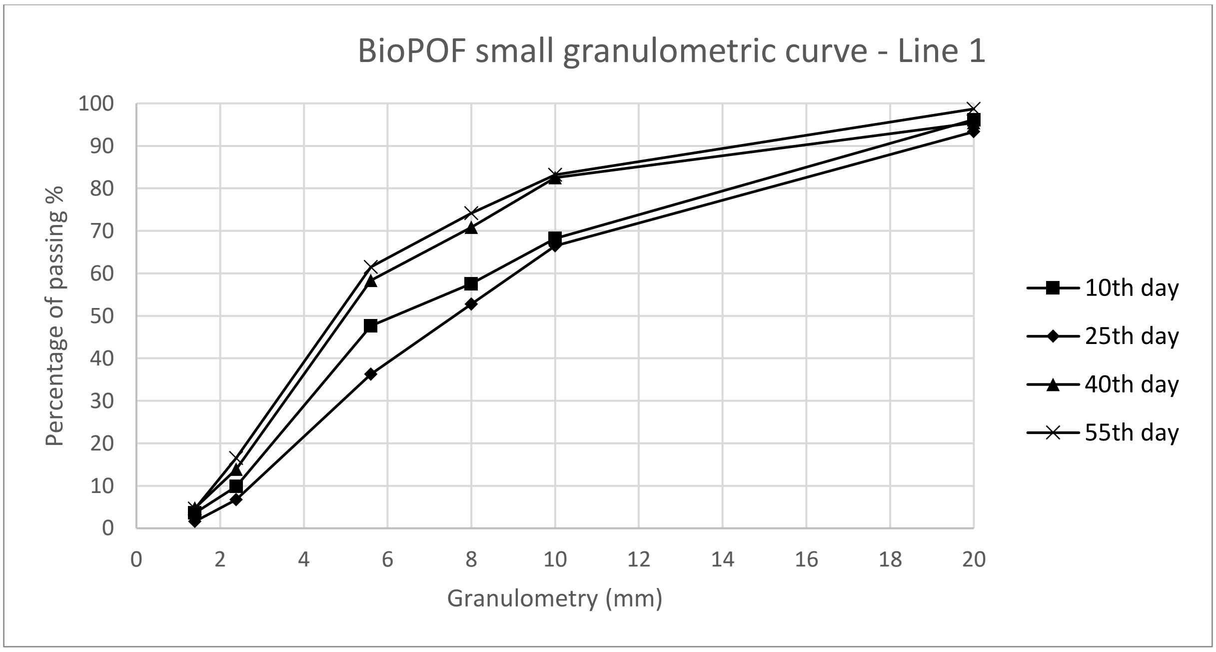


Figure 4.14-Granulometric curve example

It's fair to say that not a significant variation of seizes occurred in time; for the smallest fractions there was an increase between 10 and 15% of passing materials. So the fractions to be considered as compost, those smallest than 10 mm, reached in total an 80% of the total matrix, where the material smaller than 5.60 mm was about the half.

To give an idea of the different composted waste present in each fraction after sieving, in figure 4.15 is reported a graph with the material mainly found in the different ranges of seizes of the samples.

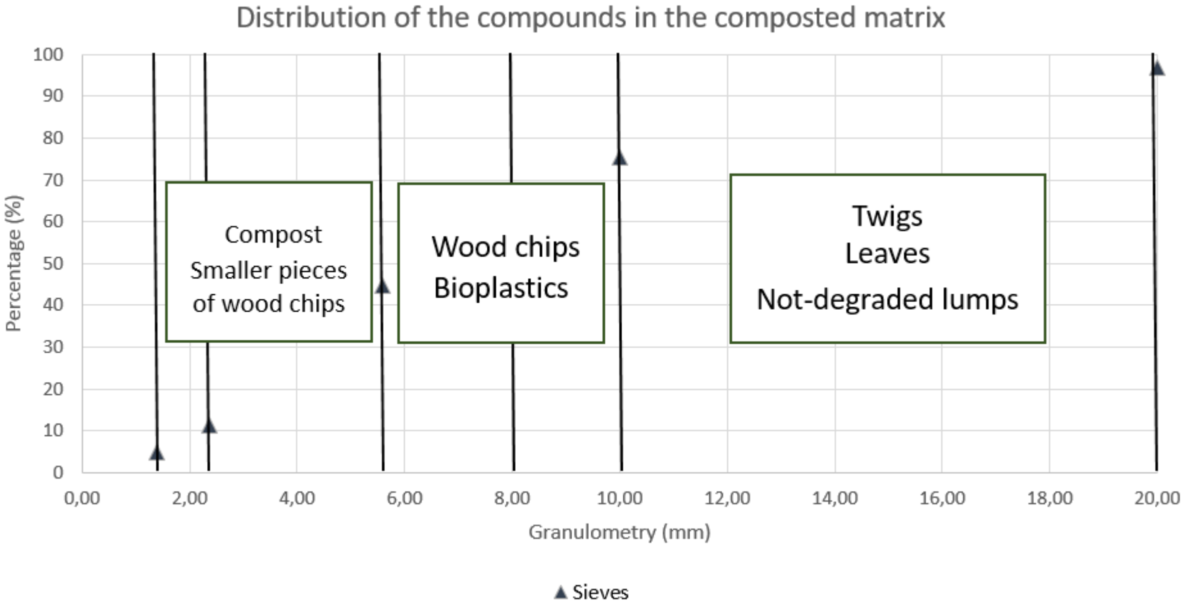


Figure 4.15-The main waste components of each granulometric fraction

4.3 Evaluation of bioplastics disintegration and degradation in composting

4.3.1 Sieving analyses of bioplastics disintegration

The results of sieving analyses are reported in this paragraph for all the four timings of sampling and for both small and big BioP of the two lines: in fact the purpose is to show on the one hand the behaviour of bioplastics disintegration during the phases of the process, describing an eventual linear or not linear trend of disintegration, and on the other hand the comparison between the results of the two lines to define if this trend is constant within all the samples or if it exists a substantial difference among big and small BioPOF and among the lines.

The results are reported in tables from 4.8 to 4.11, referring both to the weight of bioplastics sample taken off from each witheld fraction, and to the correspondent percentage, to avoid having the influence of the difference in the initial weight of the samples taken, from a maximum of 2.5 kg for the 10th of Line 1 to a minimum of 0.5 kg in the last timings of sample, as not to remove too much bulk from the ever-smaller heaps.

Then in the histograms elaborated from these data, the values are reported only in percentage, in figures 4.18 – 4.21. All the results are divided into four sections, to show the comparison in time between the four points sampled: BioPOF small Line 1, BioPOF small Line 2, BioPOF big Line 1, BioPOF big Line 2.

Furthermore, in graphs 4.16 and 4.17 there are drawn the size of bioplastics at the beginning of the test, considering that the samples were equally distributed among the sizes of the two ranges, small BioP and big BioP.

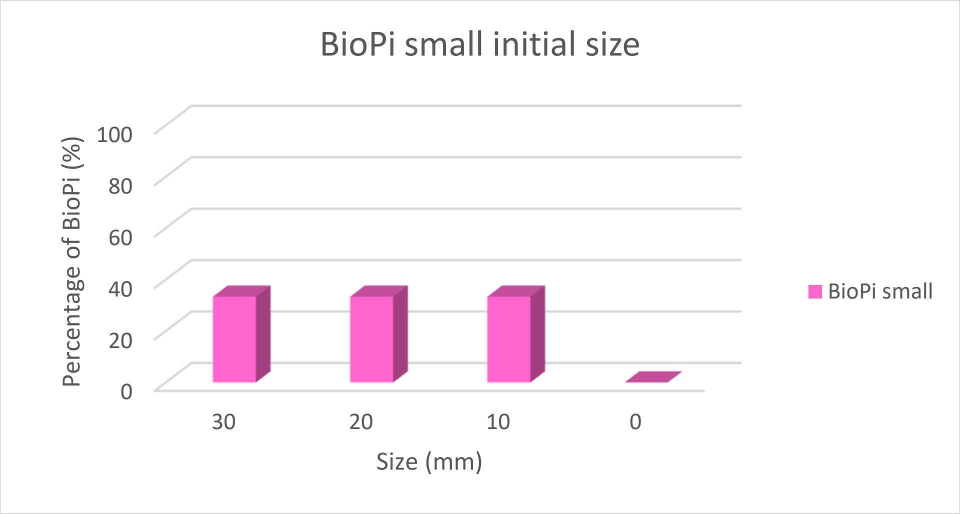


Figure 4.16-BioPi small size at the beginning of the test

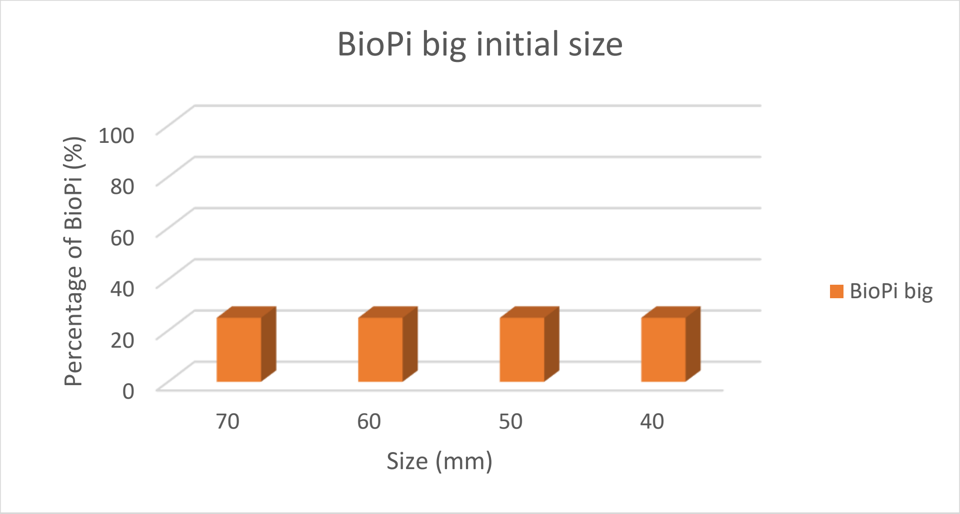


Figure 4.17-BioPi big size at the beginning of the test

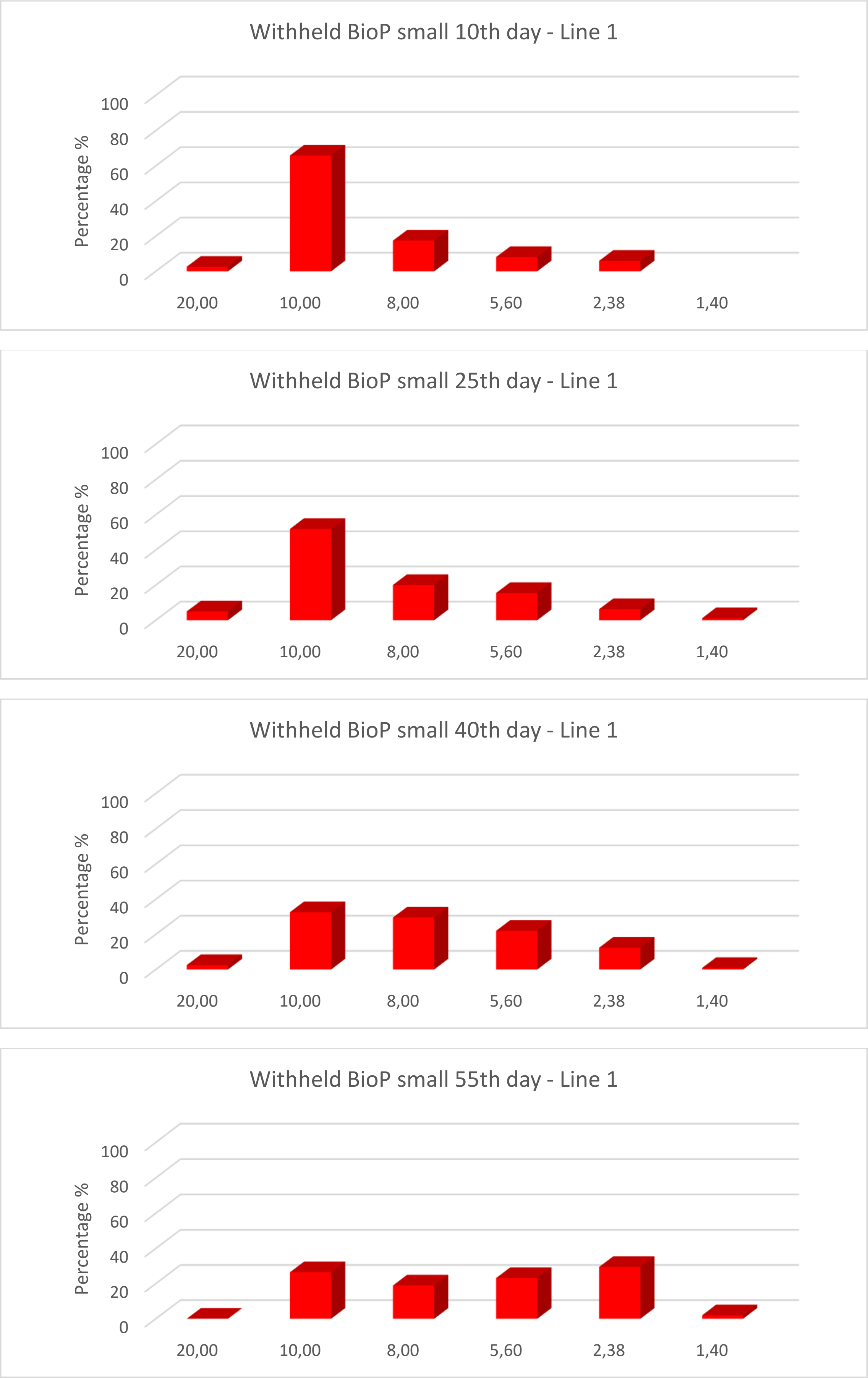


Figure 4.18-Histograms of BioP small granulometry – Line 1

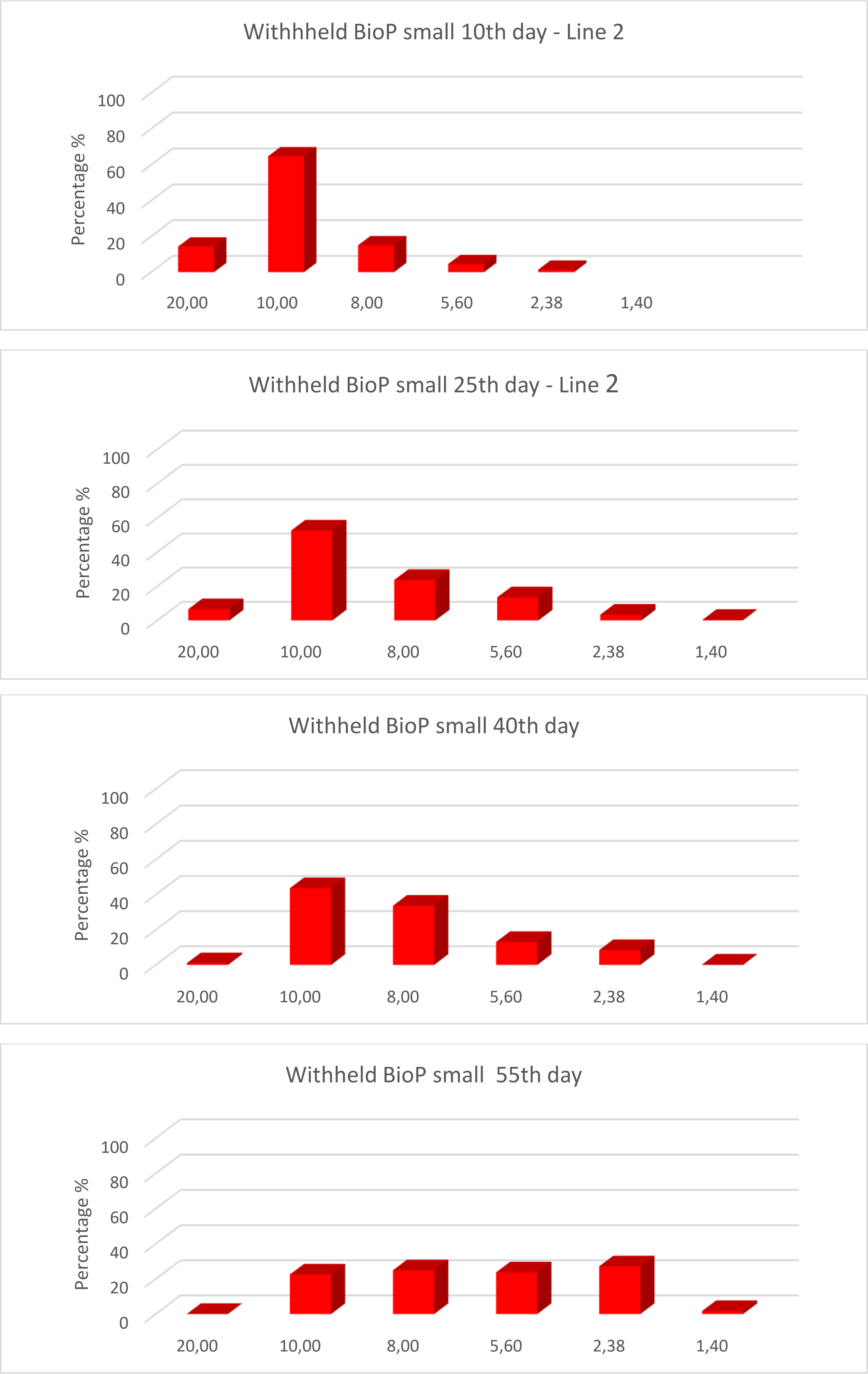


Figure 4.19-Histograms of BioP small granulometry – Line 2

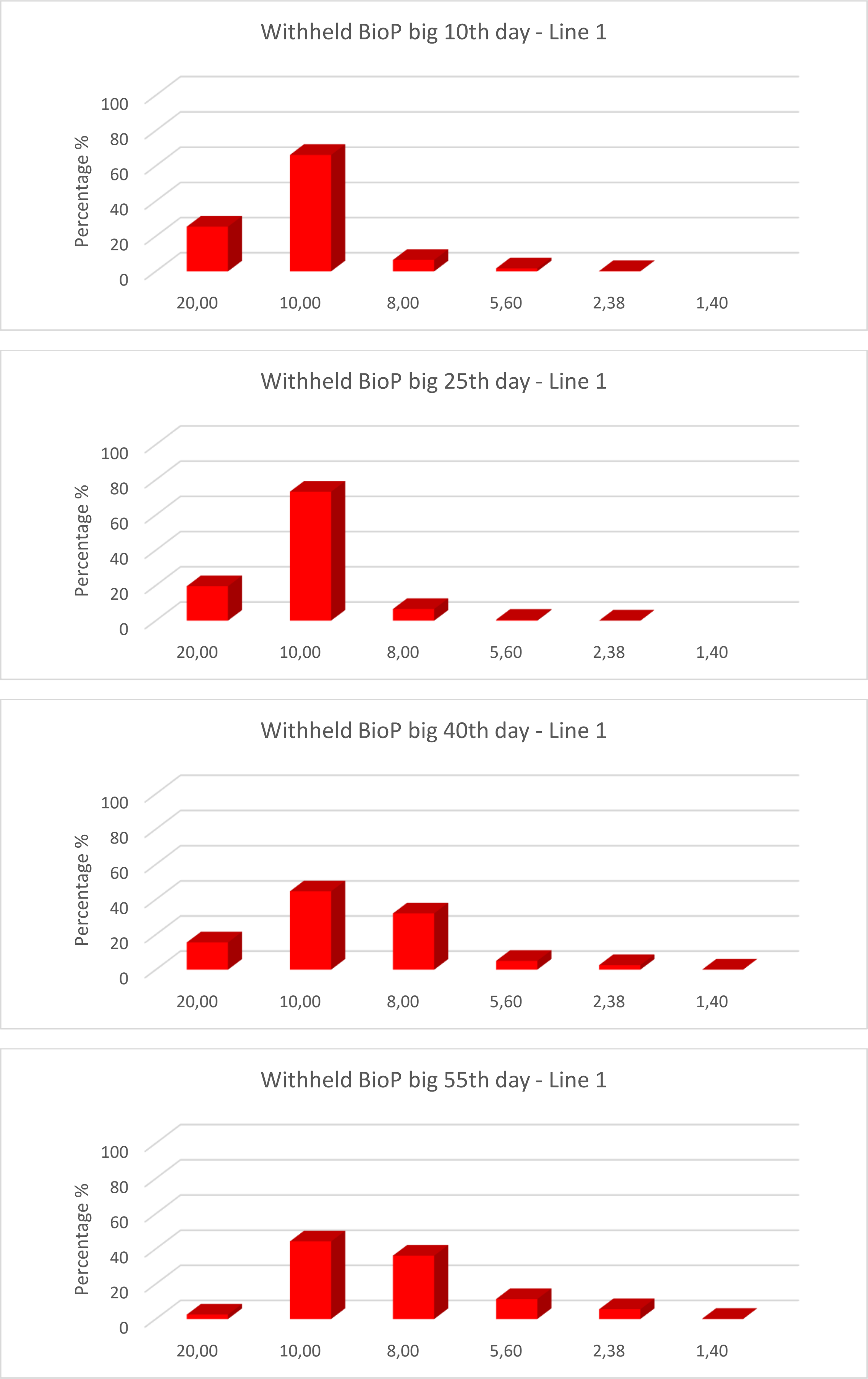
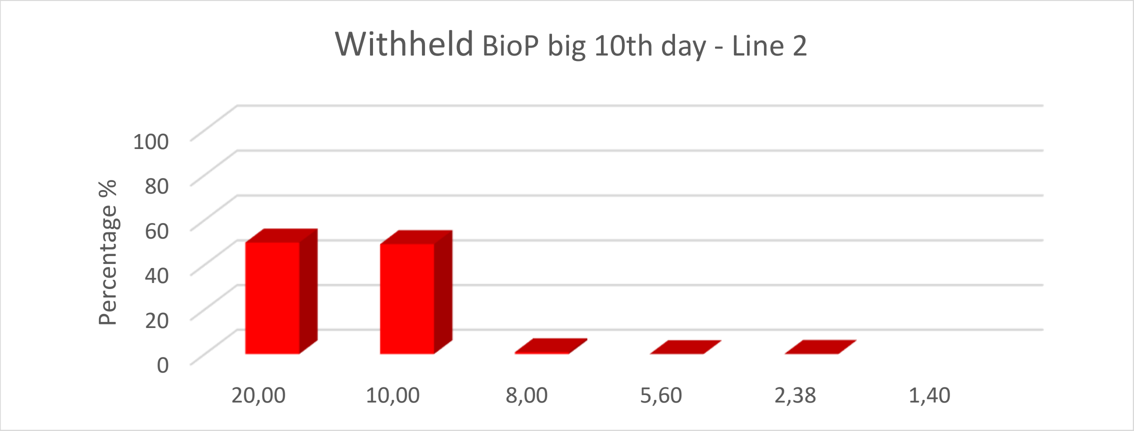
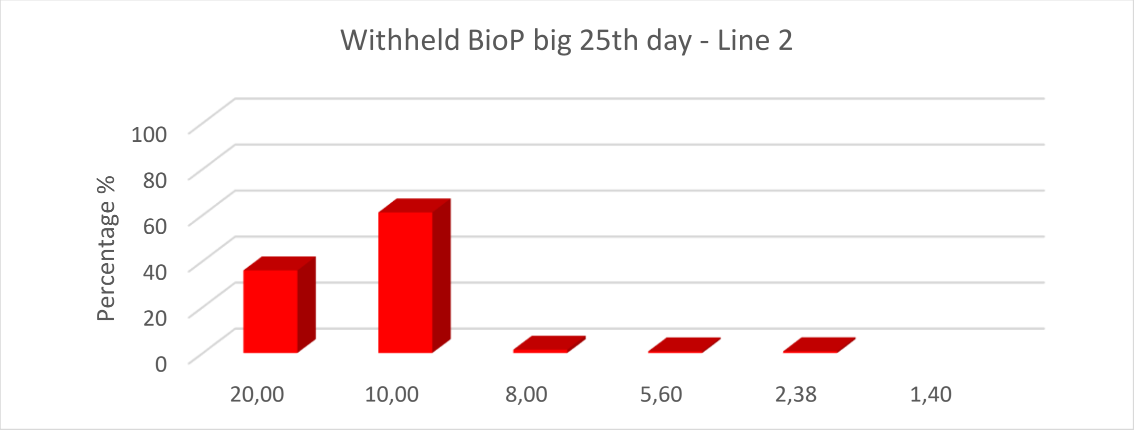
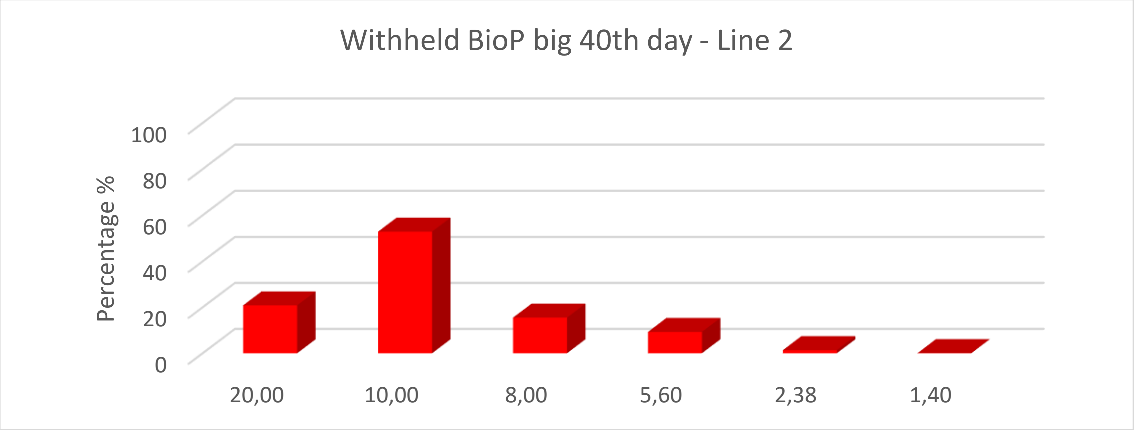


Figure 4.20-Histograms of BioP big granulometry – Line 1







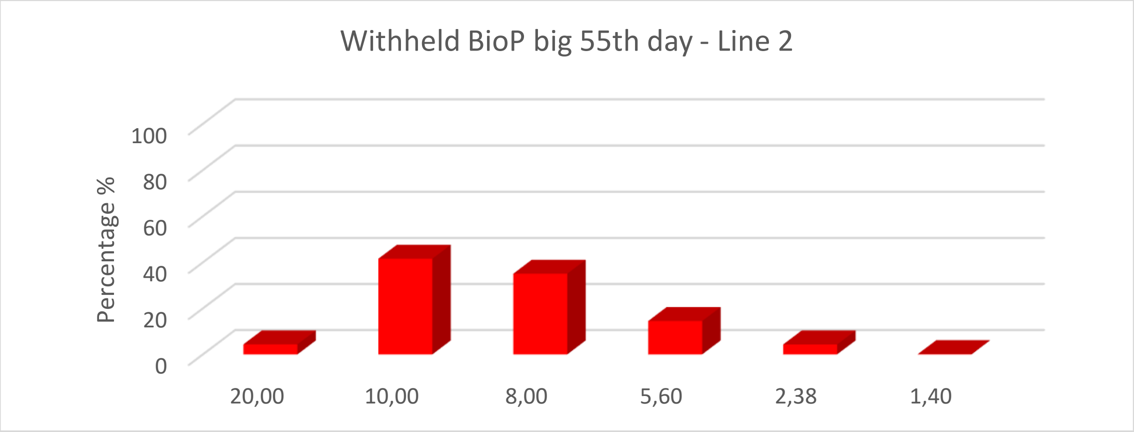


Figure 4.21-Histograms of BioP big granulometry – Line 2

Table 4.8-BioPOF small granulometry - Line 1

		BioPOF small withheld - Line 1							
		10th day		*25h day*		*40th day*		*55th day*	
Sieve	*Granulometry*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*
3/4	20	0,883	3	1,337	5	0,206	3	0	0
3/8	10	22,462	66	13,867	52	2,6781	33	2,8168	26
5/16	8	5,969	17	5,357	20	2,4321	30	2,0169	19
3,5	5,6	2,765	8	4,140	16	1,8094	22	2,4682	23
8	2,38	2,052	6	1,685	6	1,0202	12	3,1427	29
14	1,4	0,000	0	0,057	0	0,0724	1	0,2106	2

Table 4.9-BioPOF small granulometry - Line 2

		BioPOF small withheld - Line 2							
		10th day		*265h day*		*40th day*		*55th day*	
Sieve	*Granulometry*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*
3/4	20	3,612	14	1,494	7	0,137	1	0,0012	0
3/8	10	16,323	65	12,003	53	6,462	44	2,4152	23
5/16	8	3,797	15	5,392	24	4,987	34	2,675	25
3,5	5,6	1,138	5	3,078	13	1,934	13	2,5431	24
8	2,38	0,350	1	0,761	3	1,248	8	2,9155	27
14	1,4	0,000	0	0,074	0	0,029	0	0,184	2

Table 4.10-BioPOF big granulometry - Line 1

		BioPOF big withheld - Line 1							
		10th day		*265h day*		*40th day*		*55th day*	
Sieve	*Granulometry*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*
3/4	20	9,603	25	7,340	20	1,0914	16	0,1792	3
3/8	10	24,985	66	27,474	73	3,1363	45	3,1464	44
5/16	8	2,453	6	2,489	7	2,2545	32	2,5702	36
3,5	5,6	0,636	2	0,191	1	0,3534	5	0,809	11
8	2,38	0,076	0	0,029	0	0,1839	3	0,3972	6
14	1,4	0,000	0	0,000	0	0,002	0	0,0108	0

Table 4.11-BioPOF big granulometry - Line 2

		BioPOF big withheld - Line 2							
		10th day		*25th day*		*40th day*		*55th day*	
Sieve	*Granulometry*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*	*(g)*	*(%)*
3/4	20	10,480	50	13,373	36	5,010	21	0,3012	4
3/8	10	10,334	49	22,764	61	12,732	53	2,8764	42
5/16	8	0,177	1	0,540	1	3,733	16	2,4253	35
3,5	5,6	0,001	0	0,271	1	2,235	9	1,004	15
8	2,38	0,016	0	0,285	1	0,328	1	0,2996	4
14	1,4	0,000	0	0,000	0	0,023	0	0,0098	0

From the direct observation of the data collected three considerations can be done about the development and the trend of the disintegration process of bioplastics.

It's fair to notice that it exists a uniform trend between small BioP of Line 1 and small BioP of Line 2, as for big BioP of the two lines; so the process of disintegration has a common behaviour independently on the heap.

However, the data of the 10th day for big BioP are quite different as for the sieves 10 and 20 mm; observing that this difference disappear in the later graphs, it can be associated firstly to the sampling of few grams in a big heap, and secondly to the less linear behaviour of the thermophilic phase with respect to the maturation phase.

The second consideration is about the difference which occurs among the small and big size: in fact it is noticeable from the percentages that the small BioP became microplastics just since the 25th day, with an average percentage between the two lines of 20%, up to 55% at the 55th day.

Meanwhile, as for the big BioP, the sieving analyses of the 25th day showed a percentage of MicroBioP less than 1%, increasing up to 20% at the 55th day.

Thus, as supposed in the initial hypotheses of the research, it exists a creation of microplastics during the composting process of BioP, which, in accordance with the size at the beginning of the treatment, leads to having after a certain point more micro than normal bioplastics.

In the sieving analyses required by the standards, the sample after twelve weeks is passed through a sieve of 2 mm to demonstrate that the weight of bioplastics bigger than this fraction is less than 10%. But, as seen from the data collected in the experimental part of the thesis, this observation is not sufficient to demonstrate the disappearance of the bioplastics during the composting process, just only their disintegration.

In order to have a possible prevision of the time needed by the bioplastics of the small scale experiment of this thesis to become finest than 2 mm and finally disappear, it was built a model that exploits the linearity of the cooling and the maturation phase.

Starting from the values obtained in tables 4.8-4.11, it was done a weighted average between the sizes of bioplastics in each timing of sampling, and it was found the mean size of each day of sampling for the four heaps. In table 4.12 there are reported all these values.

It was also evaluated the percentage of size reduction with respect to the previous day of sampling. The aim was to demonstrate that it subsisted a substantial difference in the trend of size reduction between the phases of the composting process.

The equations to obtain the mean size of the bioplastics are:

$$\Sigma(Sieve\ (mm) * Withheld\ BioP\ (\%)) = Means\ size\ of\ BioP\ day\ x, Line\ y\ (mm) \qquad (9)$$

$$\frac{Mean\ size\ Line\ 1 + Mean\ size\ Line\ 2}{2} = Mean\ size\ of\ BioP\ day\ x\ (mm) \qquad (10)$$

The equation for the evaluation of size reduction is written as follows:

$$\frac{d(i+1)}{d(i)} * 100 = \%\ size\ reduction \qquad (11)$$

Table 4.12-Mean size of bioplastics during the composting process

	Mean size mm		% Size reduction	
Day	*BioP small*	*BioP big*	*BioP small*	*BioP big*
1st	20,00	50,00	50	73
10th	9,96	13,64	9	7
25th	9,11	12,66	13	14
40th	7,93	10,87	22	20
55th	6,21	8,67	29	28

From the values reported in the table it’s fair to notice that during the thermophilic phase the percentage of size reduction is much higher than between the values obtained during the cooling and the maturation phase; thus, in order to elaborate a general model (Figure 4.22) able to give information about the time needed for the bioplastics to disappear, the first ten days and so the first percentage value of reduction was not considering in the experimental data used to implement the forecast tendency line of the model because they would have greatly altered the final results.

Furthermore, the thermophilic phase was closed after ten days, and all the proceeding of the composting after the 55th day was a maturation phase, so having the same trend and behaviour of the last forty-five days.

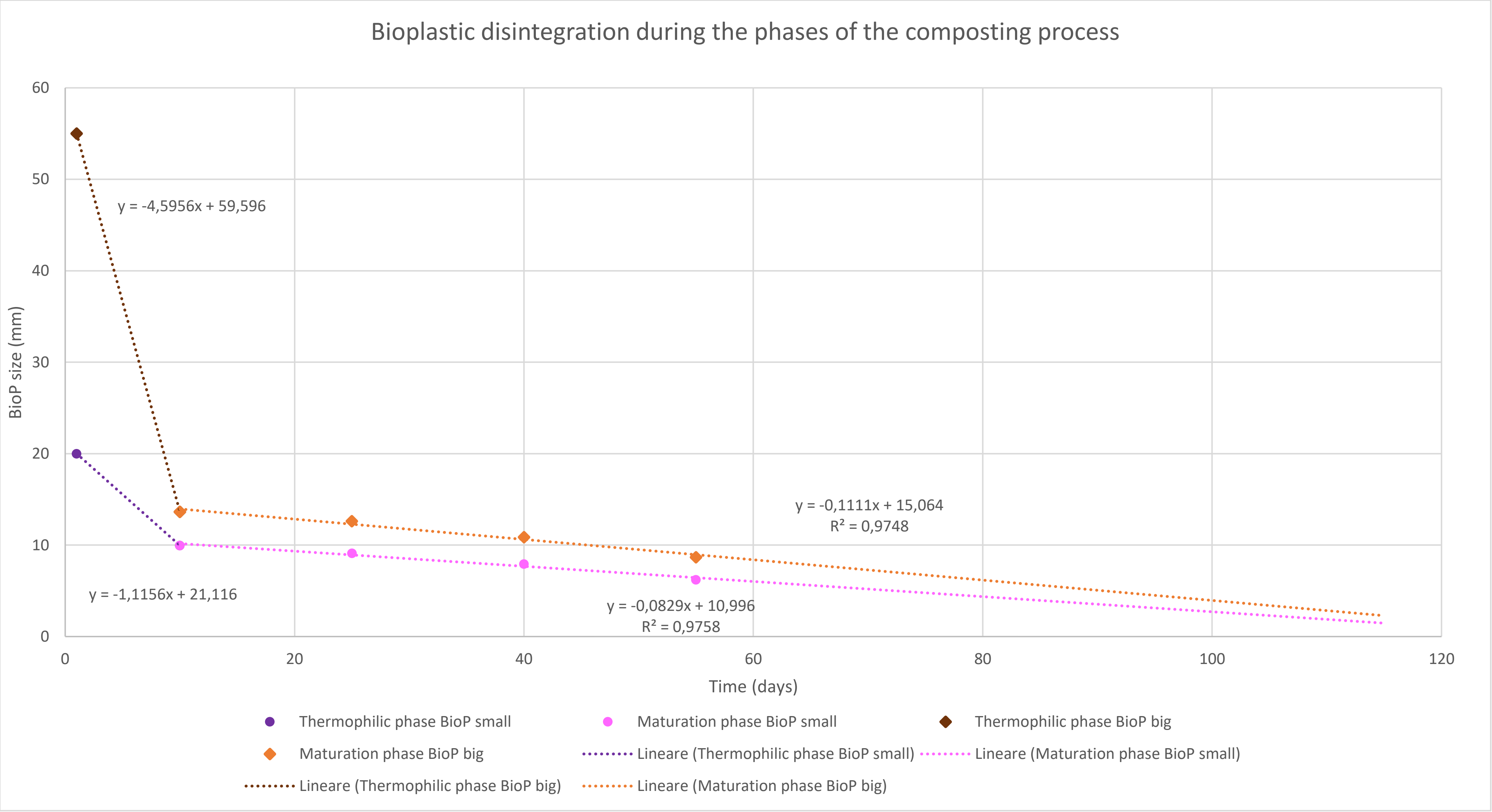


Figure 4.22-Model of prevision of bioplastics disintegration

This model presents a fundamental positive aspect; the advantage involves the square error obtained from both the lines, so near to 1 that it shows basically a model of almost a perfect linearity. Thus, following the model it is possible to affirm that after 115 they would be finer than 2 mm.

It means four months, or better 16.5 weeks, to become finer than 2 mm as required by standards.

On a small scale, starting from 25 kg, it is not possible to proceed with the collection of further data after the 55th day because the heap would become too small to allow the taking of other samples without compromising the total bulk of the heap and consequently the possibility for the composting process to follow a natural evolution similar to the real composting plants.

An eventual variable not verifiable through this small scale test concerns the possibility of a slowdown in the trend of disintegration when the bioplastic pieces become smaller and smaller after the 55th day.

The hypothesis of this variable arose from the observation of the two lines of the graph; in fact the bioplastics started with a bigger size have a disintegration velocity higher than which of bioplastics starting from the smaller size.

To conclude with the elaboration of the results of this analysis of the disintegration, it’s fair to underline again the discrepancy between the thermophilic and the maturation phase in their effect on the reduction of bioplastics size.

With the further analyses, it will be analysed if the same situation can be observed also for disintegration or if this trend is valid only for the disintegration.

4.3.2 Bioplastics concentration

The values of concentration found for each sample during the analyses are reported in tables 4.13 and 4.14: they have been subdivided in accordance with the respective line and the heap of origin, small or big BioPOF.

In the tables below, not only the values of concentration of each single fraction are reported, but also the values of the total amount of BioP within the heap, and of the microplastics less than 5.60 mm.

Table 4.13-BioP small concentration in BioPOF

		BioPOF small - Line 1				**BioPOF small - Line 2**			
Sieve	**Granulometry**	*10th day*	*25th day*	*40th day*	*55th day*	*10th day*	*25th day*	*40th day*	*55th day*
3/4	20,00	0,008	0,014	0,009	0,000	0,027	0,015	0,011	0,000
3/8	10,00	0,029	0,034	0,041	0,018	0,031	0,028	0,035	0,016
5/16	8,00	0,023	0,023	0,043	0,023	0,014	0,021	0,051	0,031
3,5	5,60	0,010	0,014	0,029	0,022	0,004	0,009	0,016	0,023
8	2,38	0,002	0,002	0,005	0,007	0,001	0,001	0,003	0,007
14	1,40	0,000	0,000	0,002	0,002	0,000	0,001	0,000	0,002
Total BioP	≤ 20,00	0,017	0,015	0,016	0,011	0,013	0,015	0,015	0,011
MicroBioP	≤ 5,60	0,0015	0,0018	0,0037	0,0055	0,0005	0,0010	0,0023	0,0050

Table 4.14-BioP big concentration in BioPOF

		BioPOF big - Line 1				**BioPOF big - Line 2**			
Sieve	**Granulometry**	*10th day*	*25th day*	*40th day*	*55th day*	*10th day*	*26th day*	*40th day*	*55th day*
3/4	20,00	0,055	0,061	0,091	0,014	0,070	0,095	0,010	0,017
3/8	10,00	0,047	0,056	0,039	0,020	0,018	0,048	0,073	0,020
5/16	8,00	0,010	0,010	0,040	0,020	0,001	0,002	0,036	0,022
3,5	5,60	0,001	0,001	0,004	0,005	0,000	0,001	0,012	0,007
8	2,38	0,000	0,000	0,001	0,001	0,000	0,000	0,001	0,001
14	1,40	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Total BioP	≤ 20,00	0,019	0,019	0,014	0,007	0,011	0,019	0,012	0,007
MicroBioP	≤ 5,60	0,0001	0,0000	0,0007	0,0008	0,0000	0,0004	0,0007	0,0006

It's fair to immediately notice the increase of concentration from the beginning of the process to the times of sampling.

Three main reasons that can justify this increase are described as follows:

1. During the composting process the mass of the heaps decreases; if bioplastics don't have the same weight decreasing evolution, it will be present the same mass of bioplastics in a heap lighter than at the beginning of the process.
2. The moisture content of bioplastics increases during the composting process; it means that also their total weight increases. In fact, for having been in contact with putrescible moist waste, bioplastics, which at the beginning of the process had a moisture content of 2%, became moister up to 5-9%.

3. Bioplastic pieces tend to remain attached one to each other, in this way it's possible to have few lumps of bioplastics into the heap that increases bioplastics concentration in certain points of the BioPOF. Sampling the heap for the analyses it could be possible to take also one or more of this lumps (Figure 4.23).

Figure 4.23-Bioplastic lumps formed during the composting process

Figure 4.24 shows the variation of the total concentrations along the process: it represents a not uniform increase up to the 25th day, and a later trend of decrease up to the 55th day when the concentration returned near to the initial one.

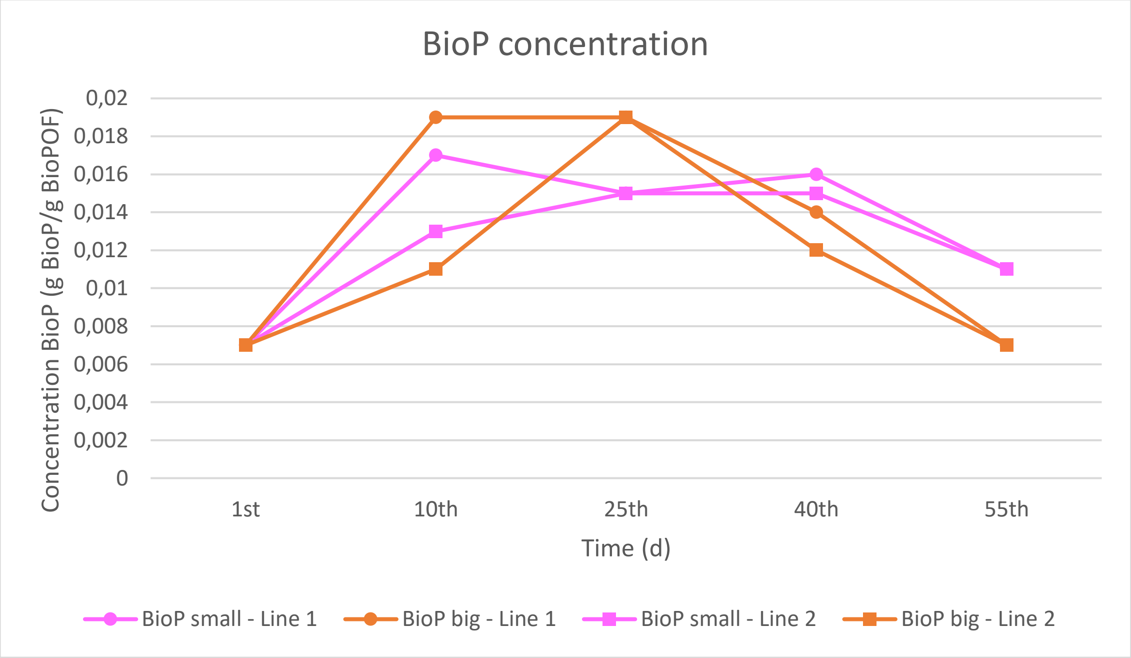


Figure 4.24-BioP concentration trend during the composting process

As typical of the polluting substances, even if they potentially represent a risk for the environment or human health, the effective contamination is a consequence of the amount of the pollutant discharged, of its concentration in the matrix, of the duration and the time of pollution, of the space and the matrix where they are discharged. So, not all the pollutants are effectively contaminants, it depends mainly from the contour conditions.

Bioplastics is not considered a pollutant, but they could be if their presence in compost compromises field fertilizations and crops or plants growth. The state of fact coming from the experimental observation of a not constant trend in the concentration behaviour during the process, should be a suggestion for a further implementation of ecotoxicological tests which would verify the potential contamination of field through fertilization with a compost with different bioplastics concentration.

A further deduction was made having observed the concentration of bioplastics in composting samples taken; starting from the experimental data of bioplastics concentration and weight of the heaps (Table 4.1), which change along the process, it was found the amount in grams of bioplastics in 1 kg of composted matrix.

Observing the numbers obtained with equation 8, reported in the fourth column of the tables in the Annex III, it's noticeable that the grams of bioplastics in the sample often increased, an occurrence which is physically impossible.

The causes of this occurrence has to be found in the possible variables involved in the weighing of bioplastic pieces. The first two variables had been already anticipated: firstly the increase of moisture content in bioplastics ranging from 5 to 9%, secondly the increase of weight due to impurities and dirt on pieces surfaces. The range of moisture increase was empirically evaluated through total solids analysis in the oven at 105 °C, and the percentage of weight increase due to dirt was defined through experimental data obtained with the difference of weight before and after a cleaning operation of the bioplastic pieces.

In particularly, the operation was carried out on samples of five pieces, taken from different size categories, different days of analyses and different heaps of the lines: these samples were weighted as preliminary step, then each piece was cleaned using spatulas, hard brushes and tweezers for the removal of the attached pieces of other materials. This manual operation required ten to twenty minutes per pieces, and it was concluded with the weighting of the samples, gaining the percentage of dirt.

The average of the percentages obtained from the samples was substantially different between days 10th and 25th and days 40th and 55th, because the bioplastics sampled in the last two timings where dirtier than the previous ones. So the two ranges of percentage are 10-20% and 20-30%.

The last point to take into account is the distribution of bioplastic pieces inside the sample; in fact, even if during the composition of the compostable heaps, the tested material was equally distributed among the other components of waste, turning, mixing, weighting of heaps and the composting process itself, may have changed the distribution. The consequence is that, when sampling the heap for the granulometric analysis, it exists a range of probability that the initial bioplastic concentration in the chosen is 10% higher or lower than 0,007.

A percentage of 10% was chosen in accordance with the small scale of the experiment which limited the alteration of the initial pieces' distribution in the sample, and considering that attention was paid in taking samples as homogeneous as possible.

If the test was carried out on a full scale, this range should probably be expanded, while, working with smaller baskets where all the initial matrix is used as sample and analysed, this variable is equal to zero because it is exactly known the initial concentration of the sample itself.

In table 4.15 these variables are summarized, defining a minimum and a maximum value for each variable.

Table 4.15-Range of variability in bioplastics weight

Variable	Max %	Min %
Moisture content	+ 9	+ 5
Sampling	+ 10	-10
Dirt	+ 20/30	+ 10/20

At this point it was made the sum of the minimum and the maximum parameters: to the values obtained directly from the bioplastics concentration and the samples weight with equation 8, it was subtracted from a minimum of 15-25% to a maximum of 39-49%, obtaining the values in table 4.16 and in graph 4.25.

The graph is reported only for bioplastics small of Line 2, but all the tables with calculations and the graphs with ranges of weight variability are in Annex III.

Table 4.16-Bioplastics weight variation range in percentage, with respect to the initial value

	BioP small %		**BioP big %**	
	Line 1	Line 2	Line 1	Line 2
1st	100	100	100	100
10th	87-122	75-104	98-136	62-87
25th	52-73	48-67	71-99	61-85
40th	35-51	39-58	36-53	29-42
55th	23-34	25-37	14-21	15-23

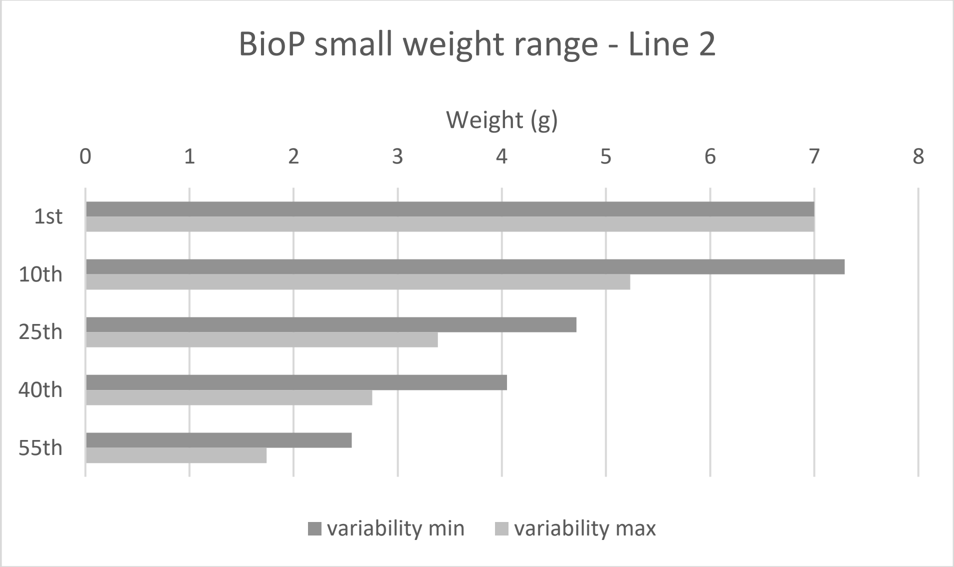


Figure 4.25-Range of BioP small weight during the composting process

Both numerically and graphically it is observed a decrease in weight during the process: it was excluded a completely disappearance of a certain amount of the tested material because through the granulometric study of disintegration it was clearly pointed out that the trend of size decrease didn't move fast towards the smallest fractions. So, it is not due to disintegration up to microparticles that the weight decreases, but due to a process of biodegradation that leads to a simplification of bioplastics and to the transformation of a part of organic material into CO_2 emitted in the air and into water.

Linking now the values obtained from this model with the values obtained from the disintegration model, it is noticeable that even if during the thermophilic phase the trend of disintegration was faster than during the maturation phase, the weight losses don't follow the same trend: the direct conclusion is that the effect of temperature leads to a disintegration of bioplastic pieces, but the thermophilic bacteria are not as able as the fungi, actinomycetes and mesophilic bacteria to contribute to the biodegradation of bioplastics.

The next IR analyses will confirm this observation, showing that it is during the maturation phase that, as the weight losses already demonstrated, the most of the degradation occurred.

The last consideration that closes this paragraph about bioplastics concentration involves a comment about microplastics.

At the beginning of the research it was supposed that the composting process leads to a progressive disintegration of the tested material up to 5 mm, it means up to microplastics. With the experimental data gotten during the tests, it was demonstrated that the concentration of microplastics in the composted matrix tended to increase along the process (Figure 4.26).

From this observation it’s fair to deduce that compost discharged in the environment could effectively be reached in micro-bioplastics, with the important unknown of how much time these pieces need to completely disappear, as already discussed in paragraph 4.3.1.

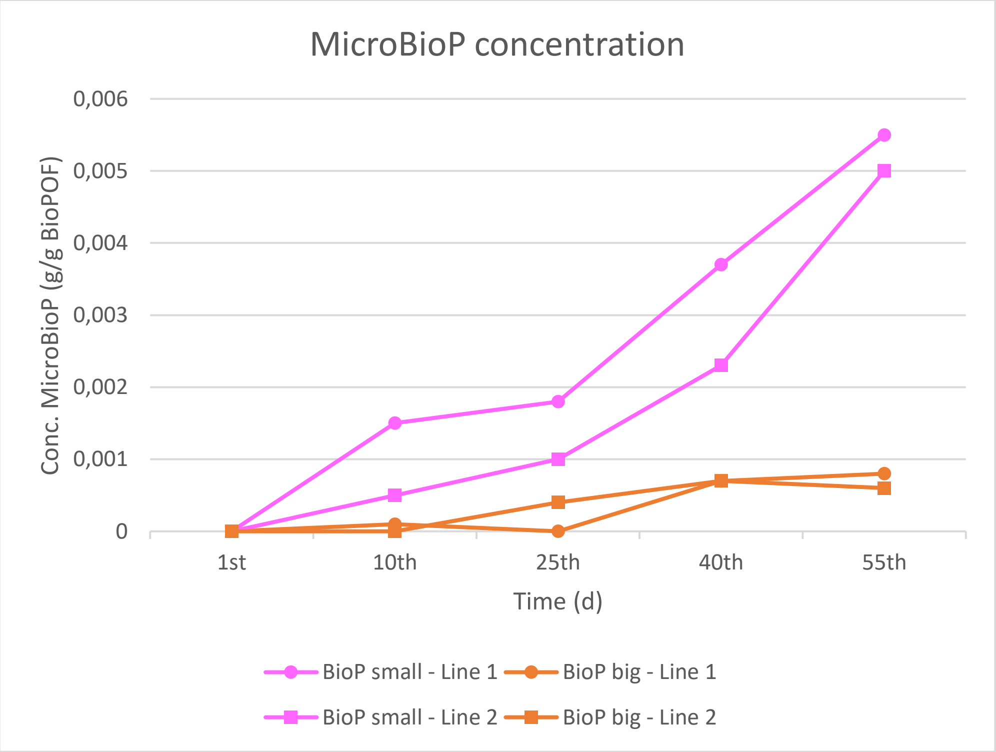


Figure 4.26-MicroBioP concentration during the composting process

4.3.3 IR analyses of degrading bioplastics spectra

The evolution of the spectrum along time was used to identify if a biodegradation occurred in the material: so, IR analyses were done on bioplastic samples taken from BioPOF during the sieving analyses of the 10th, 25th, 40th and 55th days.

A multitude of samples were submitted to the analyses to observe if among the pieces of the same day there were a similarity, and some of these spectra are reported in Annex IV.

In this paragraph the comparisons between the spectrum of bioplastics at the beginning of the process and during the composting are reported in the same graph for each period of analysis, just to permit a visible comparison and a direct association between the explanation given and the spectra drawn.

It starts from the 10th day, in figure 4.27, and proceeds with samples of 25th, 40th and 55th day, with the comparison of the spectrum of the 1st day and of two pieces of the sampling day, one from a fine fraction and one from a big fraction.

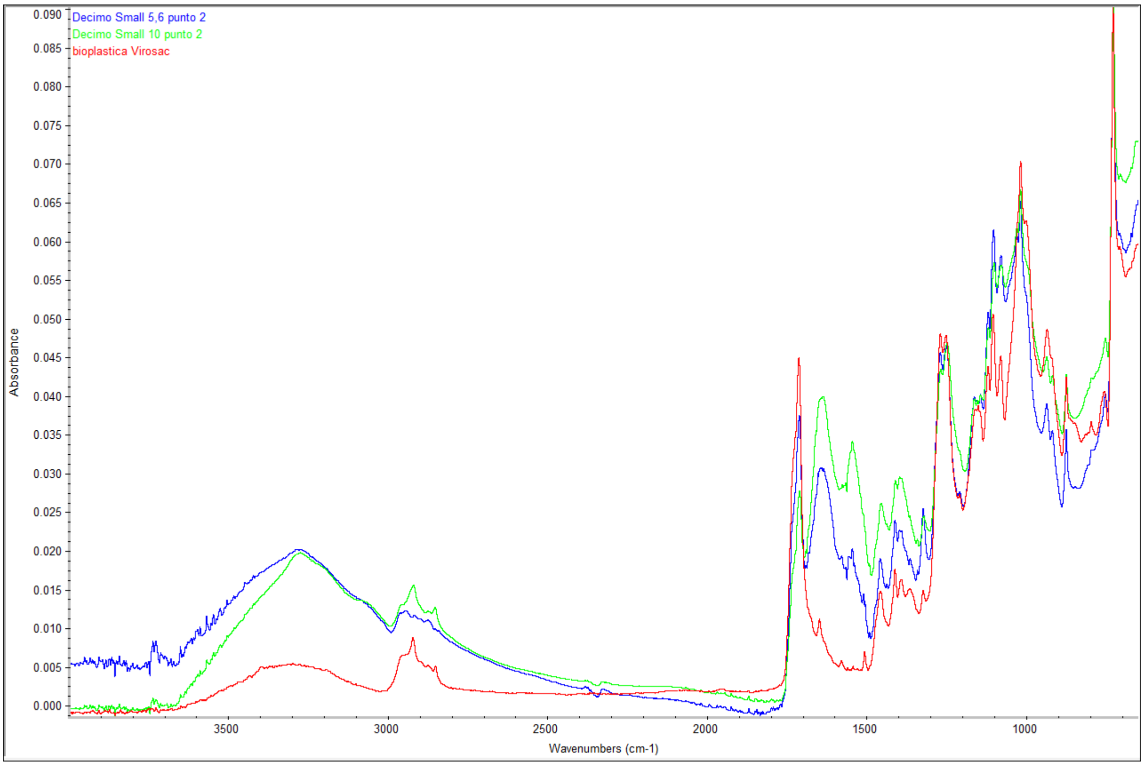


Figure 4.27-comparison between 10th and initial spectra of BioP

Some considerations can be done observing the comparison between these spectra.

It is present an increase of the first peak, around 2919 cm^{-1}, even if it is necessary to notice that the increase of the absorbance is just of less than 0,015. It means that, with respect to the next spectra, here it didn't occur a great change.

However, the reason for the increase of the bounds in this wavelength, which includes single bounds, is to be found in the breaking of the most complex bounds into simpler one, so for example from double to single. In fact the first action of bacteria on a complex polymer is the hydrolysis, to make it more available: the complex molecules are broken into simpler ones.

It can be observed also the rise of new peaks in the range 1650-1500 cm^{-1}, which corresponds mainly to the bound C=O. Considering that the increase of a peak represents an increase in the concentration of the correspondent bound, a reason for these peaks can be found it the breaking of the longest chains, but maintaining inside the new smaller chains this group, while other components are removed; as a consequence the concentration of the C=O bound increases in the broken molecule.

As the chemical structure of the PBAT composing Mater-Bi class N is mainly composed on C=O and single bounds within its chain (Figure 4.28), the increasing concentration of the peaks in the correspondent wavelengths confirms that it exists a degradation of the molecule in simpler molecules, up to reach the final formation of CO_2 and water.

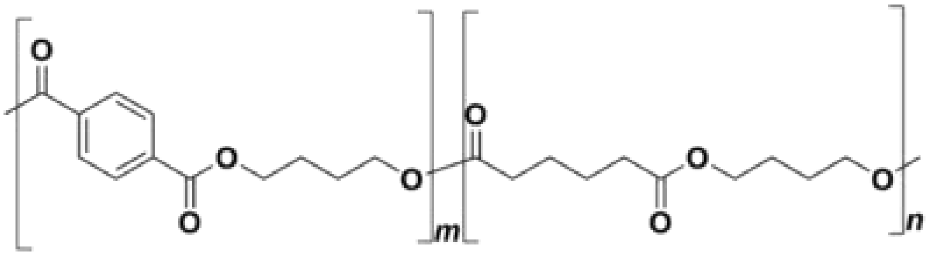


Figure 4.28-PBAT chemical structure

It's fair to underline that the spectra of the samples taken from the 10th day are quite similar to each other (Annex IV for the figures), showing that even if there are pieces disintegrated more than others, the biodegradation at the 10th day has the same trend in all the analysed sampled.

The same IR analyses were carried out on samples of the 25th day, in figure 4.29.

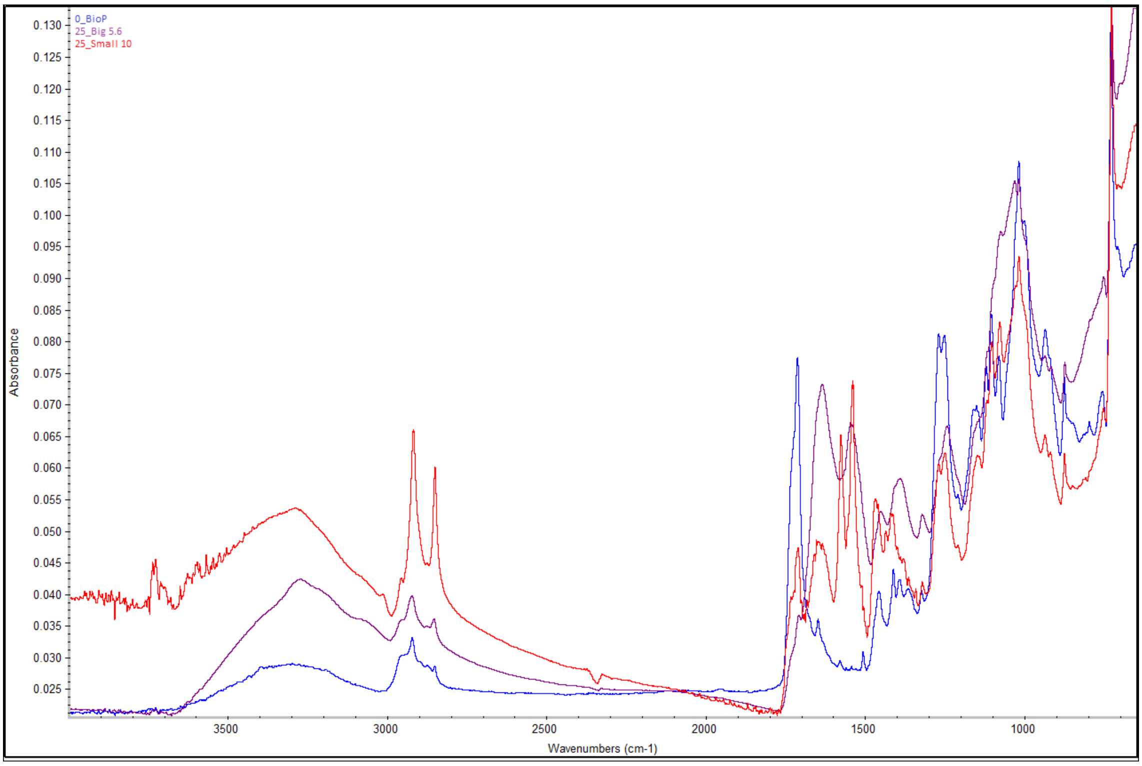


Figure 4.29-Comparison between 25th and initial spectra of BioP

From the analyses of these spectra it was observed that for few samples, in particularly big BioP larger than 2 cm and for small BioP larger than 1 cm, the peaks are equal to the initial spectrum, just no signs of biodegradation.

For the sample of small BioP, withheld by the sieve of 1 cm, two peaks of 2919 and 2848 cm^{-1} have an evident increase of concentration. Furthermore, the peak of 1710 cm^{-1} decreases in favour of the rise of peaks in the range from 1600 to 1400 cm^{-1}, and from 1300 cm^{-1} the absorbance of the initial peaks shows a decrease in the spectra of the 25th day.

A new peak in the wavelength of the single bounds appeared for the sample of big BioP withheld by sieve 5.60 mm, confirming the hypothesis of the breaking of the more complex molecules in simpler ones.

More than the IR analyses on the samples of the 10th day, it was done now also an IR analyses on the smallest, withheld by the sieve 2.38 mm: the spectra were quite disturbed due to the dirty surface of the sample, but it was still possible to see the main peaks.

Passing now to the spectra elaborated with IR analyses on the samples of the 40th day, in figure 4.30 compared with the spectrum of the 1st day, it's noticeable how the trend of increase of the peaks in the wavelength between 1600 and 1000 cm^{-1} was still constant, while in all the analysed samples the peaks of 2919 and 2848 cm^{-1} were disappeared in favour of an increase of the peaks of wavelength from 3300 to 2750 cm^{-1}, representative of the simplest bounds of the polymer.

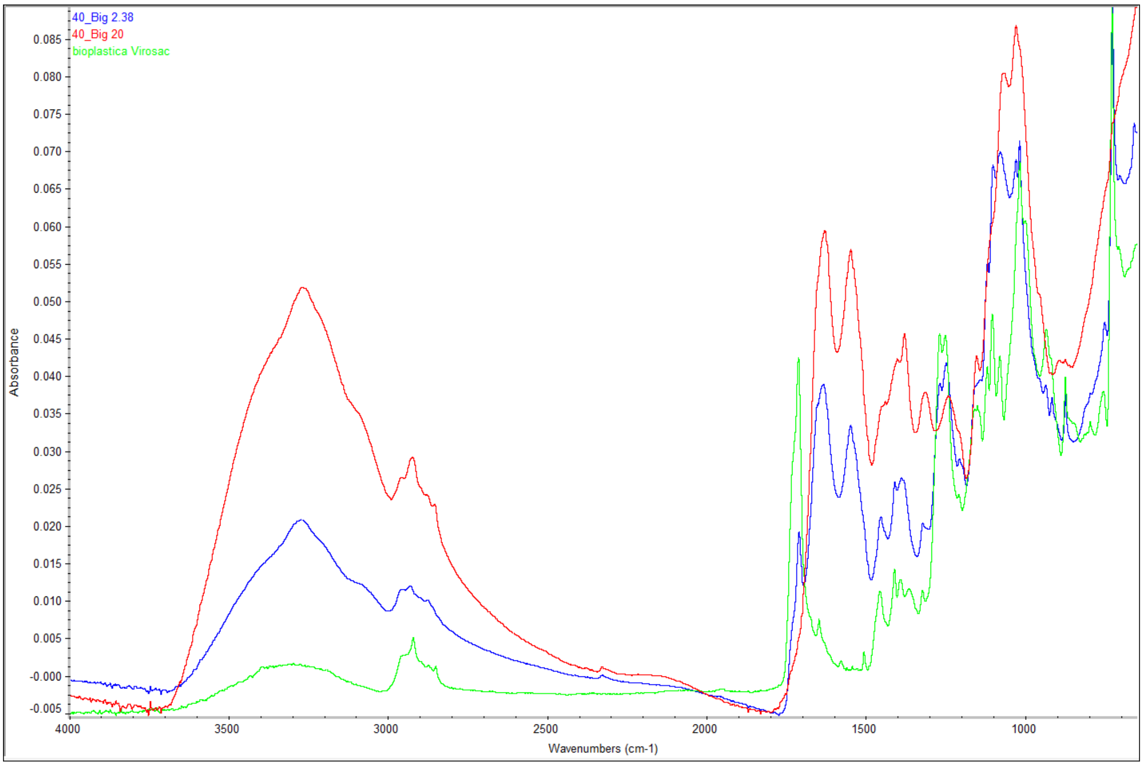


Figure 4.30-Comparison between 40th and initial spectra of BioP

The last IR analyses on the samples of the 55th day didn't present a significant difference with respect to the previous ones, defining that the main points of bioplastics degradation are the increase of single bound and of C=O bounds.

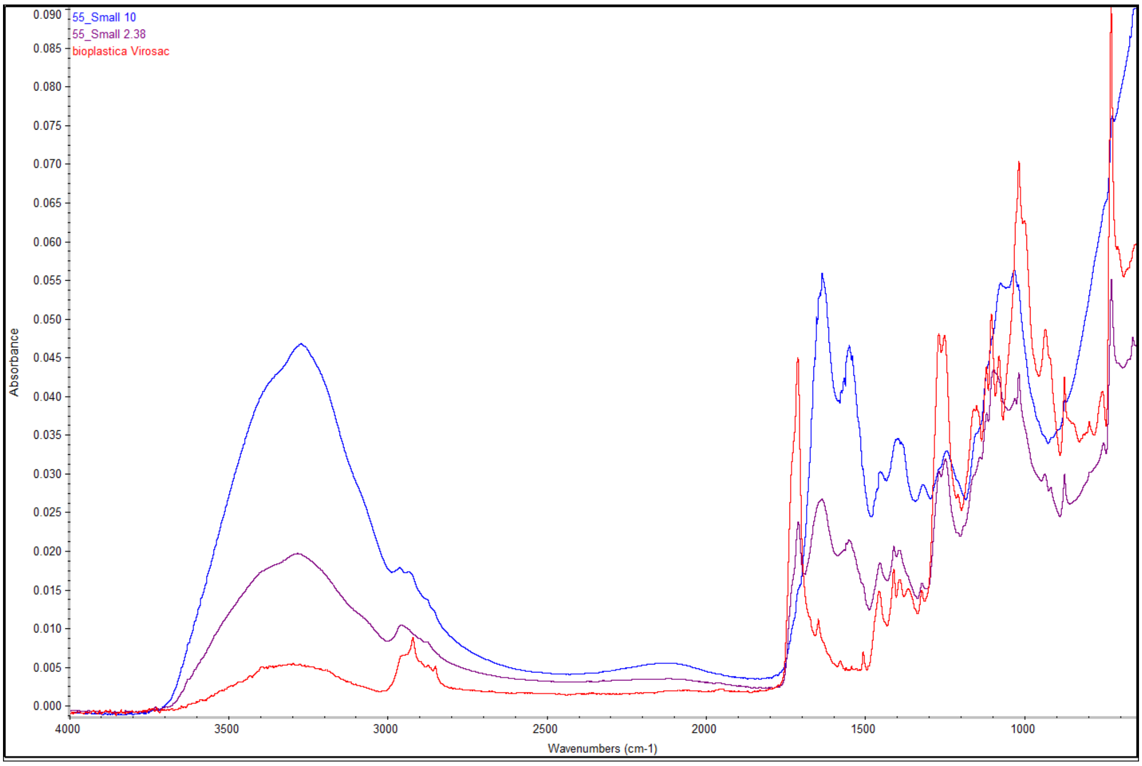


Figure 4.31-Comparison between 55th and initial spectra of BioP

The spectra of one sample taken for each day of analyses are put together in the graph in figure 4.32 to show the evolution from the beginning to the end of the period of the test.

From this graph it is noticeable how the spectrum of the 1st day in reality is very similar to the initial spectrum of the virgin bioplastic: while during the maturation phase it is evident the evolution of the spectra toward the simplest bounds and the creation of C=O peaks: this conclusion is in accordance with what was already observed in the analyses of the concentration.

During the thermophilic phase the prevalent action is that of the temperature, which leads to a disintegration of the bioplastics; however, in this phase the degradation observed is almost negligible, as seen in the change of the spectrum and of the weight, so the thermophilic bacteria are supposed not to be suitable in biodegrading this material.

On the contrary, the maturation phase is suitable for the growth of bacteria and fungi able to biodegrade bioplastics, even if the disintegration during this period has a clear and strong slowdown with respect to the thermophilic phase, confirming the hypothesis that is the action of the temperature that has a great influence in this process.

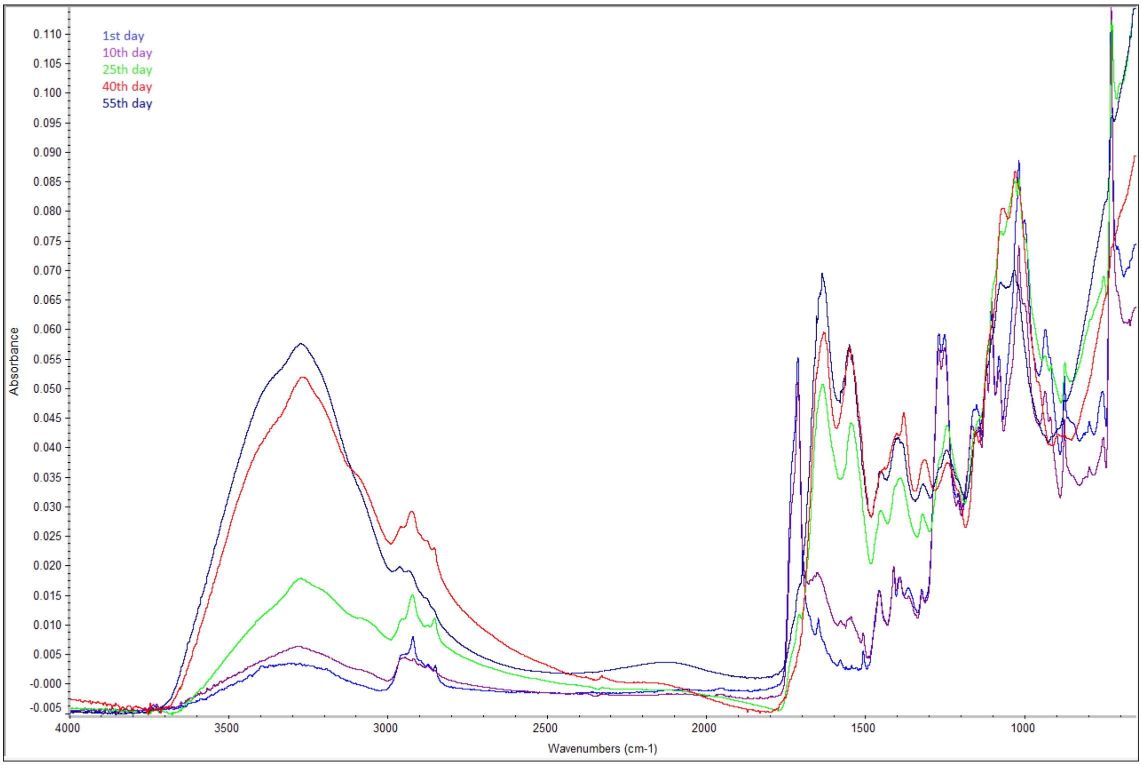


Figure 4.32-Comparison between spectra of BioP during the composting process

To conclude with this third type of analysis, it was also done an IR on a piece of bioplastic submitted for 2 days in the oven to a temperature of 60 °C, simulating the thermophilic phase of the composting process; the purpose was to define the effect of temperature on the changes in the peaks, but it was observed that, with the exception for a small increase in the concentration of all the peaks, the shape of the spectrum is unchanged.

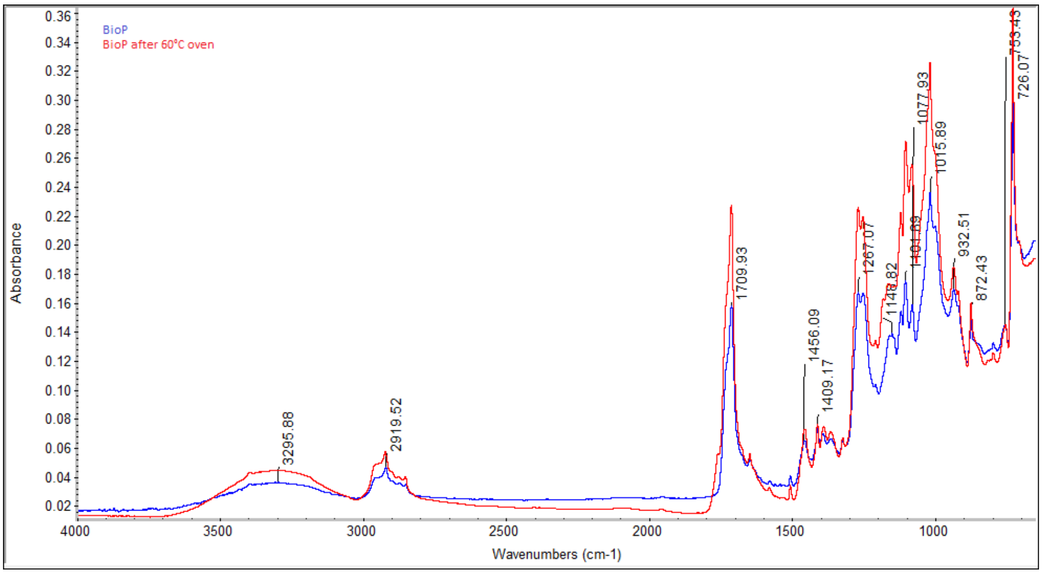


Figure 4.33-Spectrum of a BioP sample submitted to a temperature of 60 °C in the oven

4.3.4 Visual analyses of bioplastics changing features

To carry out a visual inspection of the surface of bioplastic pieces, some photographs of the samples were taken during the timing of the analyses, and in figure below they are reported: it was immortalized one sample for each withheld fraction, at the four days of the analyses.

10° day – 20 mm
10° day – 10 mm
10° day – 8 mm
10° day – 5,6 mm
10° day – 2,38 mm
25° day – 20 mm
25° day – 10 mm
25° day – 8 mm
25° day – 5,6 mm
25° day – 2,38 mm
25° day – 1,4 mm
40° day – 20 mm
40° day – 10 mm
40° day – 8 mm
40° day – 5,6 mm
40° day – 2,38 mm
40° day – 1,4 mm
55° day – 20 mm
55° day – 10 mm
55° day – 8 mm
55° day – 5,6 mm
55° day – 2,38 mm
55° day – 1,4 mm

Figure 4.34-Photographs of bioplastic samples taken during the composting process (F. Ruggero, 2017)

Having a complete view of the aspects of bioplastics removed from the composted matrix, some considerations involving the changes observed can be done.

The samples taken from the first two samplings are cleaner than the older ones, and it is noticeable a change of the colour of the smallest fractions from white to yellow-orange.

The pieces prenset a curling especially of the exyernal borders, together with an evident erosions of the sides, sign that bacteria have attaked the material in these parts.

Few holes are present in the pieces, and they are probable related to the probes used to take temperature and humidity, or because they were pierced by twigs and wood chips during the mixings.

Moreover, the aspect of the bioplastics, in particularly the smallest ones, become ever more similar to compost for colour, consistency and sizes.

In figure 4.35 it was focused the aspect of the microplastics prelevated from the samples of the 55th day, to show how much difficult it was their identification due to the color and the dirt around them, even if it is surely not feasible to say that they are no more plastics.

Micro-bioplastics after 55 days of composting

Figure 4.35-MicroBioP aspect after 55 days (F. Ruggero, 2017)

Another observation concernign the aspects and the characteristics of bioplastic after having stayed in the composting process is linked with their stickiness. In fact, pieces of biobag tend to remain attached to all the other components of the composted matrix, from wood chips to degrading food waste.

This characteristic is developed exspecially during the thermophilic phase of composting, due to theramal abiotic degradation, which is one of the possible degradation forms that take place for bioplastics.

Thermal degradation of thermoplastic polymers is not always possible during the composting process, beacuase it depends on the melting temperature of the polymer; for bioplastics made on Mater-Bi t_m is equal to 64°C (Lucas et al., 2008), allowing the partial melting of the tested material during the first week of the process when temperatures rose between 55 and 60°C.

Bioplastics stickiness can cause troubles not only during the degradation process but also after the release of compost in the environment. First of all, if during composting bioplastic pieces remain attached each others or to other components of the matrix, this decreases the specific surface avialiable for bacteria both in the piece of bioplastic and in th piece of food or wood. Secondly the release of some glue or other pastes after melting could discourage biodegradation or make matrix less appetizing.

Morevore, when released in the environment in form of compost and used as fertilezer for food crops or vegetables cultivation, small bioplastic pieces with some residues of stickiness after the composting process may remain attach to the food growing in the fertilized field, or to the soil.

As a consequence it may be ingested with food, not only by animals such as insects or birds, but also by people who eat those products.

Figure 4.36-Bioplastics stickiness (F. Ruggero, 2017)

To conclude with the analysis of the stickiness and confirm that it is an element of disturbance in the process of biodegradation, it was done an IR on a piece of bioplastic which was folded; it was found that the spectrum of the external part, which stayed in contact with the compostable matrix and was submitted to the action of bacteria, showed a higher degradation than the internal part. In fact, this spectrum is almost equal to the spectrum of the initial BioP, demonstrating that when these bioplastic pieces remain attached one to the other or to other components of the BioPOF their surface is not attachable by microorganism, thus biodegradation is not able to start or it is stopped (Figure 4.37).

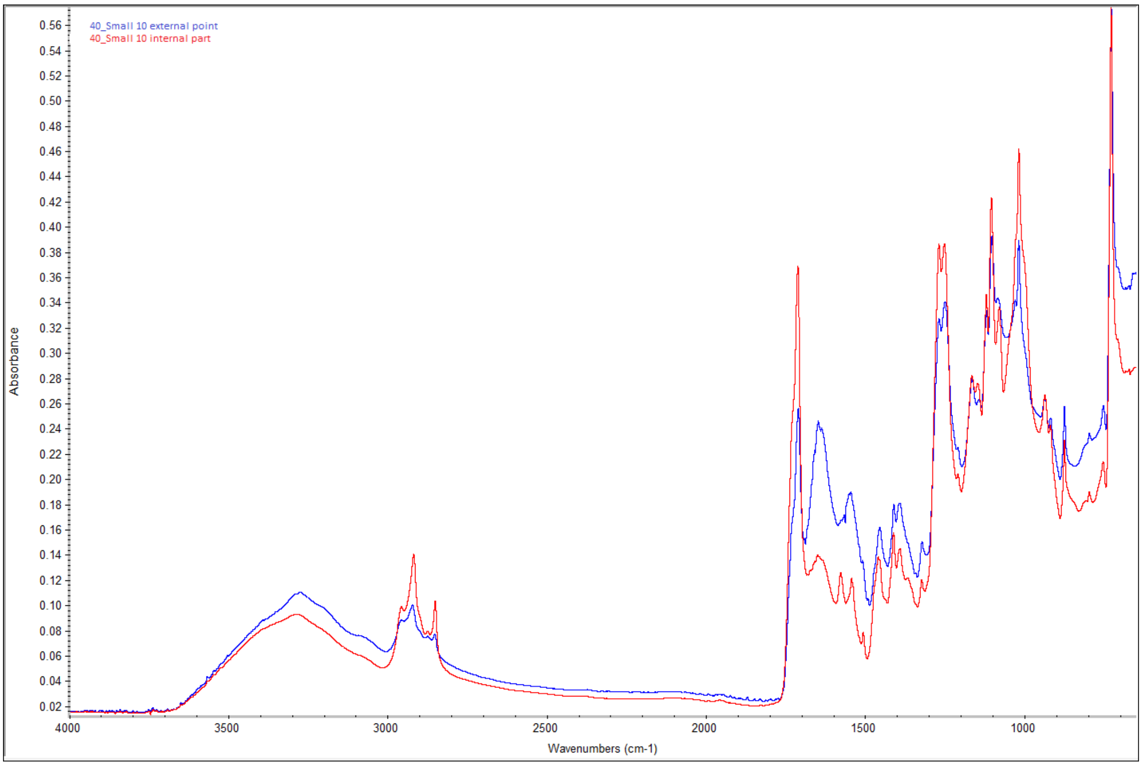


Figure 4.37-Comparison between the internal and the external side of a sticky bioplastic piece

5. CONCLUSIONS

The results of the research should be evaluated on two sides: the composting process carried out on a small scale and the analyses obtained on the tested material.

As for the composting process, the most of the conclusions are positive: it passed through the typical thermophilic phase of this treatment, even if it lasted a little bit less than in the real composting plants, and during the maturation phase it was observed the growing of actinomycetes and fungi, which are the main organisms acting on bioplastics degradation.

Furthermore, the analyses carried out on the samples, taken during the phases of the process and at the end of the period of the research, showed a positive match with the requirements for a good quality compost. The results for the C/N, the moisture content, the pH, the final temperature and the respirometric index corresponded to the values generally achieved at the end of the full scale composting process, confirming that the small scale tests for this type of process are completely feasible.

The two aspects that revealed a possible improvement for a future development of the research are on the one hand the initial mixture of waste, and on the other hand the initial conditions in which the heap should be put.

As for the mixture, the amount of wood chips included in the mixture was too high, fact that was demonstrating by the final results obtained in the analyses of TOC and volatile solids: in fact the lignin of the wood chips is the last element to be degraded by fungi, so that in two months its degradation is still not completed.

It’s also true that an amount of wood is required within the mixture destined to a composting process because the matrix of waste needs a good level of structure, so for a possible further implementation the suggestion earnt from this experience is to put within the waste wood twigs and small branches of a size big enough to be removed with a sieve of 20-10 mm, as happens in the real plants.

The second point involves the initial conditions to be preserved: in fact, as the small heap make difficulties in keeping heat and cold, and moisture content, due to the few bulk, it should be helped through maintaining it in an environment without excessive thermal swings.

Focusing now the attention on the results obtained about the disintegration and the degradation of bioplastics, four conclusions can be taken at the end of the two months of the test.

Firstly, it was observed that the higher disintegration activity was done during the thermophilic phase, with a percentage of size decrease of 50-70% with respect to the initial dimensions. However, the IR analyses carried out on bioplastic pieces after ten days of composting showed a not significant change in the spectrum, linked with a not substantial biodegradation activity by the thermophilic bacteria.

On the contrary, during the maturation phase it occurred a slowdown in the disintegration trend, but the IR analyses, especially on the 40th and 55th days, resulted in a change of the spectrum recallable to the degradation activity carried out by fungi and actinomycetes during the cooling and the maturation phase.

To conclude with this first consideration, it's fair to say that the effect of the temperature leads to a disintegration of the material, thanks to the fact that the reached temperature is almost equal to the melting temperature of the bioplastics. Meanwhile, it can be said that the major action of biodegradation occurs during the maturation phase, by mesophilic and psychrophilic bacteria, and fungi.

In addition to this, the same analyses carried out on the disintegration, revealed that the time required theoretically to achieve a size less than 2 mm is equal to four, up to four and half, months, thus more than the three months of the European standards used as reference, and a little bit more than the time generally reserved for the composting process in the real plants.

The third conclusive information achieved with this research involves the fact that having observed the number of bioplastic pieces within the samples taken during the process, it didn't decrease a lot among the samples of the different timings, even if the weight decrease and the spectra confirmed the effective degradation of these bioplastics.

So the hypothesis is that the action of microorganisms is mainly on the thickness of these materials, including that if a thicker material was used and disposed in composting plants, maybe its degradation and disintegration time would not be the same of the biobags, and it could have a slowdown which would lead to an increase in the time required for its disposing.

The research developed with this thesis work gave the possibility to explore a new field, and to observe that other implementations of this project could be done, in order to define a more general vision of the biodegradation and disintegration of bioplastic products.

In particularly the suggestions for some further implementations could involve an ecotoxicology study carried out to evaluate if it exists a level of bioplastics concentration in compost that could be polluting for plants growth and worms' life.

The second interesting implementation could be a microbiologic study of those microorganisms active during the composting process for bioplastics degradation: thus, it would carry out a confirm of the action of fungi and actinomycetes as the main microorganism able to biodegrade bioplastics, developed during the cooling and the maturation phase of the process.

Another interesting point that could be evolved in a further study is that involving the disintegration and degradation model: in fact, firstly the analyses carried out on biobag can be expanded also to the new products proposed on the market, such as cutlery and coffee capsules, and secondly also the variable of quantity could be taken into account to obtain a model with a more general evolution of the process.

At the conclusion of my thesis work I would like to get a glance on the fieldwork of the new materials, processes, technologies and products immitted on the markets in these last decades. Often the focus of the producers is on the birth of the products from the cradle of the industries: so the attention is posed on the use of renewable resources, both for materials and energies, in the use of less amount of water, in the reduction of the emissions during the process, in accordance with the LCA at the basis of the production.

It's also true, though, that the same responsibility is not felt at all in the disposing of the products after their life, thing that would be an important part of a LCA study when a new creation is proposed on the market.

The sensitization to the environment should be extended from the cradle to the grove in the life of a product, and the research around the development of a new product should be done before the immision on the market not only to obtain a more sustainable substance at the beginning of its production chain, but also to leave at the end of the chain a waste with a clear, suitable and economically and environmentally sustainable way of disposal.

In this view, from the cradle to the grove, the generations of this century will be able to manage in a sustainable way the beginning of the production chain, as far as the end of the same chain, and whenever they will leave to the future generations the disposal of their long-life products, they will have already found a safe and sustainable treatment for the waste management of these products, in accordance with the view of the sustainable development.

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ANNEXES

I. ANNEX: Composting process parameters

In the Annex I there are reported graphs and tables with all the data collected during the analyses of the composted matrix: the order of the analyses reported is the same of chapter 4.1.

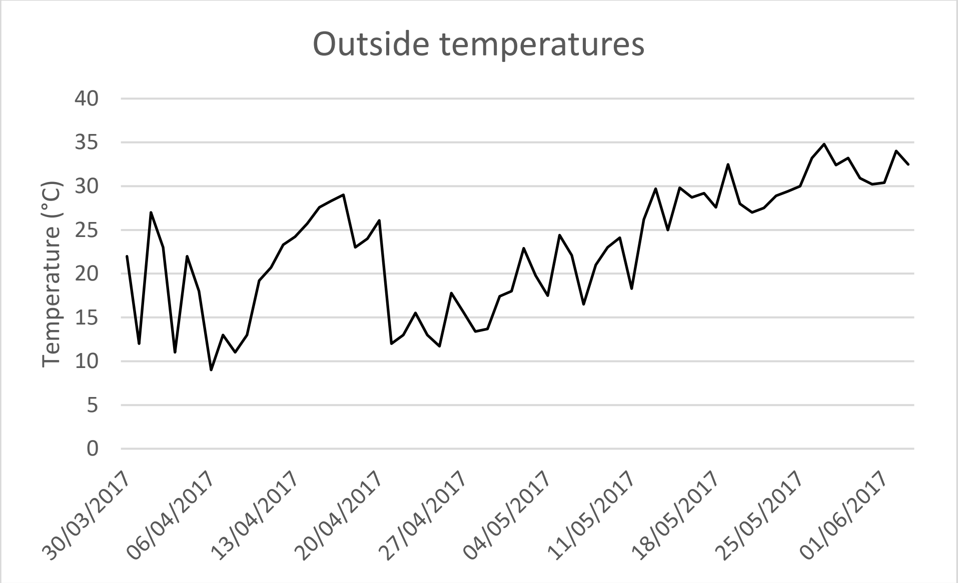

Figure I.1-Outside temperature during the small scale test

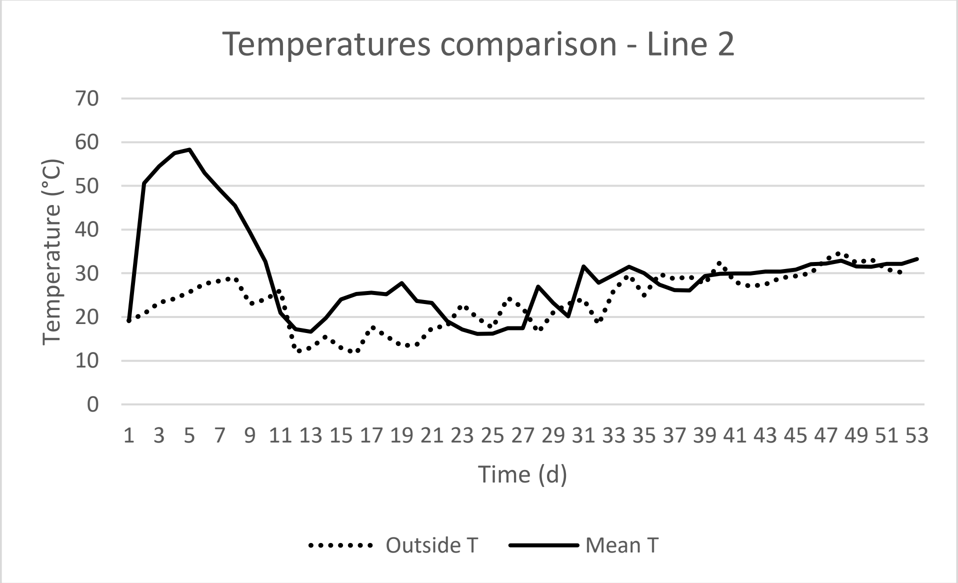

Figure I.2-Comparison between outside temperature and heaps temperature - Line 2

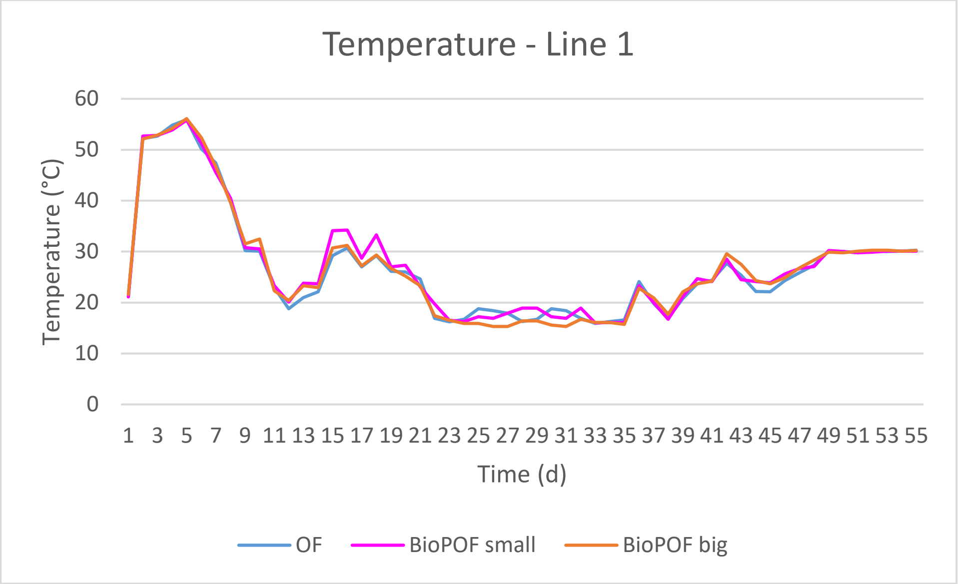

Figure I.3-Temperature during composting process - Line 1

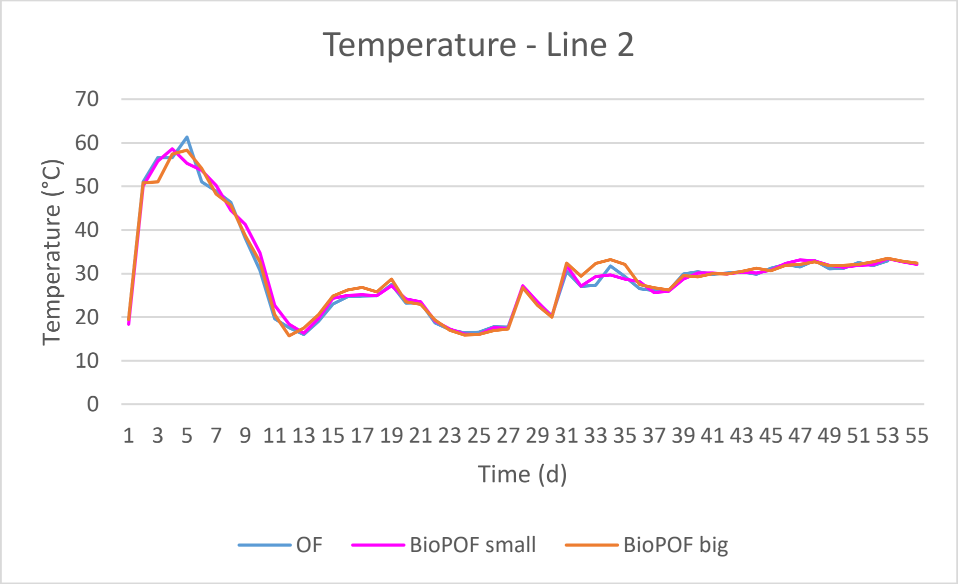

Figure I.4-Temperature during composting process - Line 2

Table I.1-Moisture content

MOISTURE %					
	Line 1				
	1st	10th	25th	40th	55th
OF	56,5	44,5	37,9	43,9	41,9
BioPOF s	56,7	43,3	36,9	44,7	43,1
BioPOF b	56,8	44,1	37,6	44,2	41,7
Mean	56,7	44,0	37,5	44,3	42,2
	Line 2				
	1st	10th	25th	40th	55th
OF	55,8	44,1	39,7	46	41,4
BioPOF s	55,9	43,5	37,9	47	41,5
BioPOF b	56,6	44,1	40,1	45,7	41,6
Mean	56,1	43,9	39,2	46,2	41,5

Table I.2-Total solids

TOTAL SOLIDS %					
	Line 1				
	1st	10th	25th	40th	55th
OF	43,5	55,5	62,1	56,1	58,1
BioPOF s	43,3	56,7	63,1	55,3	56,9
BioPOF b	43,2	55,9	62,4	55,8	58,3
Mean	43,3	56,0	62,5	55,7	57,8
	Line 2				
	1st	10th	25th	40th	55th
OF	44,2	55,9	60,3	54	58,6
BioPOF s	44,1	56,5	62,1	53	58,5
BioPOF b	43,4	55,9	59,9	54,3	58,4
Mean	43,9	56,1	60,8	53,8	58,5

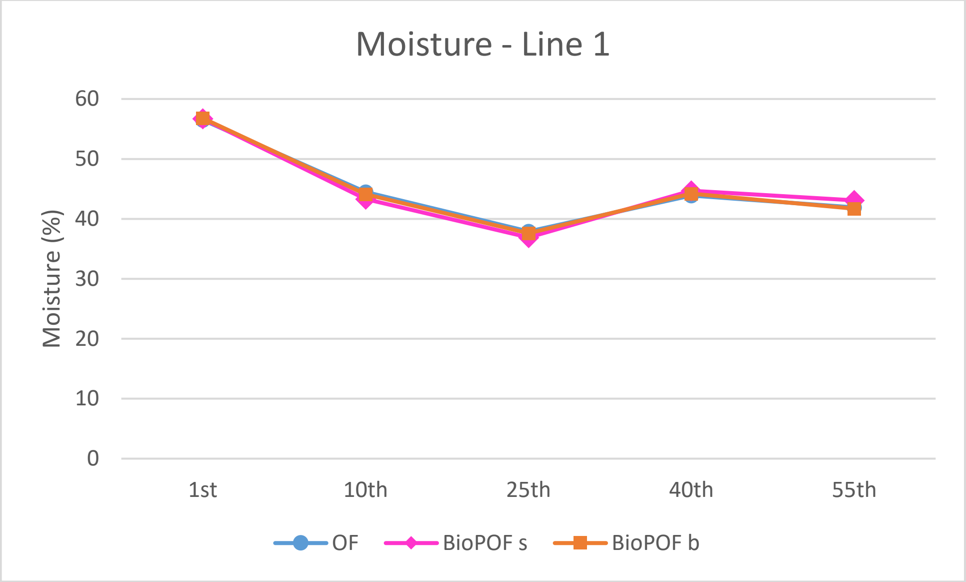

Figure I.5- Moisture content - Line 2

Table I.3-Volatile solids

VOLATILE SOLIDS %					
	Line 1				
	1st	10th	25th	40th	55th
OF	90,7	89,8	89	87	85,5
BioPOF s	90,1	89,9	89,3	87,2	85,7
BioPOF b	90,2	89,9	88,9	87,1	85
Mean	90,3	89,9	89,1	87,1	85,4
	Line 2				
	1st	10th	25th	40th	55th
OF	90,7	88,8	88,1	87,9	80,8
BioPOF s	90,2	88,9	88,7	88,4	81,9
BioPOF b	90,5	89,1	88,3	87,8	82,1
Mean	90,5	88,9	88,4	88,0	81,6

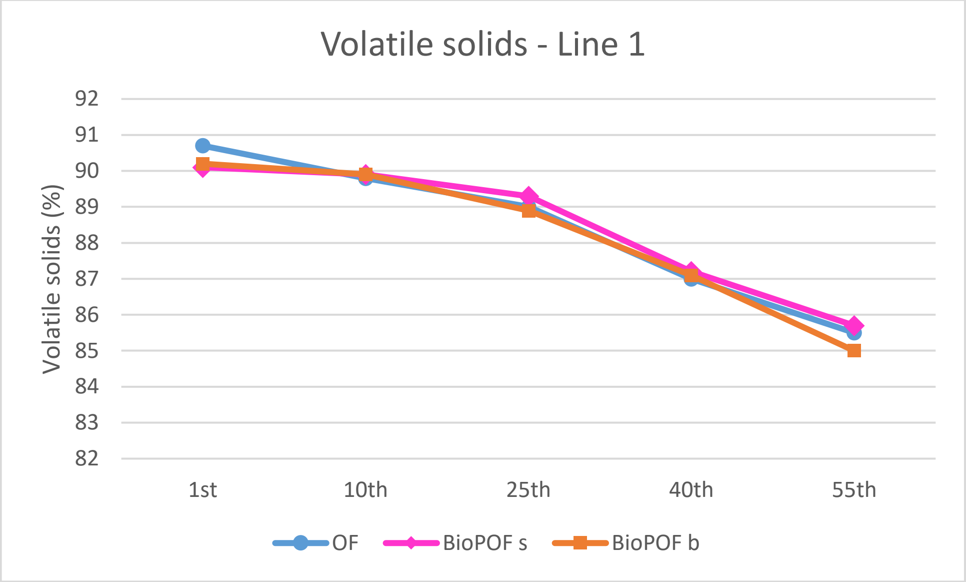

Figure I.6-Volatile solids - Line 1

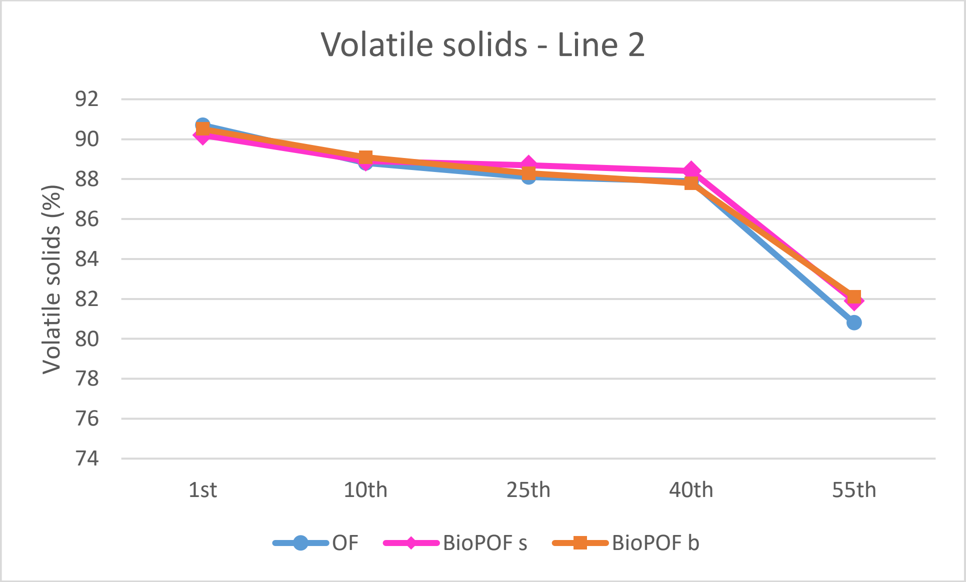

Figure I.7-Volatile solids - Line 2

Table I.4-TKN normalized with total solids

TKN g/kg TS					
	Line 1				
	1st	10th	25th	40th	55th
OF	17,8	22	32,9	25,4	31,5
BioPOF s	20,2	24,7	25,1	20,3	32,4
BioPOF b	21,8	24,9	26,1	24,9	33,7
Mean	19,9	23,9	28,0	23,5	32,5
	Line 2				
	1st	10th	25th	40th	55th
OF	20,1	25,3	25,8	27,5	31,9
BioPOF s	22,4	26,7	32,4	32,8	34,1
BioPOF b	15,7	25,1	31,3	31,4	34,6
Mean	19,4	25,7	29,8	30,6	33,5

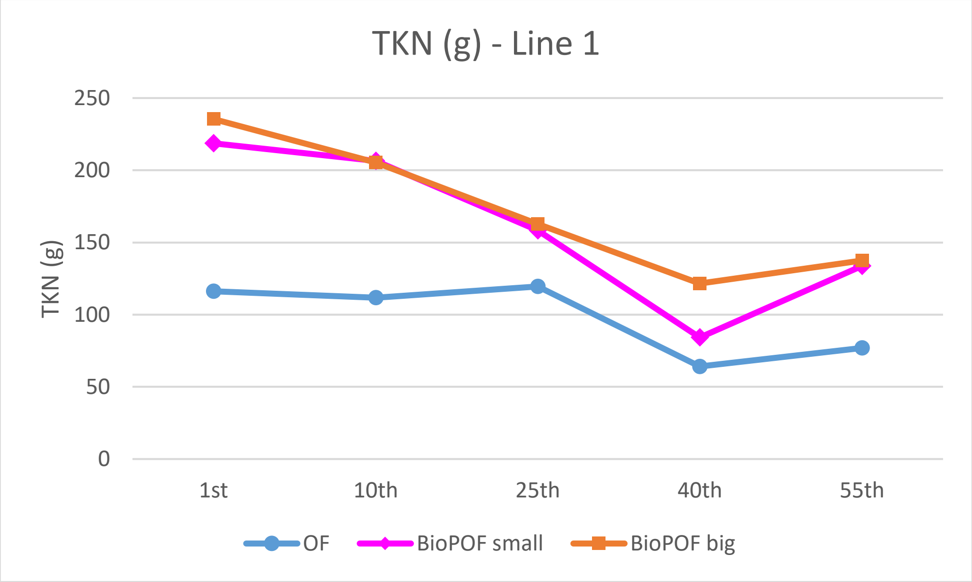

Figure I.8-TKN behaviour during the composting process - Line 1

Table I.5-TOC normalized with TS

TOC g/kg TS					
	Line 1				
	1st	10th	25th	40th	55th
OF	511	462	431	433	385
BioPOF s	513	459	425	448	413
BioPOF b	518	463	415	447	418
Mean	514,0	461,3	423,7	442,7	405,3
	Line 2				
	1st	10th	25th	40th	55th
OF	512	469	472	456	419
BioPOF s	516	464	463	452	390
BioPOF b	501	455	447	439	409
Mean	509,7	462,7	460,7	449,0	406,0

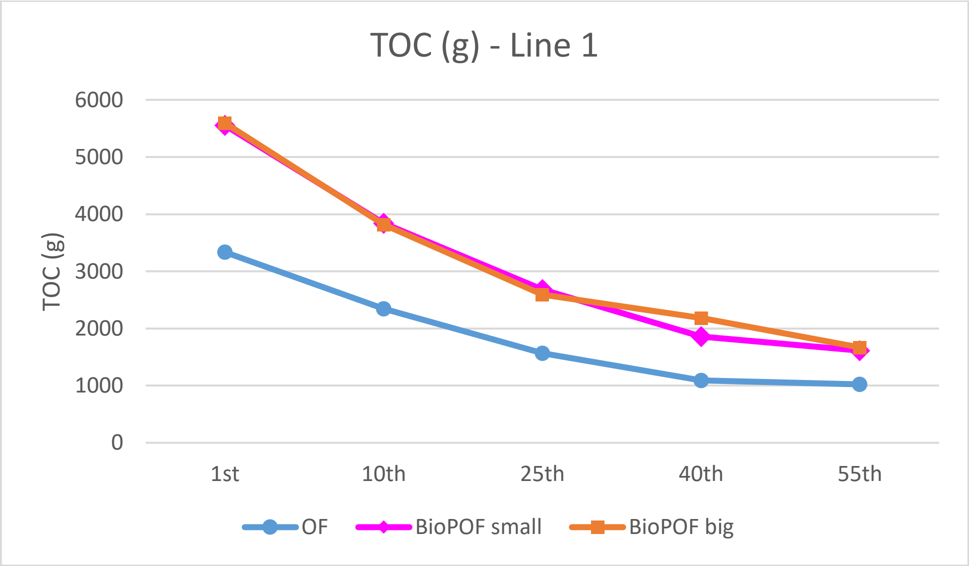

Figure I.9-TOC behaviour during the composting process - Line 1

Table I.6-RI 4 normalized on total solids

RI4 mgO2/g TS					
	Line 1				
	1st	10th	25th	40th	55th
OF	110,3	60,8	44,8	41,3	2,7
BioPOF s	112,5	62,7	49,3	52,2	7,0
BioPOF b	109,8	58,5	51,8	47,2	9,2
Mean	110,9	60,7	48,6	46,9	6,3
	Line 2				
	1st	10th	25th	40th	55th
OF	108,1	63,8	46,6	21,5	18,1
BioPOF s	107,1	65,3	51,5	36,7	13,9
BioPOF b	111,2	64,2	52,2	26,4	17,6
Mean	108,8	64,4	50,1	28,2	16,5

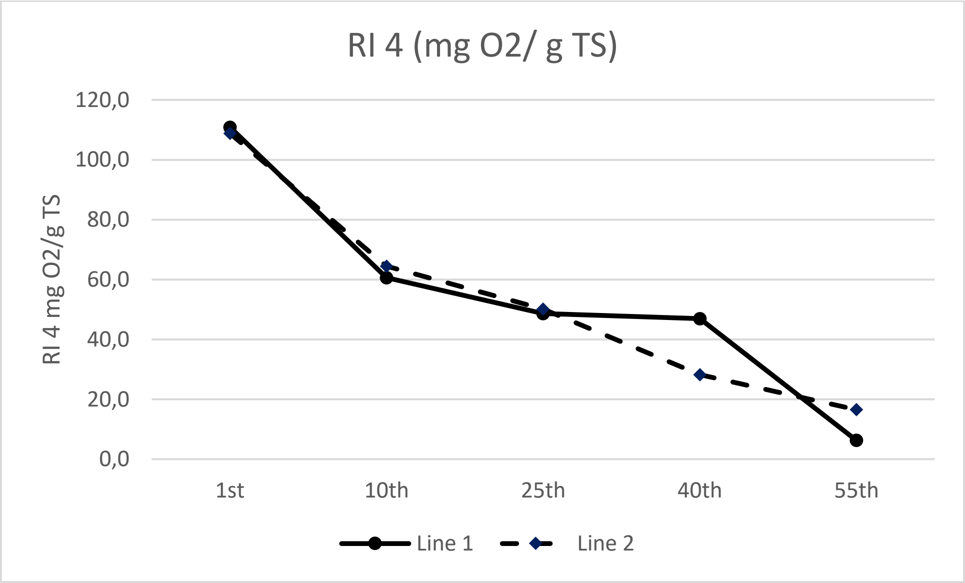

Figure I.10-RI 4 normalized on total solids

Table I.7-RI 7 normalized on volatile solids

IR7 mgO2/g VS					
	Line 1				
	1st	10th	25th	40th	55th
OF	81,5	68,7	57,7	42,9	4,02
BioPOF s	81,9	69,1	65,5	45,9	5,98
BioPOF b	84,8	75,5	69,5	50,6	9,4
Mean	82,7	71,1	64,2	46,5	6,5
	Line 2				
	1st	10th	25th	40th	55th
OF	82,5	58,5	51,2	23,9	22,74
BioPOF s	80,9	53,1	56,4	42,1	17,53
BioPOF b	83,6	58,2	56,1	27,2	21,75
Mean	82,3	56,6	54,6	31,1	20,7

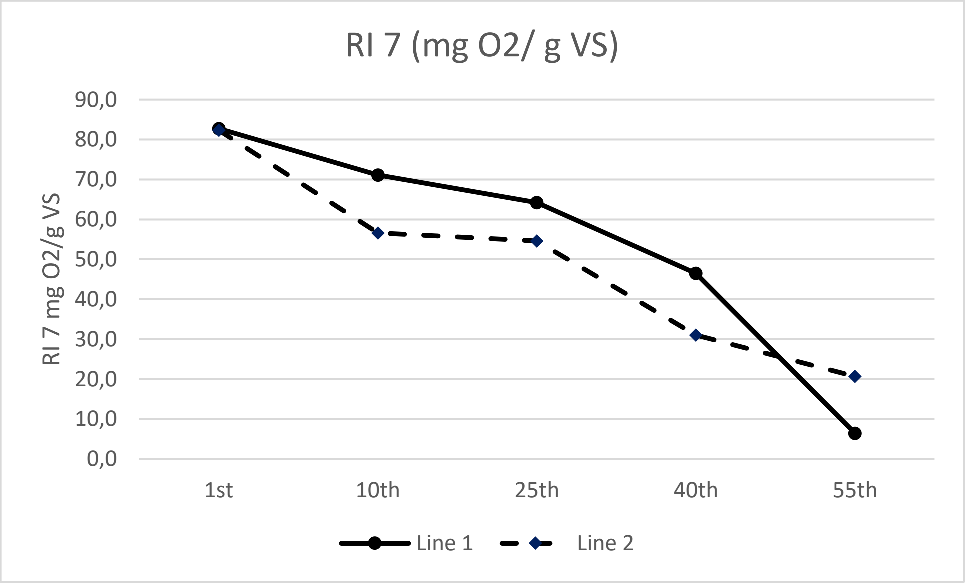

Figure I.11--RI 7 normalized on volatile solids

Table I.8-RI 7 normalized on total solids

RI7 mgO2/g TS					
	Line 1				
	1st	10th	25th	40th	55th
OF	161,3	83,3	68,3	67,2	5,94
BioPOF s	168,5	79,5	78,7	71,8	8,84
BioPOF b	164,5	95,4	82,5	79,4	13,51
Mean	164,8	86,1	76,5	72,8	9,4
	Line 2				
	1st	10th	25th	40th	55th
OF	167,1	77,4	74,2	38,5	31,71
BioPOF s	164,1	84,2	80,1	69,78	24,45
BioPOF b	166,2	78,2	82,1	44,36	30,34
Mean	165,8	79,9	78,8	50,9	28,8

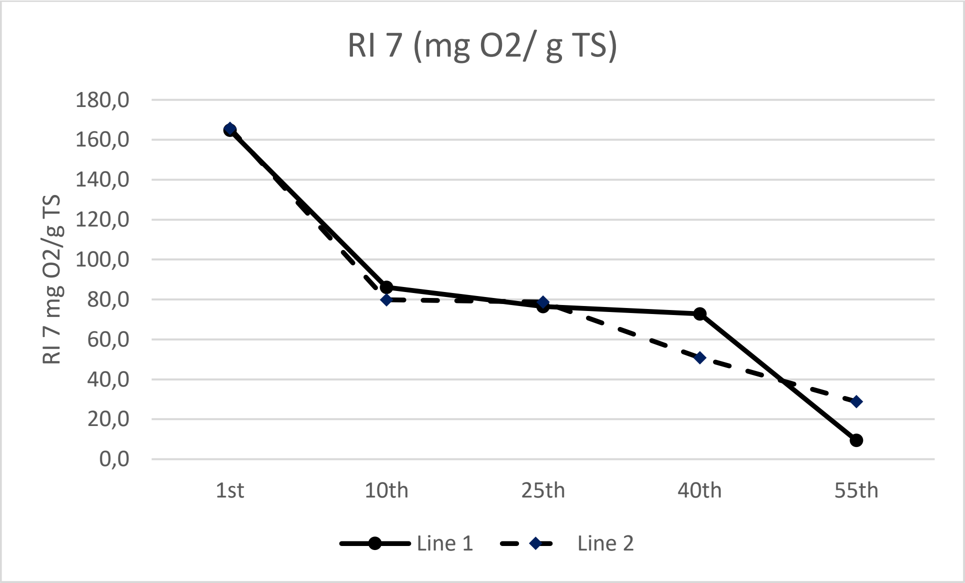

Figure I.12-RI 7 normalized on total solids

II. ANNEX: Granulometric curves

Graphs and tables of granulometric analyses are reported as a reference for paragraph 4.2. The granulometric curve is done on the passing fractions and follows the disintegration of the composted matrix during the process.

Each graph is accompanied by the reference table with all the data in weight and percentages.

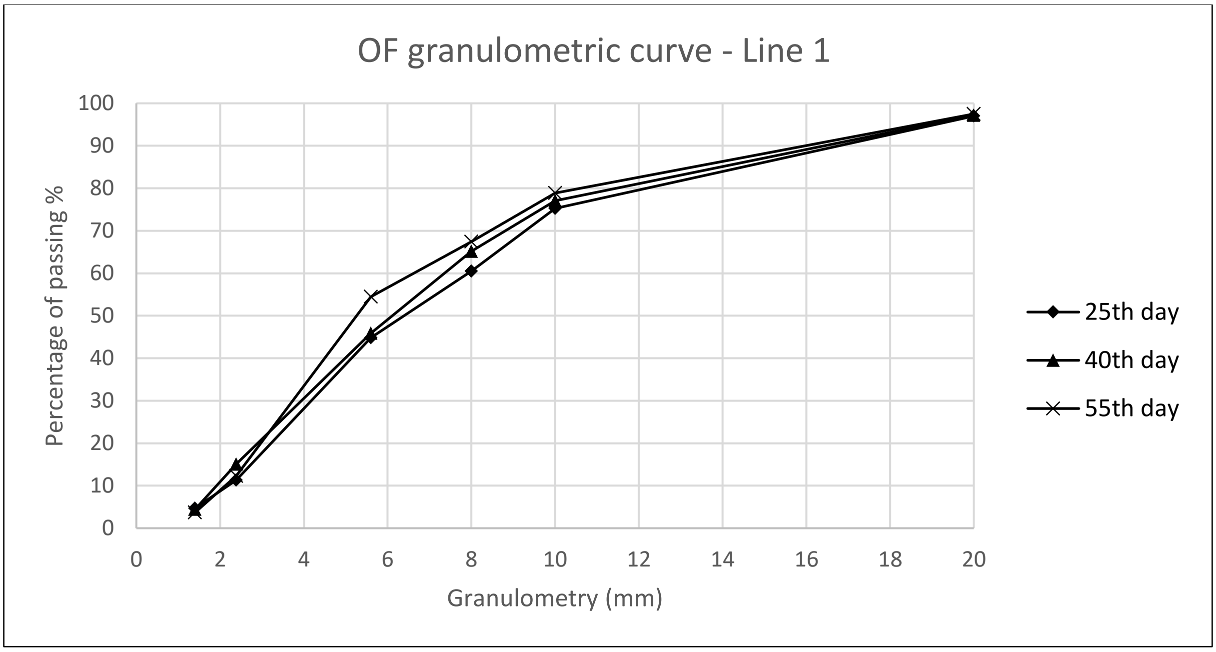

Figure II.1-Granulometric curve OF

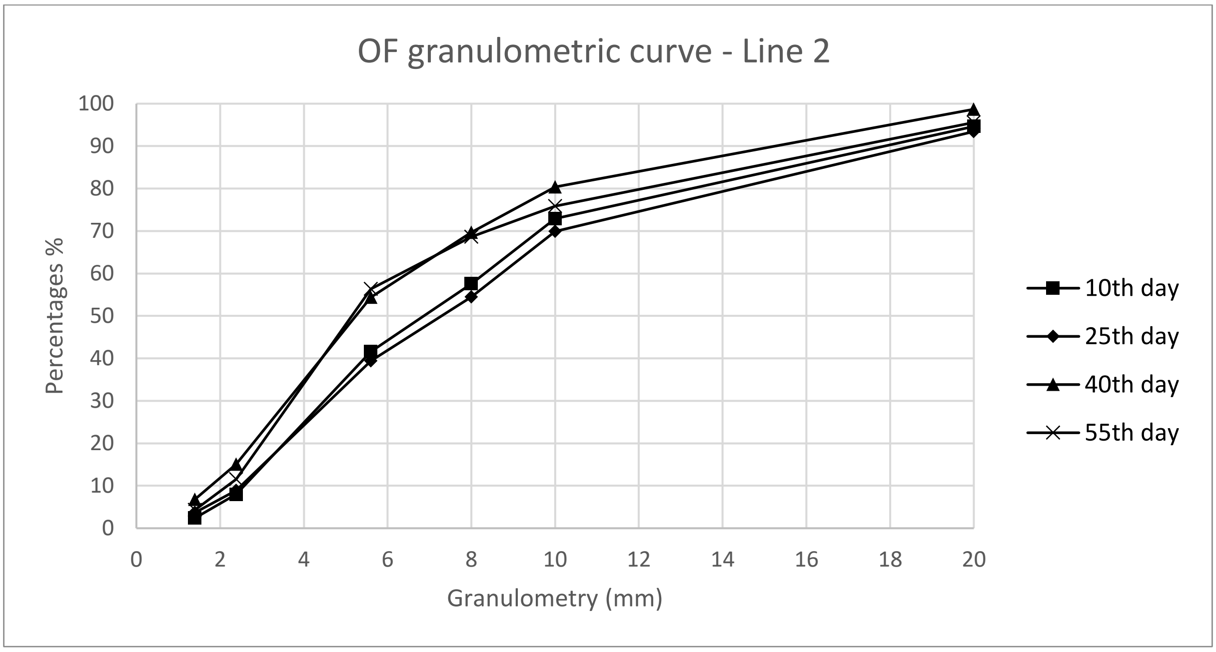

Figure II.2-Granulometric curve OF

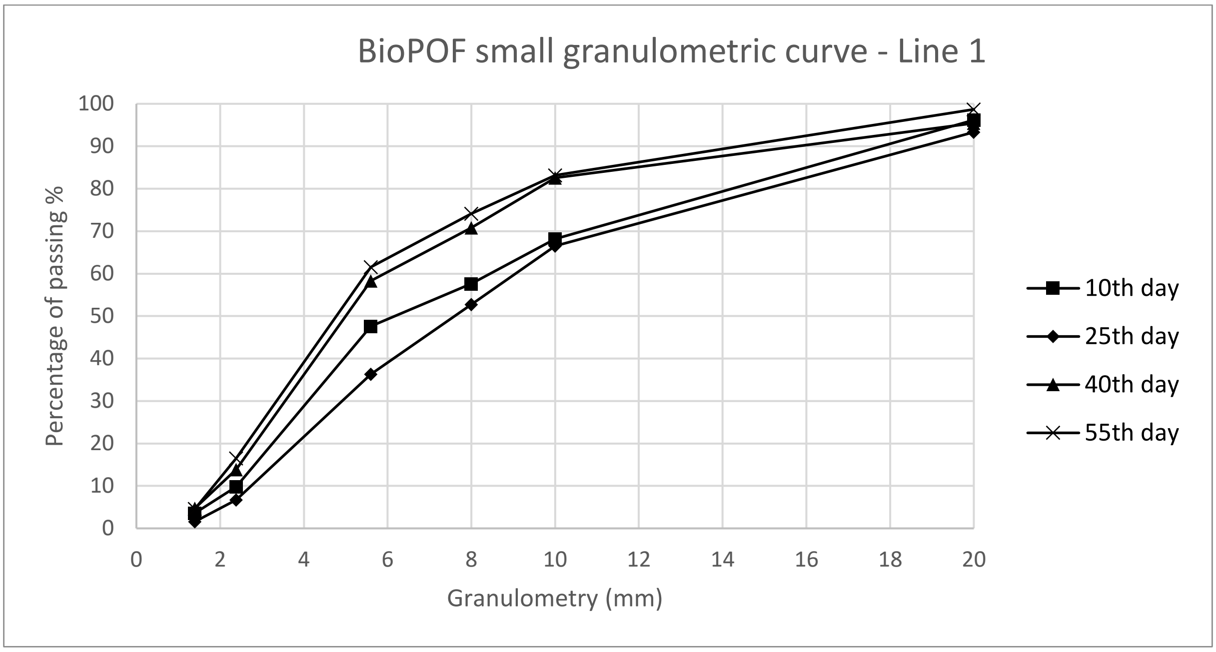

Figure II.3-Granulometric curve BioPOF small

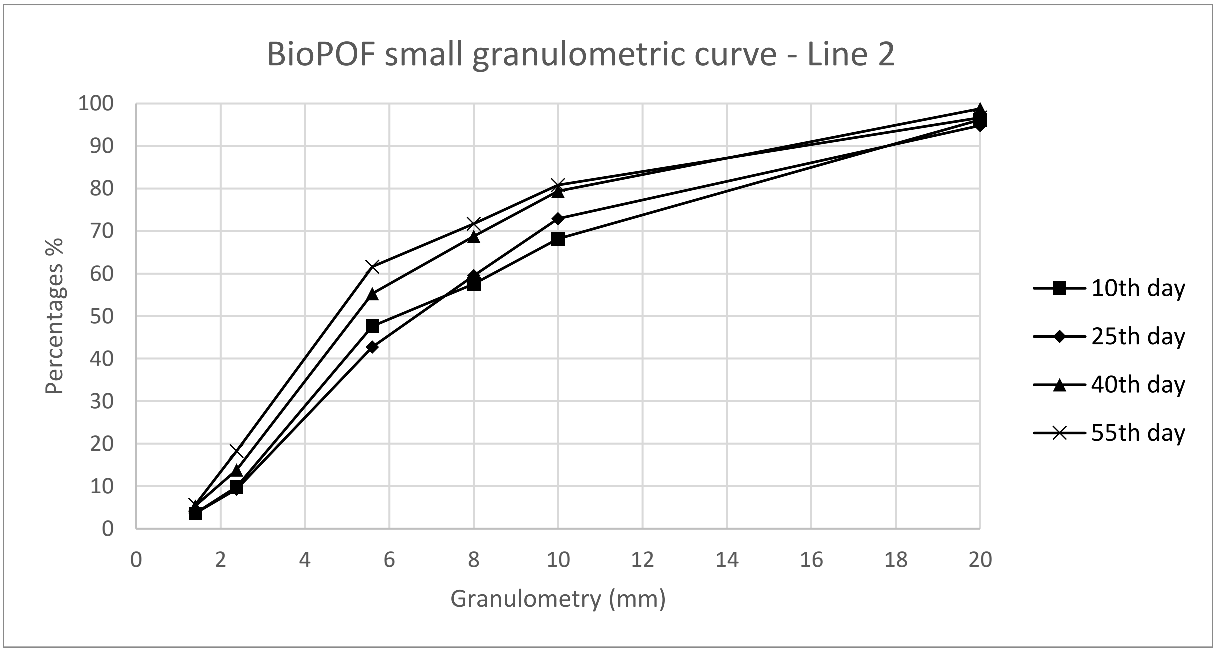

Figure II.4-Granulometric curve BioPOF small

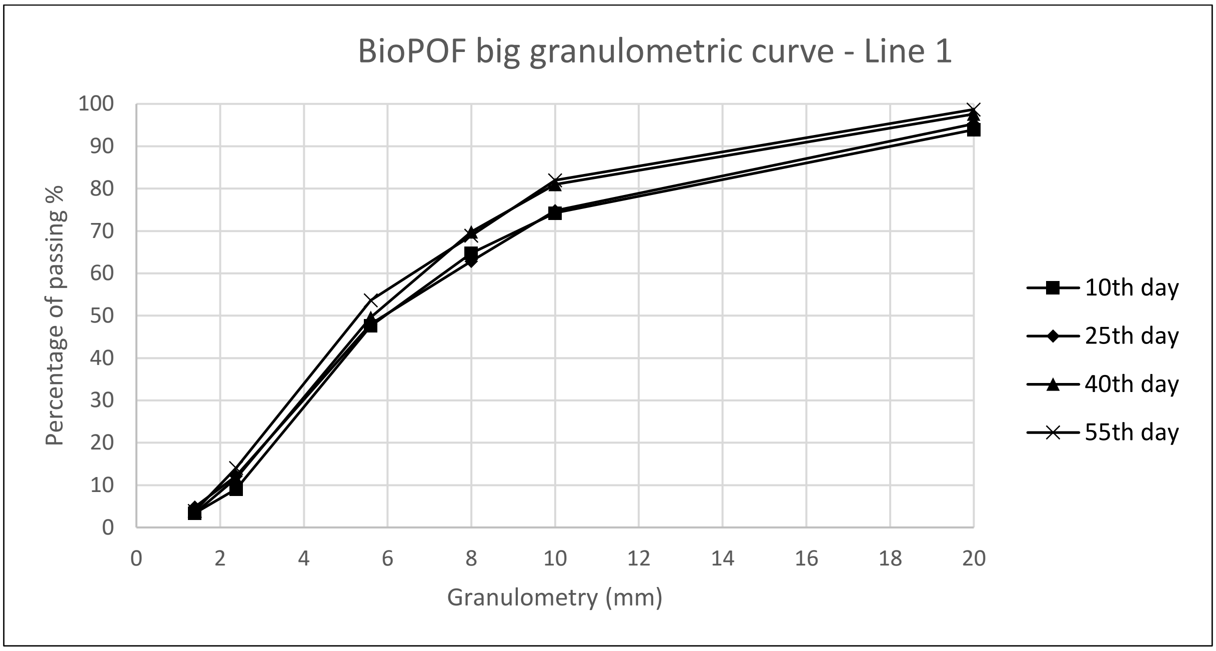

Figure II.5-Granulometric curve BioPOF big

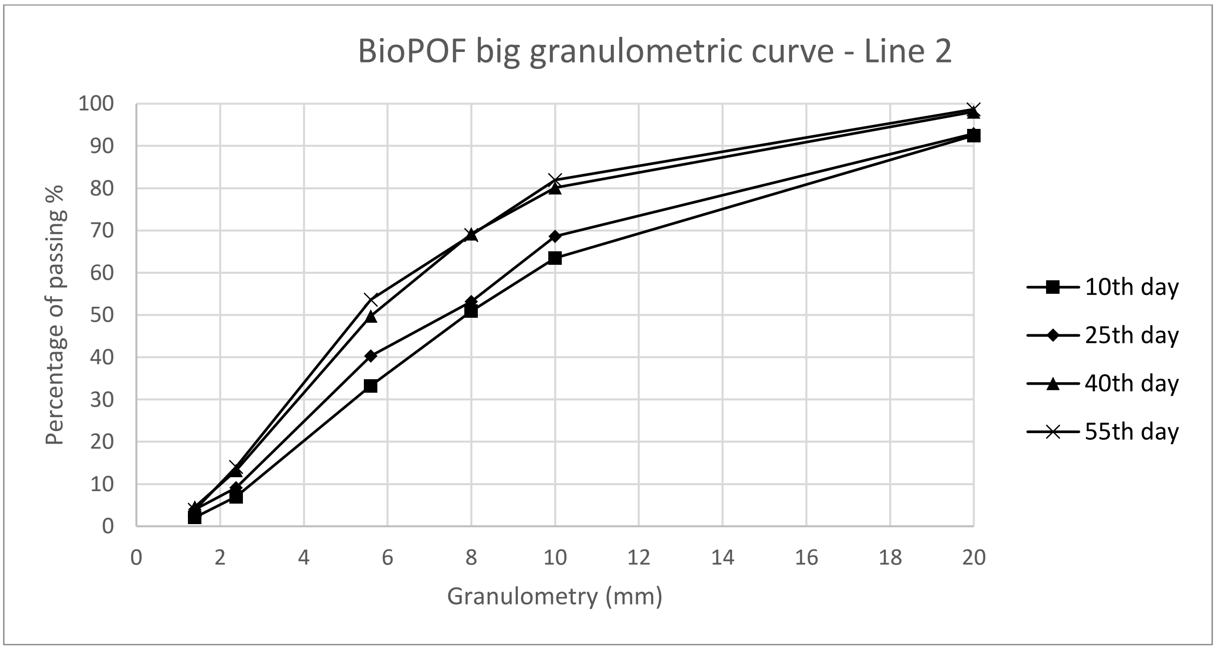

Figure II.6-Granulometric curve BioPOF big

Analyses on the 10th day

For OF the analyses were carried only on Line 2, because blanks of Line 1 are in a smaller amount and it was decided to keep them for the further sampling.

Table II.1-Granulometry 10th day OF

		OF - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
¾	20,00	1,889	95	0,107	5
3/8	10,00	1,456	73	0,418	21
5/16	8,00	1,149	58	0,304	15
3,5	5,60	0,831	42	0,306	15
8	2,38	0,159	8	0,668	33
14	1,40	0,048	2	0,112	6

Table II.2-Granulometry 10th BioPOF small

		BioPOF small - Line 1				BioPOF small - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	2,77	96	0,11	4	1,86	93	0,133	7
3/8	10,00	1,964	68	0,786	27	1,325	66	0,529	27
5/16	8,00	1,659	58	0,263	9	1,051	53	0,266	13
3,5	5,60	1,372	48	0,272	9	0,723	36	0,323	16
8	2,38	0,283	10	1,082	38	0,134	7	0,582	29
14	1,40	0,104	4	0,178	6	0,032	2	0,1	5

Table II.3-Granulometry 10th day BioPOF big

		BioPOF big - Line 1				BioPOF big - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	2,679	94	0,174	6	1,844	92	0,150	8
3/8	10,00	2,118	74	0,536	19	1,266	63	0,567	28
5/16	8,00	1,847	65	0,237	8	1,015	51	0,248	12
3,5	5,60	1,357	48	0,478	17	0,663	33	0,347	17
8	2,38	0,258	9	1,081	38	0,14	7	0,520	26
14	1,40	0,097	3	0,158	6	0,042	2	0,097	5

Analyses on the 25th day

Table II.4-Granulometry 25th day OF

		OF - Line 1				OF - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20	0,97	97	0,03	3	1,851	93	0,13	7
3/8	10	0,753	75	0,215	22	1,385	70	0,458	23
5/16	8	0,605	61	0,145	15	1,079	54	0,306	15
3,5	5,6	0,448	45	0,148	15	0,781	39	0,297	15
8	2,38	0,113	11	0,334	33	0,176	9	0,6	30
14	1,4	0,047	5	0,065	7	0,073	4	0,102	5

Table II.5-Granulometry 25th day BioPOF small

		BioPOF small - Line 1				BioPOF small - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	1,901	95	0,094	5	1,887	95	0,103	5
3/8	10,00	1,493	75	0,404	20	1,451	73	0,433	22
5/16	8,00	1,254	63	0,236	12	1,184	59	0,256	13
3,5	5,60	0,958	48	0,292	15	0,850	43	0,334	17
8	2,38	0,243	12	0,71	36	0,185	9	0,659	33
14	1,40	0,097	5	0,145	7	0,072	4	0,109	5

Table II.6-Granulometry 25th BioPOF big

		BioPOF big - Line 1				BioPOF big - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	1,878	94	0,121	6	1,847	93	0,141	7
3/8	10,00	1,381	69	0,495	25	1,364	69	0,474	24
5/16	8,00	1,13	57	0,247	12	1,057	53	0,305	15
3,5	5,60	0,802	40	0,328	16	0,802	40	0,248	12
8	2,38	0,175	9	0,624	31	0,182	9	0,618	31
14	1,40	0,067	3	0,107	5	0,079	4	0,103	5

Analyses on the 40th day

Table II.7-Granulometry 40th day OF

		OF - Line 1				OF - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,483	97	0,014	3	0,983	99	0,013	1
3/8	10,00	0,383	77	0,097	20	0,801	80	0,178	18
5/16	8,00	0,324	65	0,058	12	0,694	70	0,105	11
3,5	5,60	0,228	46	0,093	19	0,542	54	0,152	15
8	2,38	0,075	15	0,153	31	0,150	15	0,391	39
14	1,40	0,022	4	0,053	11	0,068	7	0,079	8

Table II.8-Granulometry 40th day BioPOF small

		BioPOF small - Line 1				BioPOF small - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,481	95	0,023	5	0,977	99	0,012	1
3/8	10,00	0,416	83	0,065	13	0,785	79	0,184	19
5/16	8,00	0,357	71	0,056	11	0,680	69	0,097	10
3,5	5,60	0,294	58	0,063	13	0,547	55	0,124	13
8	2,38	0,07	14	0,221	44	0,137	14	0,409	41
14	1,40	0,024	5	0,046	9	0,053	5	0,084	8

Table II.9-Granulometry 40th day BioPOF big

		BioPOF big - Line 1				BioPOF big - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,488	98	0,012	2	0,979	98	0,019	2
3/8	10,00	0,405	81	0,080	16	0,800	80	0,174	17
5/16	8,00	0,349	70	0,056	11	0,691	69	0,104	10
3,5	5,60	0,248	50	0,087	17	0,497	50	0,193	19
8	2,38	0,058	12	0,188	38	0,132	13	0,358	36
14	1,40	0,017	3	0,038	8	0,046	5	0,073	7

Analyses on the 55th day

Table II.10-Granulometry 55th day OF

		OF - Line 1				OF - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,975	98	0,025	3	0,951	96	0,044	4
3/8	10,00	0,789	79	0,171	17	0,755	76	0,182	18
5/16	8,00	0,674	67	0,103	10	0,683	69	0,062	6
3,5	5,60	0,545	55	0,124	12	0,561	56	0,113	11
8	2,38	0,123	12	0,414	41	0,115	12	0,446	45
14	1,40	0,037	4	0,085	9	0,043	4	0,069	7

Table II.11-Granulometry 55th day BioPOF small

		BioPOF small - Line 1				BioPOF small - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,985	99	0,013	1	0,962	97	0,033	3
3/8	10,00	0,83	83	0,153	15	0,804	81	0,151	15
5/16	8,00	0,74	74	0,086	9	0,714	72	0,079	9
3,5	5,60	0,614	62	0,111	11	0,613	62	0,101	10
8	2,38	0,165	17	0,434	43	0,182	18	0,428	43
14	1,40	0,046	5	0,108	11	0,056	6	0,118	12

Table II.12-Granulometry 55th day BioPOF big

		BioPOF big - Line 1				BioPOF big - Line 2			
Sieve	*Granulometry*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*	*Passing Kg*	*%Passing*	*Withheld Kg*	*%Withheld*
3/4	20,00	0,985	99	0,013	1	0,969	98	0,018	2
3/8	10,00	0,818	82	0,160	16	0,821	83	0,141	14
5/16	8,00	0,688	69	0,126	13	0,703	71	0,112	11
3,5	5,60	0,535	54	0,151	15	0,545	55	0,153	16
8	2,38	0,14	14	0,394	39	0,131	13	0,410	42
14	1,40	0,039	4	0,101	10	0,045	5	0,085	9

III. ANNEX: Bioplastics concentration

Annex III contains the tables and the graphs referring to the analyses on concentration of bioplastics in the composted matrix. It includes the results to which it is made reference in paragraph 4.3.2.

Table III.1-Weight range of BioP small - Line 1

Line 1 - BioP small						
	Weight (%)	*Weight (g)*	*Conc. BioP*	*BioP (g/1 kg)*	*Variability min (g)*	*Variability max (g)*
1st	100	1000	0,007	7	7	7
10th	59	590	0,017	10,03	8,5	6,1
25th	40	400	0,015	6	5,1	3,7
40th	30	300	0,016	4,8	3,6	2,4
55th	29	290	0,011	3,19	2,4	1,6

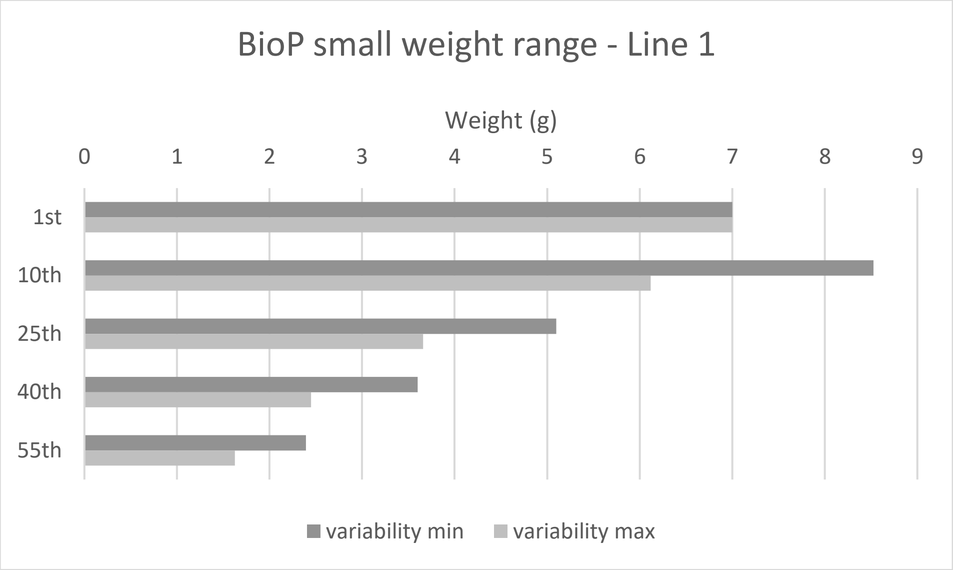

Figure III.1-Graph of weight range of BioP small - Line 1

Table III.2-Weight range of BioP small - Line 2

Line 2 - BioP small						
	Weight (%)	*Weight (g)*	*Conc. BioP*	*BioP (g/1 kg)*	*Variability min (g)*	*Variability max (g)*
1st	100	1000	0,007	7	7	7
10th	66	660	0,013	8,58	7,3	5,2
25th	37	370	0,015	5,55	4,7	3,4
40th	36	360	0,015	5,4	4,1	2,8
55th	31	310	0,011	3,41	2,6	1,7

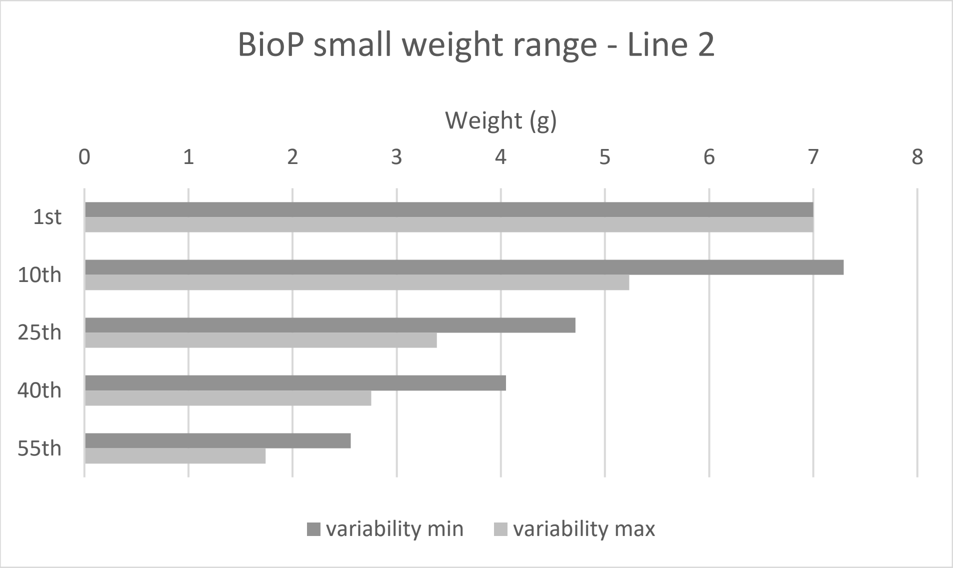

Figure III.2-Graph of weight range of small BioP - Line 2

Table III.3-Weight range of BioP big - Line 1

Line 1 - BioP big						
	Weight %	*Weight (g)*	*Conc. BioP*	*BioP (g/1 kg)*	*Variability min (g)*	*Variability max (g)*
1st	100	1000	0,007	7	7	7
10th	59	590	0,019	11,21	9,5	6,8
25th	43	430	0,019	8,17	6,9	5,0
40th	35	350	0,014	4,9	3,7	2,5
55th	28	280	0,007	1,96	1,5	1,0

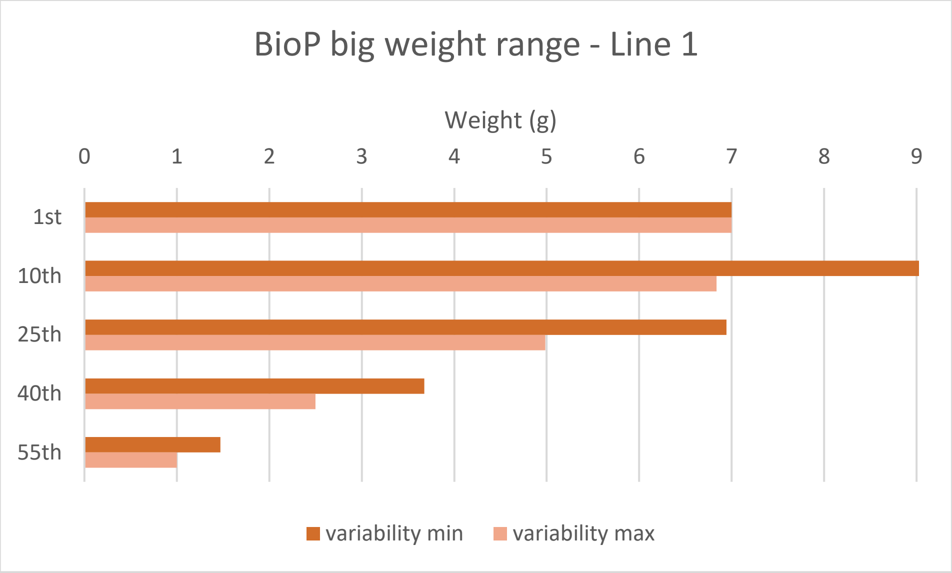

Figure III.3-Graph of weight range of big BioP - Line 1

Table III.4-Weigh range of BioP big - Line 2

Line 2 - BioP big						
	Weight (%)	*Weight (g)*	*Conc. BioP*	*BioP (g/1 kg)*	*Variability min (g)*	*Variability max (g)*
1st	100	1000	0,007	7	7	7
10th	65	650	0,011	7,15	6,1	4,4
25th	37	370	0,019	7,03	6,0	4,3
40th	33	330	0,012	3,96	3,0	2,0
55th	30	300	0,007	2,1	1,6	1,1

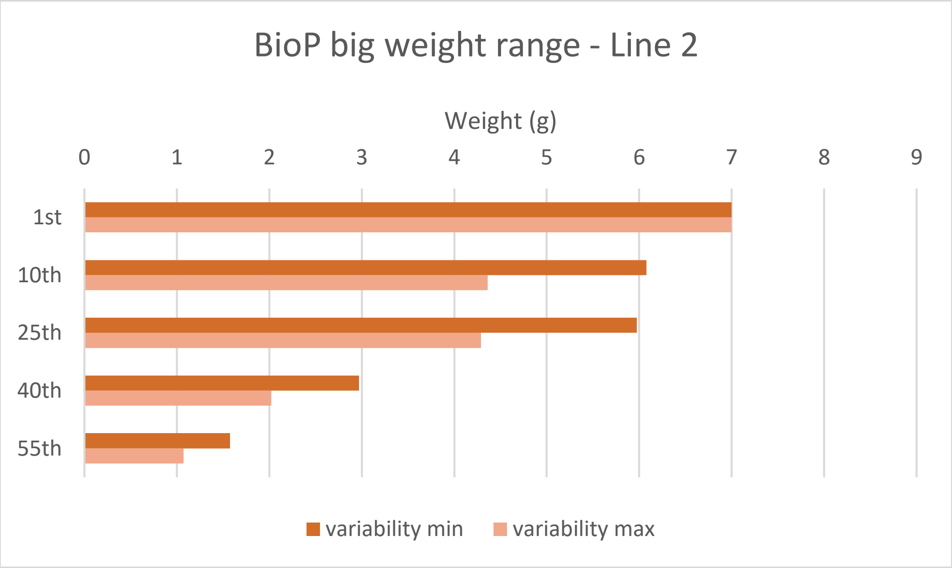

Figure III.4-Graph of weight range of big BioP - Line 2

IV. ANNEX: IR analyses

In the Annex IV the spectra of some samples of bioplastics taken during the composting process are reported, introduced with the panoramic photograph of the samples submitted to the analysis. It is referred to paragraph 4.3.3.

Bioplastics feature evolution during the composting process

Figure IV.1-Aspect of bioplastic pieces submitted to IR analysis

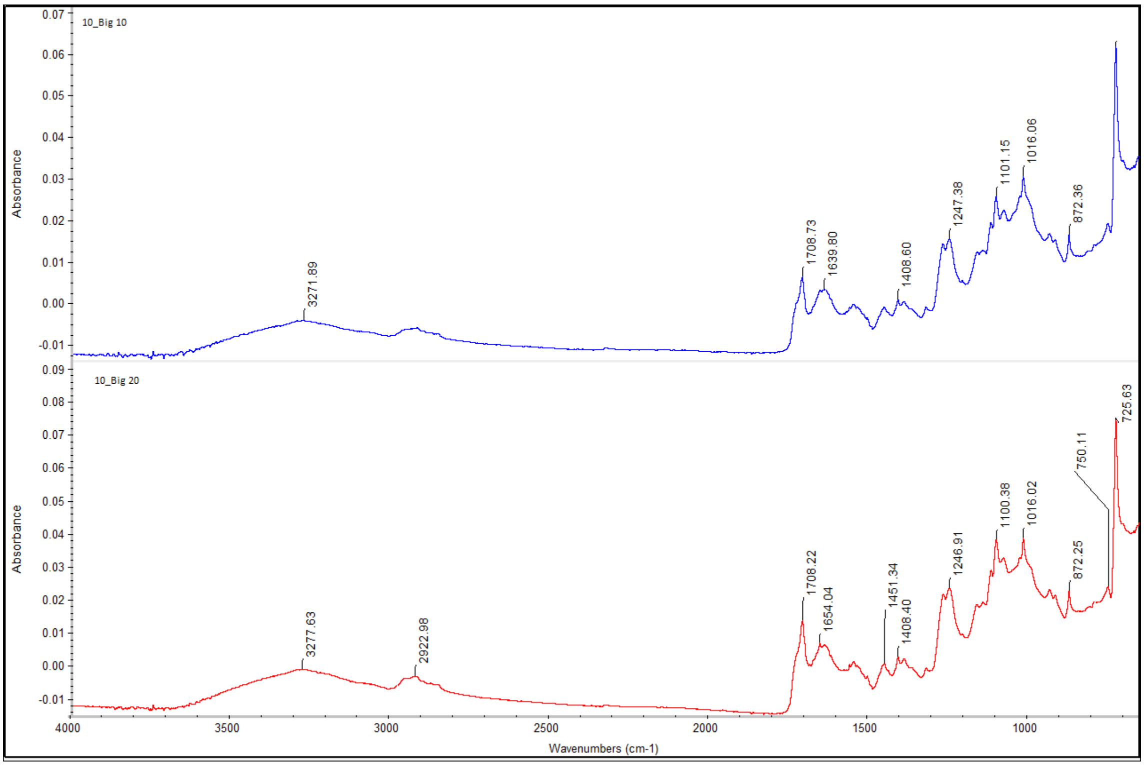

Figure IV.2-Spectra at the 10th day of the biggest granulometric fractions

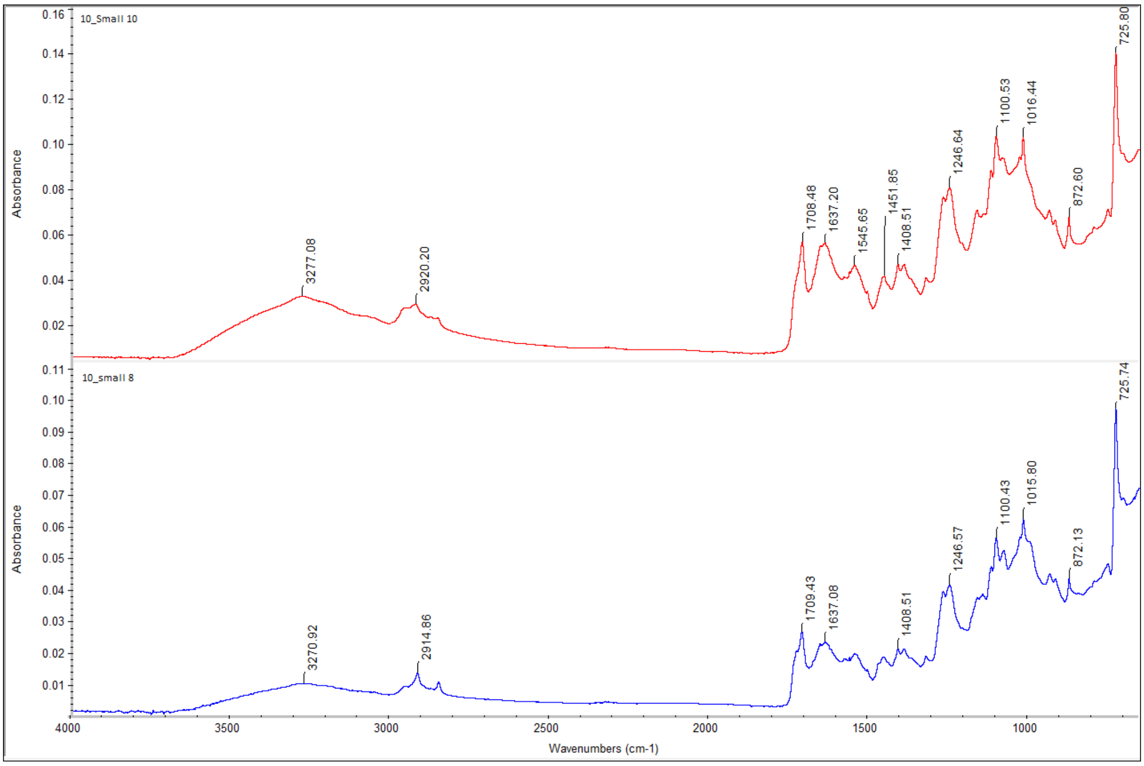

Figure IV.3-Spectra at the 10th day of the biggest granulometric fractions

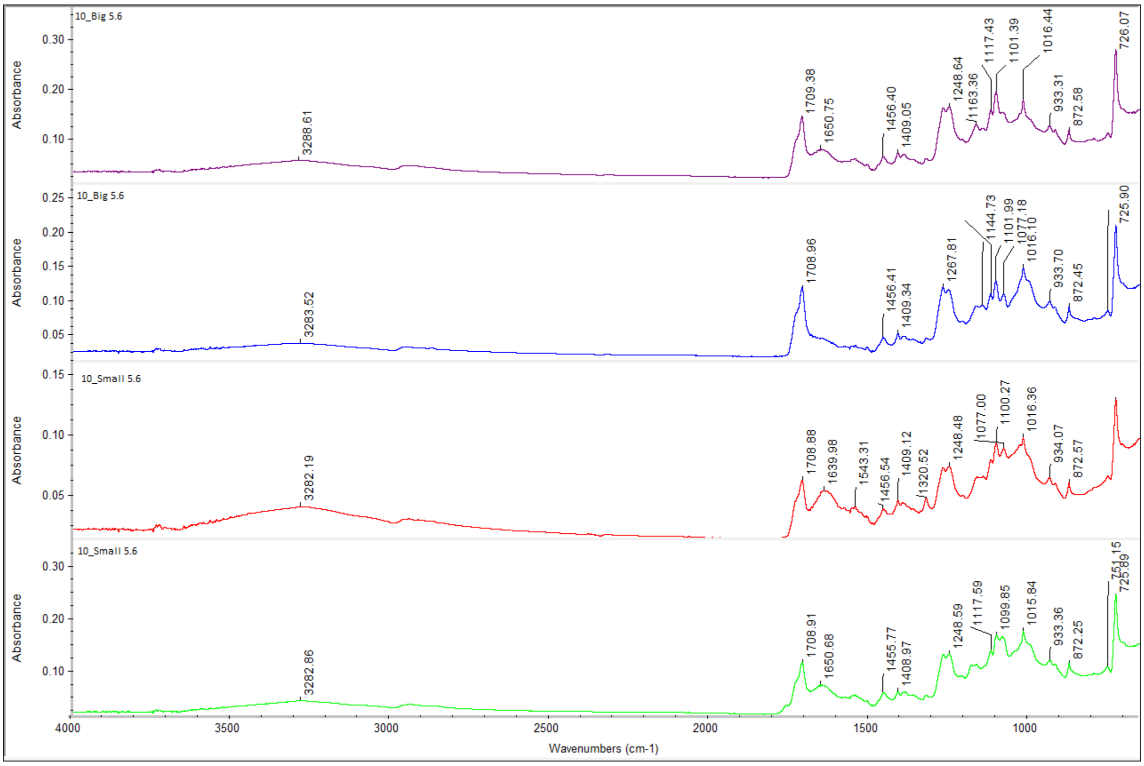

Figure IV.4-Spectra at the 10th day of the smallest granulometric fractions

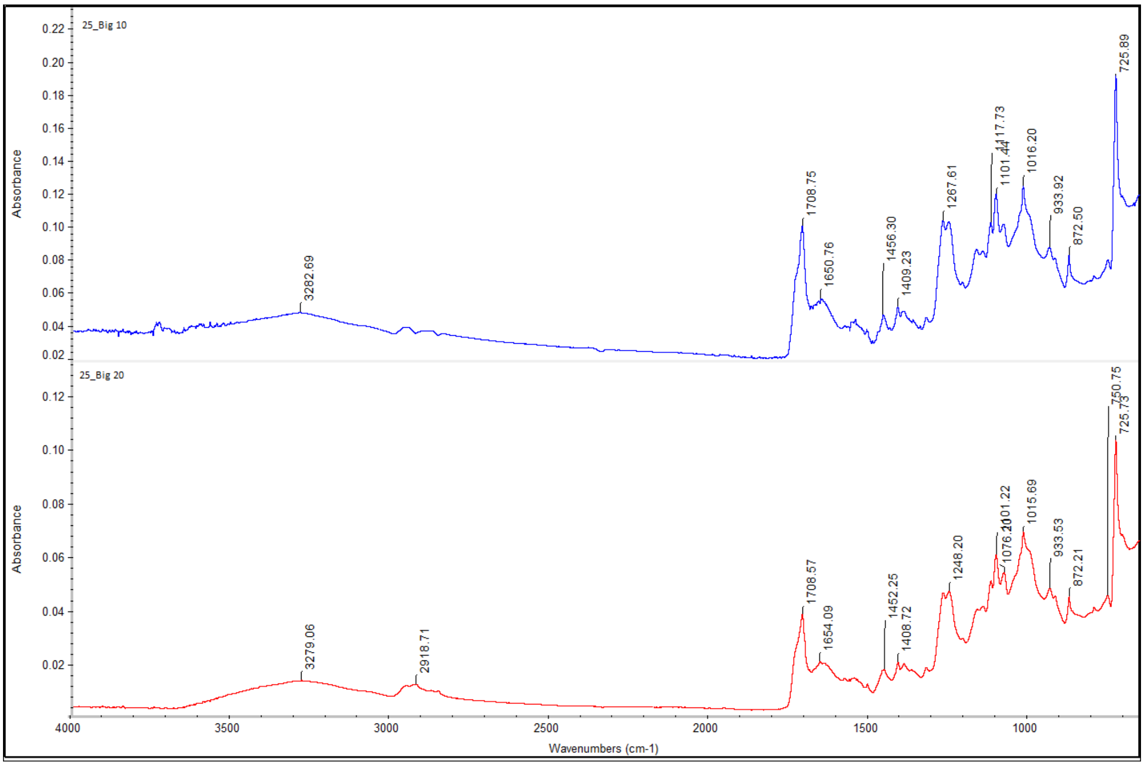

Figure IV.5-Spectra at the 25th day of the biggest granulometric fractions

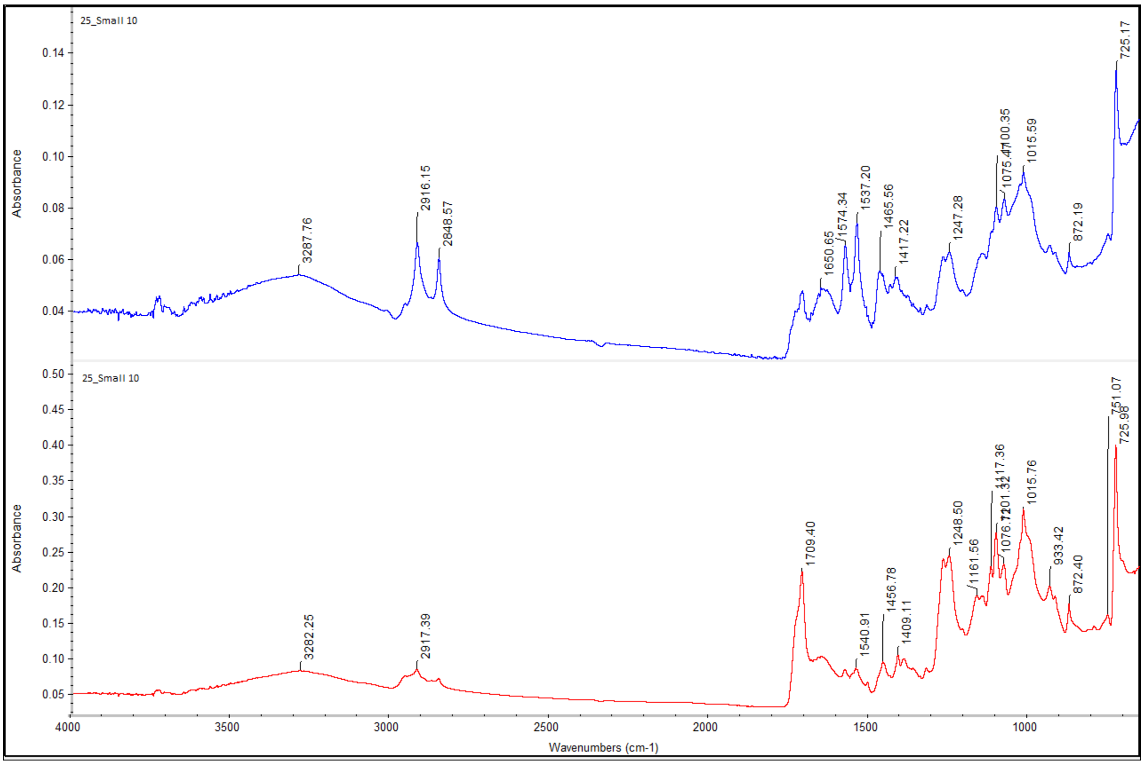

Figure IV.6-Spectra at the 25th day of the biggest granulometric fractions

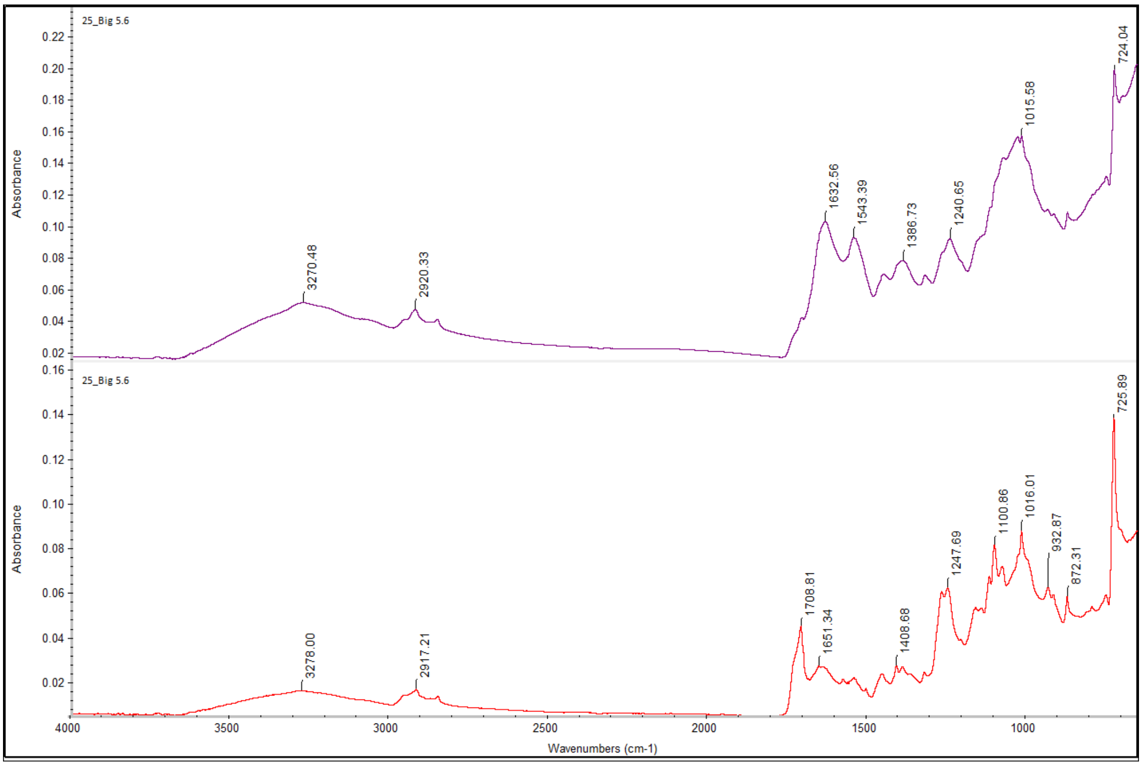

Figure IV.7-Spectra at the 25th day of the smallest granulometric fractions

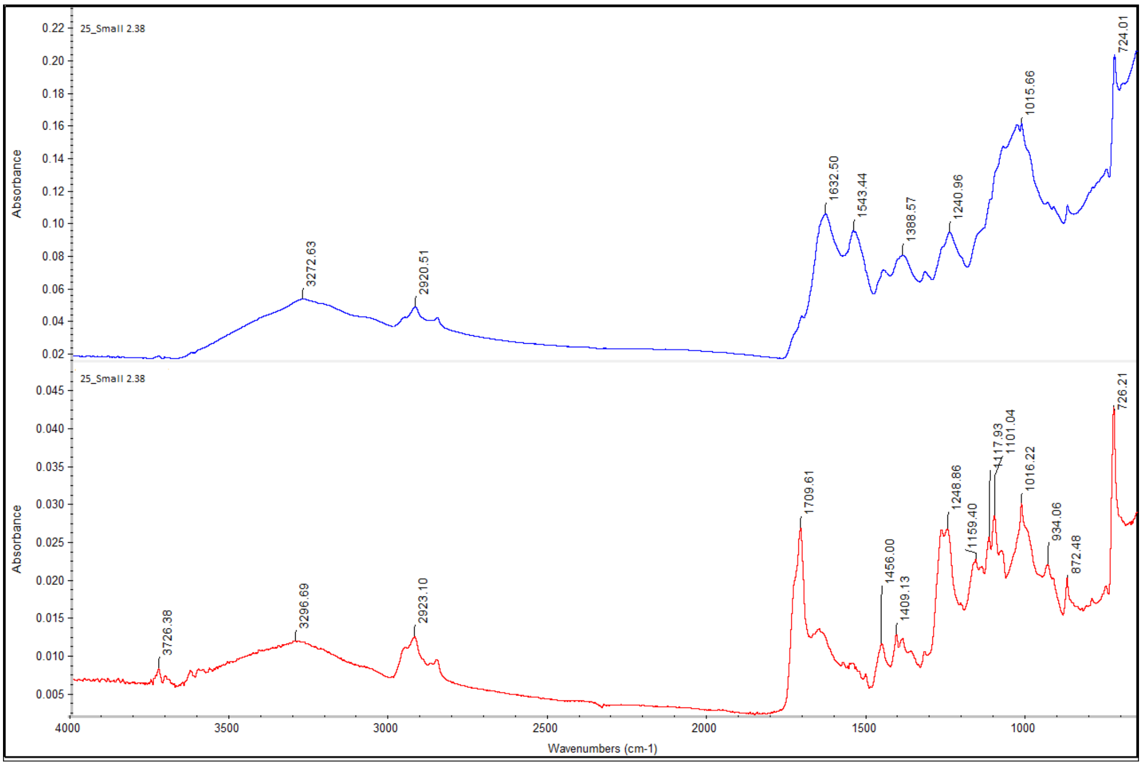

Figure IV.8-Spectra at the 25th day of the smallest granulometric fractions

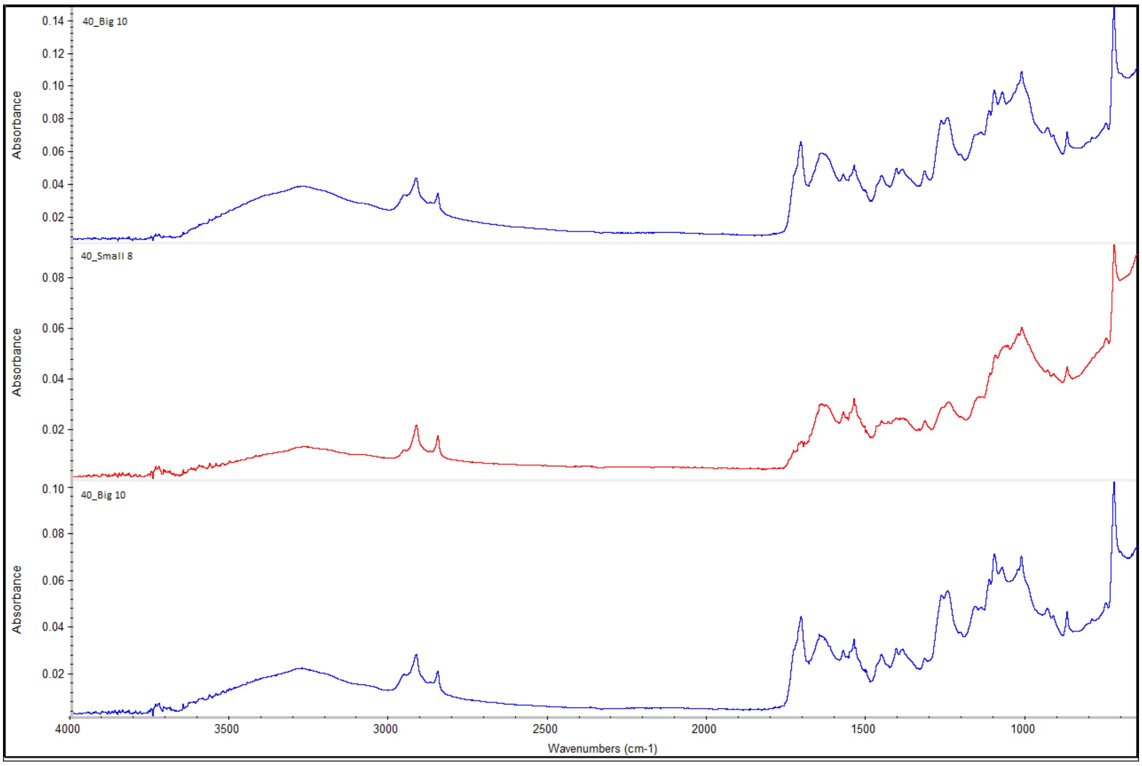

Figure IV.9-Spectra at the 40th day of the biggest granulometric fractions

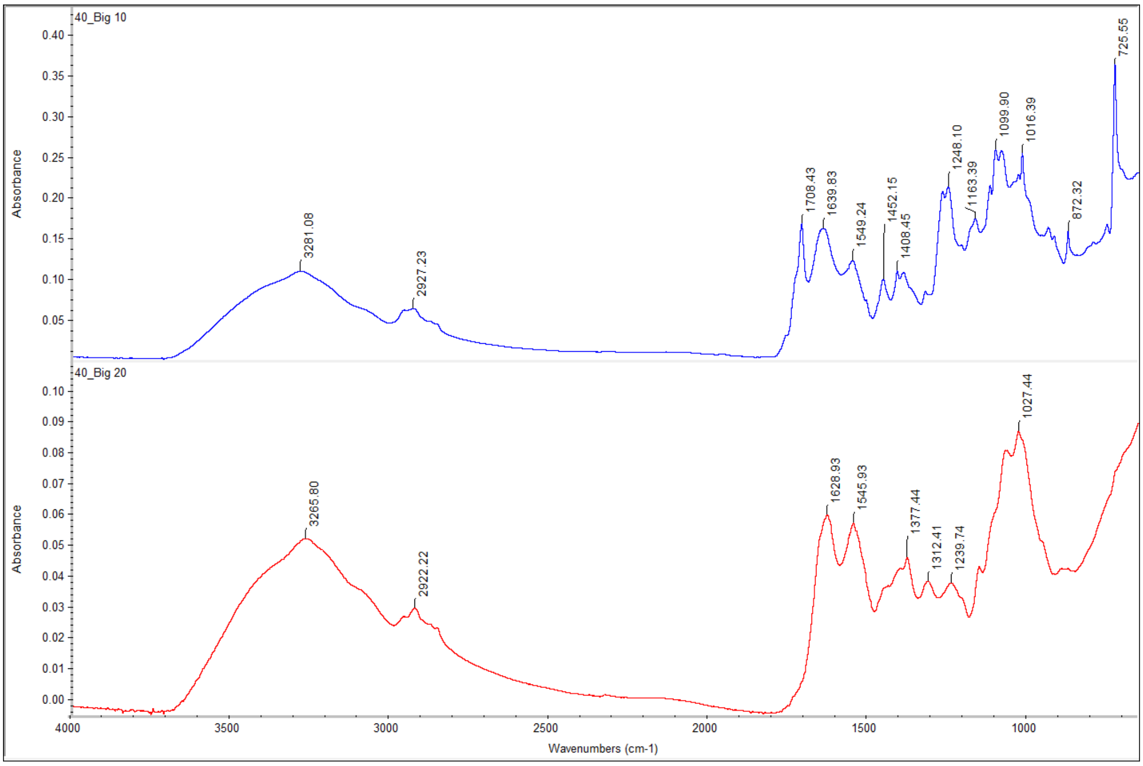

Figure IV.10-Spectra at the 40th day of the biggest granulometric fractions

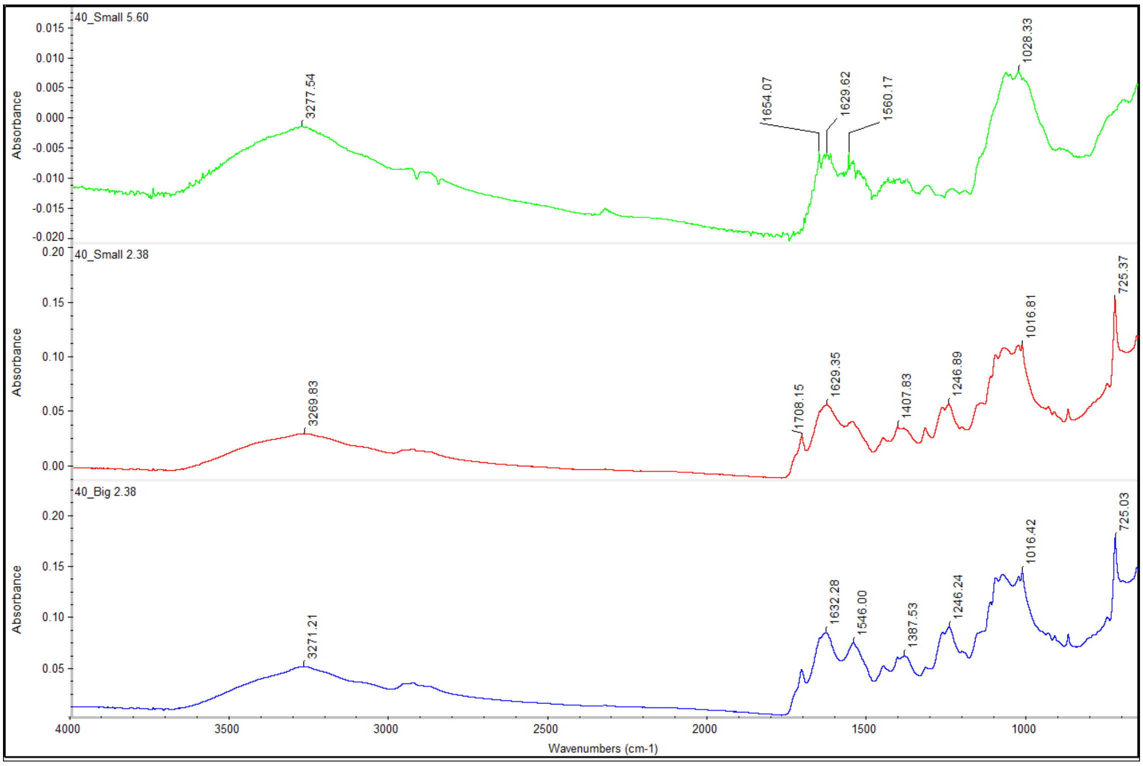

Figure IV.11-Spectra at the 40th day of the smallest granulometric fractions

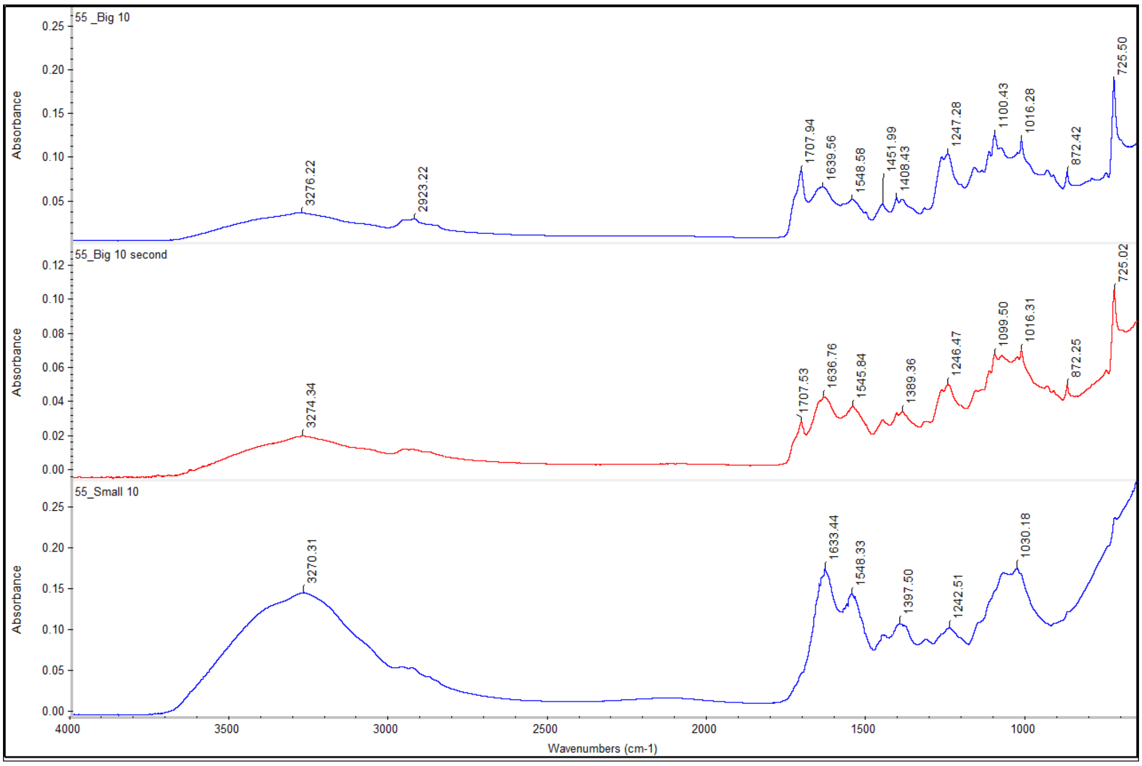

Figure IV.12-Spectra at the 55th day of the biggest granulometric fractions

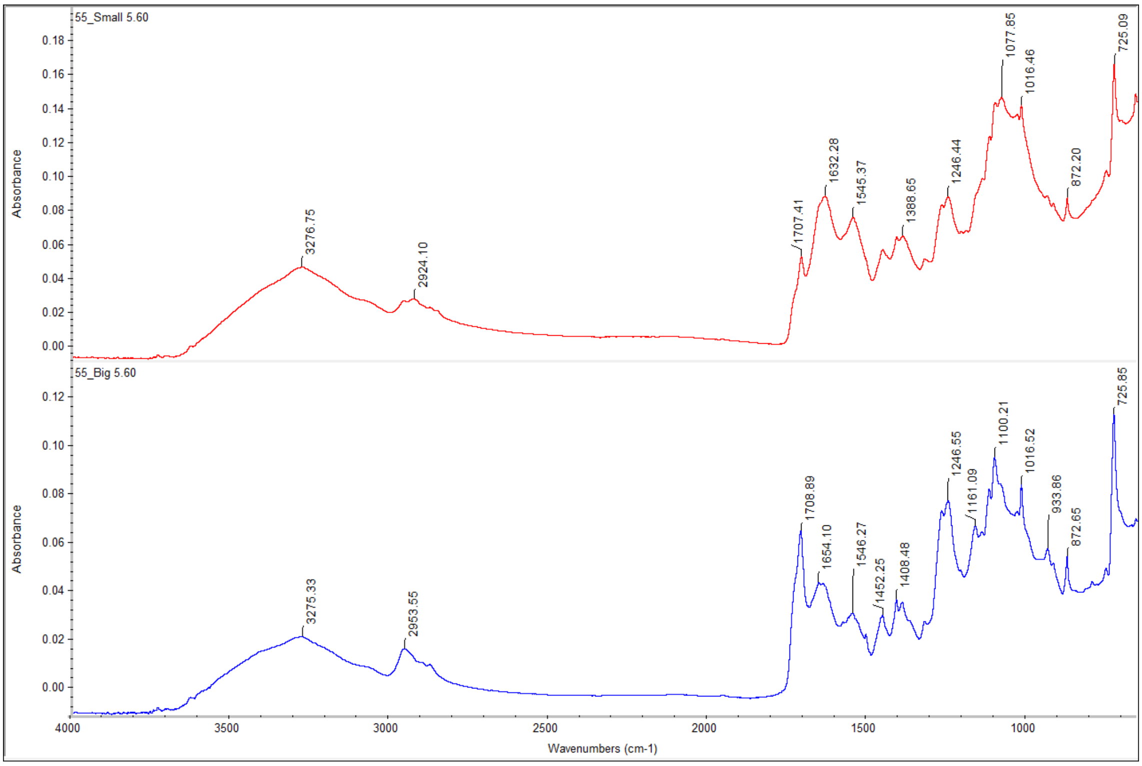

Figure IV.13-Spectra at the 55th day of the smallest granulometric fractions

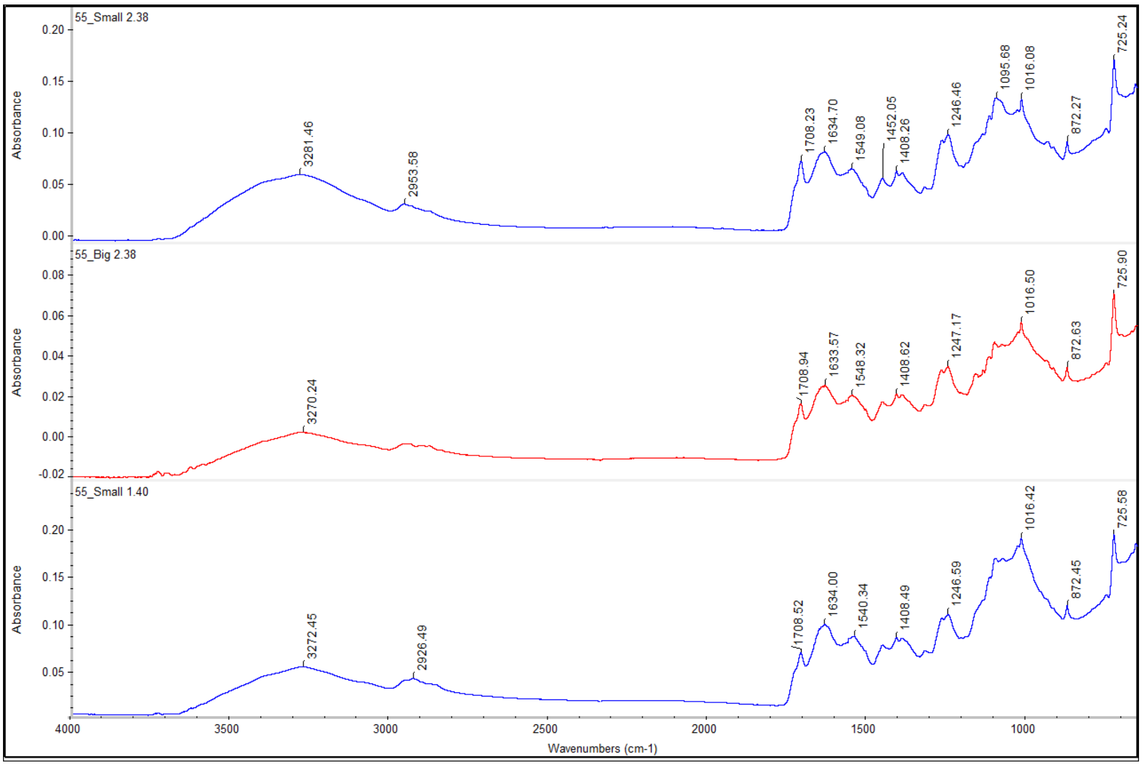

Figure IV.14-Spectra at the 55th day of the smallest granulometric fractions