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MASTER THESIS

by

Hilda, Seferi

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Evaluation of Raw Materials for the Sustainability Improvements of Single-use Plastic Shoppers

Research group: Polymer Group
Supervisor(s): Prof.Dr. Laura Mazzocchetti
Co-Supervisor(s):Dr. Tiziana Benelli, Dr. Giorgio Zattini, Vittorio Maceratesi

UNIVERSITÄT LEIPZIG

UNIVERSITY OF HELSINKI

JAGIELLONIAN UNIVERSITY IN KRAKOW

Characterization; Sustainability; Single-use shopper bags; biodegradable raw materials

ABSTRACT:

From an environmental point of view, the improvement on bio-based technologies to produce “Green-plastics” could contribute to improve the sustainability of single-use items. In this frame, the present work investigates raw materials for producing single-use plastic shopper so that they might increase their sustainability. Two approaches have been addressed: first the reuse of regenerated materials recovered from internal wastes from traditional oil based polymers, and, as an alternative, the use (and possibility or re-use) of biodegradable bio-based plastics. Hence different raw materials were analysed and their properties discussed.

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1. INTRODUCTION

1.1 Polymers

Polymer is a word derived from the Greek *poly* meaning many and *meros* which stands for parts. Polymers can be found in every basis of plants, animal life as proteins, nucleic acids and polysaccharides. The polymers are composed of many repeating units linked by covalent bonds. Polymer science was a broad field developed since 1930 when the first natural polymers were used[1,2]. In general, polymers are macromolecules composed from different repetition units and they can be differentiated according to their source, polymer chain type, way of polymerization, properties, polymerization method, monomer composition, functional group type and degradability [3,4].

At home, we found them in materials like rugs, curtains, coatings, waste paper ect. Outside our homes, they are present in our flowers, trees and soil [5].

Polymers can be divided in thermosets and thermoplastics. The ***thermoplastics*** can be melted and reshaped through the application of heat and pressure, while the ***thermosets*** decompose before they can be melted and reshaped.[5].

The most common polymers are polyolefin, polyester and polyamide due to their ease of manufacturing and their advantageous chemical and physical properties. Polyolefins are oil-based polymers and they are manufactured by an addition polymerization of the olefins such as ethylene or propylene. In general polymers are divided even according to the source like presented in Table 1[5].

Table 1. Common Polymers

Material/ Name	Typical Polymer
Styrofoam	Polystyrene
PVC pipe	Poly(vinyl chloride)
Nylon stockings	Polyamide, nylon 6,6
Concrete	Cement
Meat	Protein
Plexiglass	Poly(methyl methacrylate)
Automotive bumpers and side panels	Polyethylene and polyethylene/polypropylene blends
Potatoes	Starch
Compact disks (case)	Polycarbonate (polystyrene)
Hula hoop	Polypropylene, polyethylene
Diamond	Carbon
Silicon Sealants	Polydimethylsiloxane
Bakelite	Phenol – formaldehyde cross linked
Super glue	Poly (ethyl cyanoacrylate)
Cotton T-shirt	Cellulose
Fiberglass	Composite
Saran Wrap	PVC Copolymer
Velcro	Polyamide
Rubber band	Natural Rubber
Soda bottle	PET
Teflon	Polyetrafluoroethylene
Orlon sweater	Polyacrylonitrile
Sand	Silicon dioxide
Pillow stuffing	Polyurethane
Wood, Paper	Cellulose
Human genome	Nucleic acids

Polymers are grouped in three broad categories: thermoplastics and thermosets.

1.1.1 Thermoset Polymers

A thermoset polymer is a plastic that is irreversibly cured from a viscous liquid that it’s called pre-polymer. The thermoset polymers (macromolecular chains) are chemically joined together by cross-links, forming a rigid three-dimensional network structure (Figure 1b[6]).

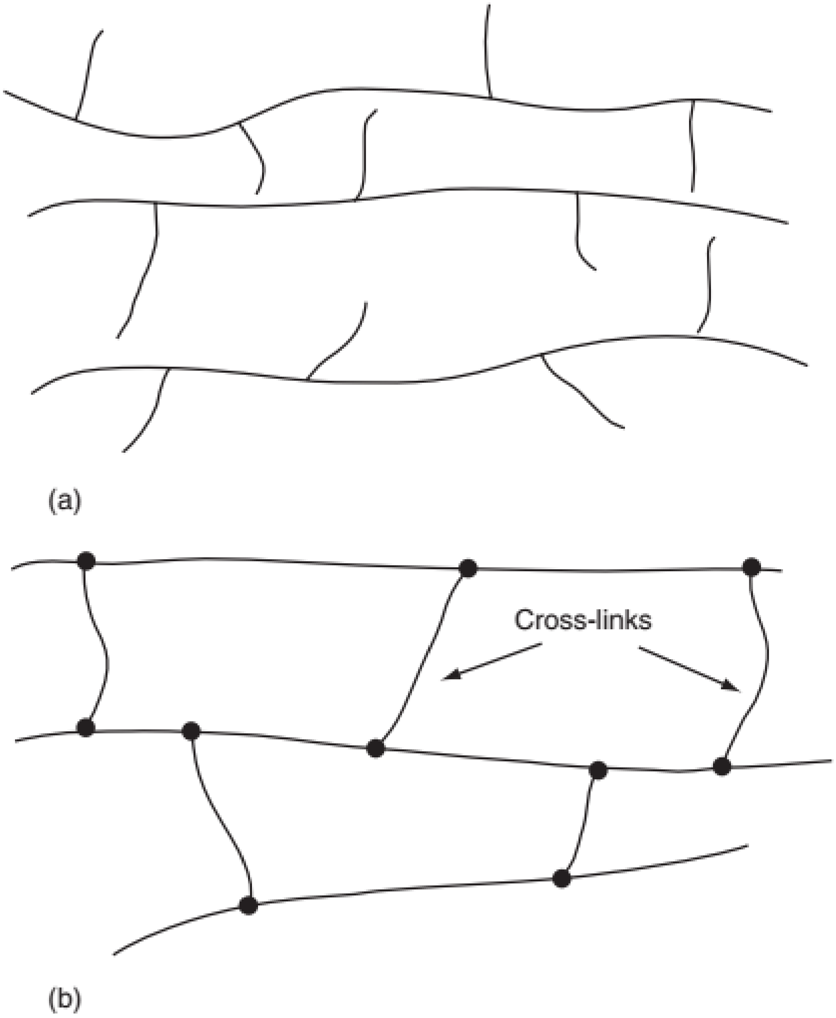


Figure 1. Schematic representation of (a) thermoplastic polymer and (b) thermoset polymer

When the material is in the uncured form, the polymer has monomers and oligomers, but during the curing reaction, cross-links are formed [7]. The addition of a second material for example monomers, oligomers or macromolecules makes them to react with themselves. During this reaction the molecules form long crosslinked macromolecular chains, causing the solidification of the material [6,7]. A particular use of thermoset polymer is as matrix in composites. One of the most used composites matrixes are the epoxy resins.

1.1.1.1 Epoxy matrix

Epoxy materials often used like starting materials are low-molecular-weight organic liquids with a number of epoxide groups like shown in Figure 2[7].

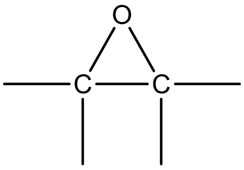
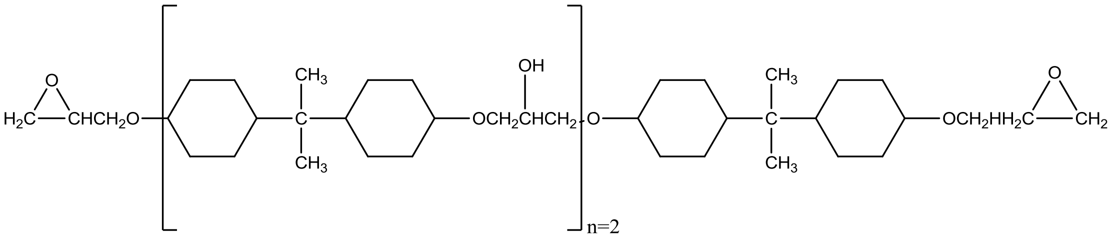
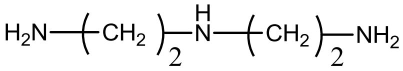


Figure 2. Epoxide group

A common starting material that is usually used is Diglycidil Ether bisphenol A (DGEBA), which contains two epoxy groups like presented in the Figure 3. In the DGEBA the reaction is between epichlorohydrin and Diglycidil Ether bisphenol A where the oligomers are formed first than is the curing process where the cross-links are formed [7].



(a)



$H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$

(b)

Figure 3. Principal components in the preparation of epoxy matrix. (a) Diglycidyl ether of bisphenol A (DGEBA) (b) Diethylene triamine (DETA) curing agent.

To form a three dimensional network structure, a curing polymerization reaction can be started by adding small amounts of a reactive curing agent such as diethylene triamine and the amine (NH_2) groups of a DETA molecule can react with the epoxide groups of DGEBA molecules like shown in Figure 4 (a, b) [7]. Of course, there are a lot of curing agents that exist, but the most used is diethylene triamine DETA.

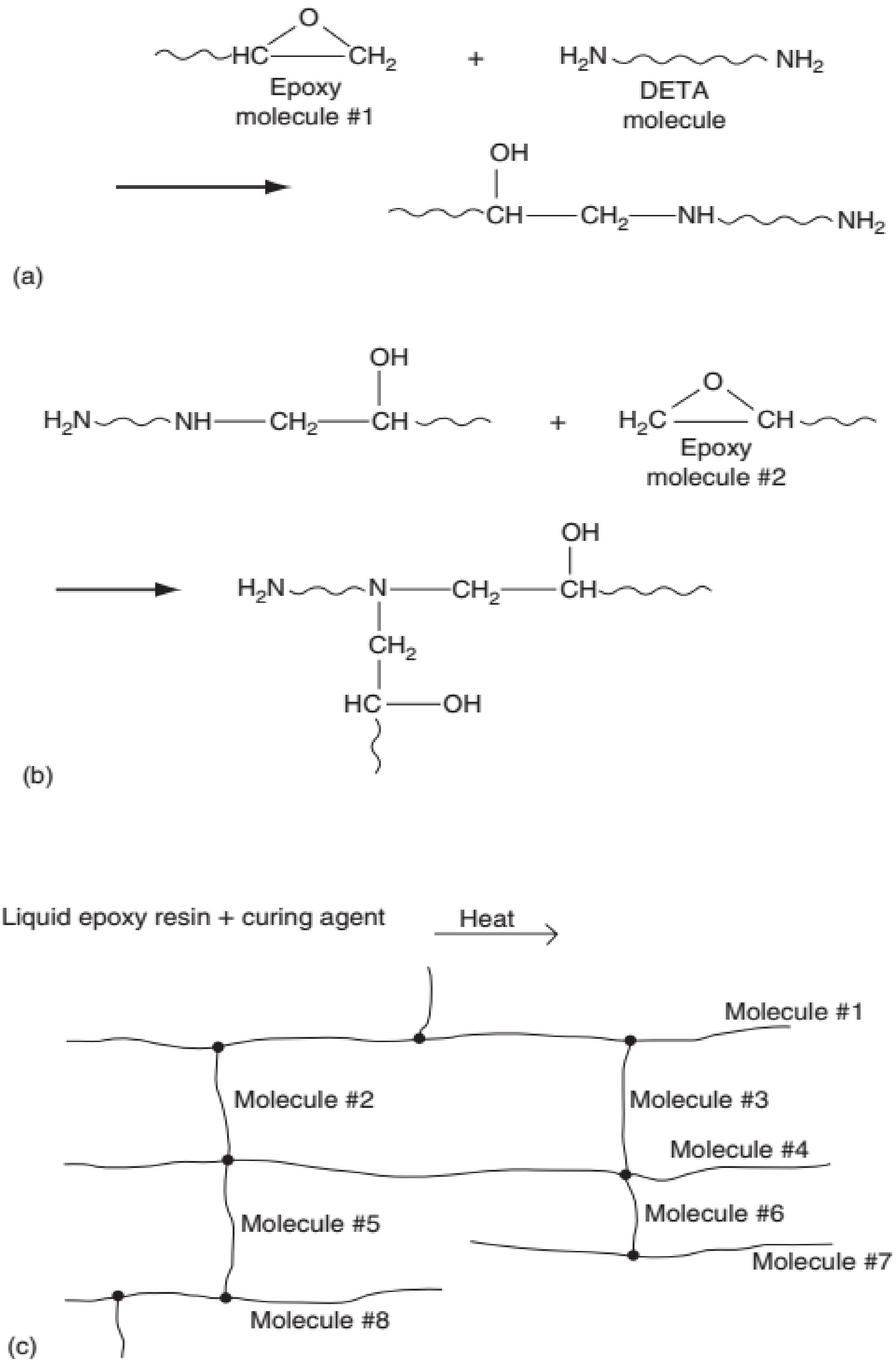


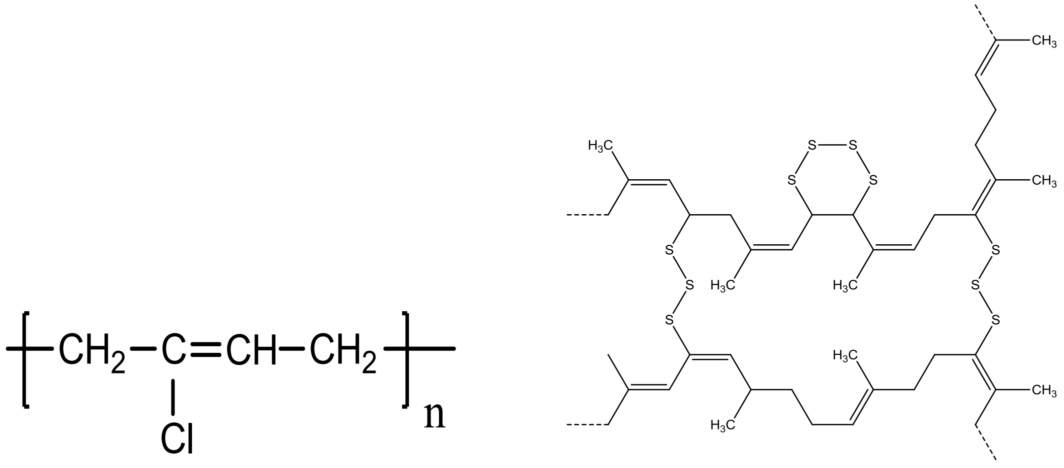
Figure 4 Schematic Representation of a cross-linked epoxy resin. (a) Reaction of epoxide group with DETA molecule; (b) formation of cross-links (c) three-dimensional network structure of solid epoxy [7]

DGEBA molecules will form cross-links to construct a solid 3D structure like in the Figure 4 (c) is shown.

Sometimes the curing reaction can be slowed down by lowering the temperature and the resin should exist in B-form, where the cross-links are widely spaced points in the reactive mass. The time and the temperature to complete the polymerization depend on the type of the curing agent. There are some curing agents that react and initiate the reactions at room temperatures, but in other cases elevated temperatures are required [7]. The finally properties of cured epoxy resin depend principally on the cross-link density (spacing between successive cross-link sites). In general, to control the cross link density is necessary to control the chemical structure of the starting liquid resin (for example the epoxide groups present and the spacing between them) and the functionally(number of active hydrogen atoms in DETA) of the curing agent and finally the reaction conditions like temperature and time [7] .

1.1.2 Elastomers

Elastomers are blend polymers like *cis*-polyisoprene (natural rubber, NR), *cis*-polybutadiene (butadiene rubber, BR), styrene-butadiene rubber (SBR), and ethylene-propylene monomer (EPM) and the crystallinity is followed by low crystal melting temperatures from 25 °C -5 °C . In addition the glass transition temperature of all these polymers are quite low, below room temperature, so all of these are soft, highly flexible and elastic [8]. In elastomeric polymers, the polymer chains are entangled together by intermolecular forces. According to these weak binding forces the polymers can be stretched. There are some “crosslinks” introduced between the chains, that help the polymer to return to the original position after the force is released. A good example are buna-S, buna-N, neoprene, etc. In Figure 5 the neoprene structure without vulcanization and the neoprene vulcanized structure[9] are shown. The vulcanization process, or differently called “curing process”, is one of the most important processes for the most of rubber technologies. The rubber compound changes form elastic to the final product that is the vulcanized rubber. The changes are due to parallel changes of chemical and physical structure. Part of vulcanization process are also physical bonds like hydrogen bond, polar and dispersed powers between individual macromolecules or their signals, which are created during the processing of the rubber. In order to make these cross-links between rubber macromolecules are often used vulcanization agents like sulfur, peroxides, metal oxides, resins, quinines and others. During the curing process different types of radiation can influence of which the energy is satisfactory to generate rubber reactive macromolecules in the form of radicals. Also microwave energy or ultrasound can cause curing creation. The vulcanization process is required for the most of the rubbers, but is not necessary for some types of thermoplastic rubbers [10].



$$\left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2- \right]_n$$

Figure 5. Neoprene Structure and the Sulfur vulcanized rubber Structure

1.1.3 Thermoplastic Polymers

A thermoplastic polymer is a plastic material where the molecules are not chemically entangled together (Figure 6) .

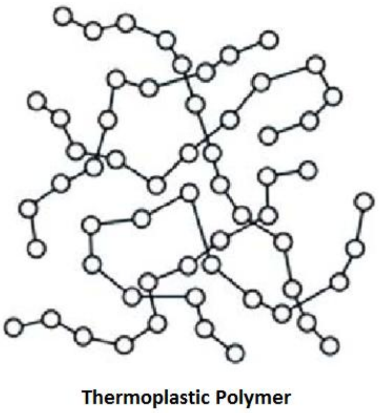


Figure 6. Arrangement of molecules in a thermoplastic polymer

The thermoplastics chains are connected together via secondary intermolecular forces, such as Van der Waals bonds and hydrogen bonds. With the application of heat, the secondary bonds can be temporarily broken and the molecules can flow to a new configuration if the pressure is applied on them. During the process of heating, the secondary bonds in the solid thermoplastic polymer can be temporarily broken and the chains can move relative to each other or flow to a new configuration if pressure is applied on them. During the cooling process, the chains can be frozen in their new configuration and the secondary bonds are restored, resulting in a new solid shape. This process can occur as many time is desired [7]. A thermoplastic material, can be compared with a set of strings that are entangled together and represent a polymer with a greater degree of entanglement like in Figure 7 [11,12] is shown.

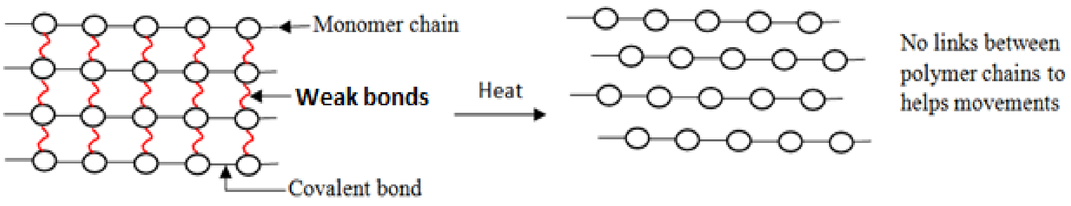


Figure 7. Thermoplastic Material

Depending on the degree of the intermolecular interactions that occur between the polymer chains, the polymer takes two different types of structures, amorphous and crystalline. In thermoplastic are semicrystalline materials with the existence of both structures (figure 8) [12].

- **Amorphous structure** -> The chains usually across each other when the polymer is pushed and pulled by external forces.
- **Crystal Structure** -> Generally this kind of structure is very ordered, which gives to the molecule strength and mobility.

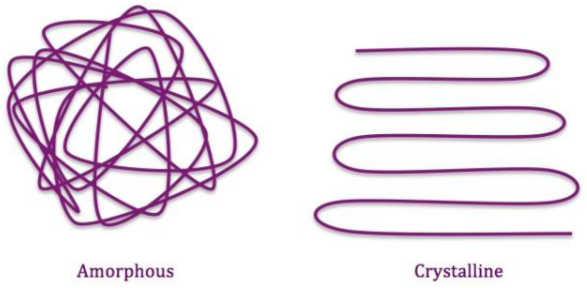
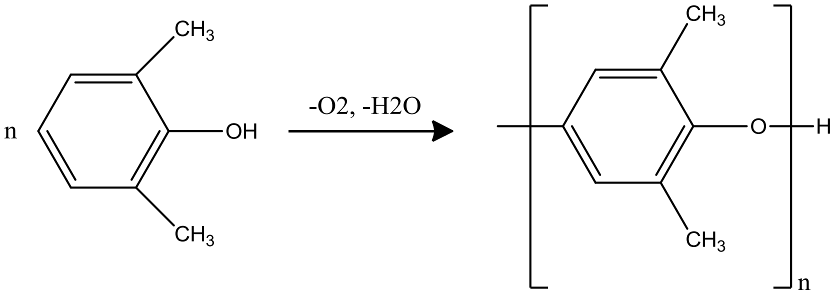


Figure 8. Representation of Amorphous and Crystalline Structure [12]

The thermoplastics, in other term s are melt-processable plastics (materials that are processed with heat). Many thermoplastic polymers are addition-type, capable of yielding very long molecular chain lengths (very high molecular weights)[12]. There are a lot of examples that are obtained by polyoxydation reactions such 2,6-Xylenol that is a starting material for polyphenylene oxide, that at high temperatures has a thermoplastic behavior with high heat resistance and chemical resistance [13]. The reaction takes place in the presence of copper catalyst by air oxydation like following :



When a thermoplastic material has a high concentration of polymers with amorphous structures, the material will have a poor resistance but a good elasticity. [12,13]

In 1988, it was established a classification system (Recycling code) developed by the "Society of Plastics Industry" to allow all the consumers to identify and classify different types of plastics. In order to do so, it was established a number in each plastic product, usually placed into the bottom like shown below in the table 2:

Table 2. Plastic recycling codes [14]

Plastic Type	General Properties	Common Household Uses
1 PETE **PETE or PET Polyethylene Terephthalate**	-Good gas and moisture barrier -High heat resistance -Clearness -Hardness -Toughness -Microwave transparency -Solvent Resistance	-Mineral Water, fizzy drink and beer bottles. -Pre-prepared food trays and roasting bags. -Soft drink & Water bottles -Some shampoo & Mouthwash bottles.
2 HDPE **High Density**	-Excellent moisture barrier properties - semi-flexibility -Soft waxy surface	- Detergent bottles - Snack food boxes - Milk drink bottles - Plastic wood, garden

Polyethylene		furniture. - Compost Containers
3 V **PVC or V Polyvinyl Chloride**	-Excellent transparency -Hardness, rigidity (flexible when plasticized) -Good Chemical resistance -Stable electrical properties -Low gas permeability	-Credit Cards -Carpet, floor covering -Window and door frames -Synthetic leather products
4 LDPE **Low Density Polyethylene**	-Toughness and flexibility -Waxy surface -Good Transparency -Low melting point -Stable electrical properties	-Films, bags, refuse sacks -Packaging films -Flexible bottles -Irrigation pipes -Some bottle tops
5 PP **Polypropylene**	-Excellent chemical resistance -High melting point -Hard, but flexible -Waxy surface -Translucent -Strong	-Most bottle tops -Ketchup & Syrup bottles -Yoghurt & Some margarine containers. -Potato crisp bags, biscuit wrappers. -Refrigerated containers.
6 PS **Polystyrene**	-Clear to opaque -Glassy Surface -Hard -Brittle -High Clarity	-Yoghurt containers, egg boxes. -Video cases -Seed trays -Low cost brittle toys
7 **Other**	There are other polymers that have wide range of use, particularly in engineering sectors.	-Nylon (PA) -Acrylonitrile butadiene styrene (ABS) -Polycarbonate (PC) -Layered or multi-material mixed polymers.

1.2 Properties of Plastics

1.2.1 Phase Transitions

The thermal properties in general include glass transition temperature (T_g), melting temperature (T_m) and flow temperature [15].

1.2.1.1Glass Transition Temperature (T_g)

Polymers can be synthetized in a various range of properties, like flexibility or rigidity, in a crystalline or amorphous nature etc. A polymeric structure during the heating process may transform itself from a state of softness to a state of hardness or brittleness. So, there is a temperature below which a polymer is hard and above this temperature, it becomes so soft that it transforms from a glassy (brittle) state to a rubbery (elastic) or a visco-elastic state. This temperature is mentioned as *glass transition temperature* (T_g). If is possible heating the polymer beyond the T_g value, it can start melting, acquiring the flow properties. The Brown's mobility of the molecules below the glass temperature (T_g) is strongly curbed by intermolecular interactions. In this moment there are no position-change of the chains [15]. At the glass temperature Brown's mobility of chain segments occur and the plastic becomes softer, but of course is still mechanical stable.

1.2.1.2 Crystalline Melting Temperature (T_m)

By reaching the crystallite melting temperature (T_m), that is responsible for crystalline forming, the crystallites start to melt and becomes liquid.. As long as we are not in the thermal degradation process, the plastic will go back reversibly in the solidified form by cooling and depending on the speed of cooling and the duration of cooling the crystallite phases will again be generated, but the size and the distribution of the crystals will be different from the original [15].

1.2.2 Specific Volume

In the thermoplastics because of an intense thermal oscillations of atoms and molecules, the plastic volume expands.

Within the glass state of amorphous thermoplastics the specific volume shows a linear increase with increasing temperature (Figure 9), described by the equation 1 [15].

$$V(T) = V0\,(1+ \beta\Delta T) \quad \text{eq.1}$$

V0 : Volume at start heating

B : Cubic expansion coefficient

ΔT: Increase of temperature

On exceeding the glass-transition temperature, the linear response rises depending on the distribution of the molecular weight. This means that with the increasing of temperature the increase of the specific volume will be intensified, caused by the decreasing strength of molecular bonds in the molten state. A graphical portrait of the temperature dependence with the specific volume for some thermoplastic materials in Figure 10 is represented.

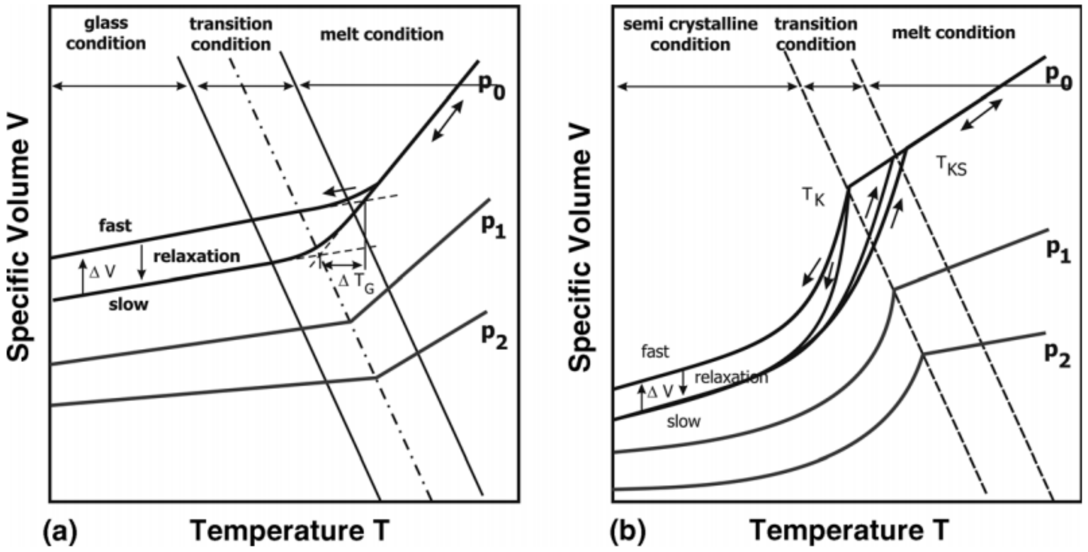


Figure 9. Schematic behavior of specific volume in dependence from the temperature for amorphous (a) and semi-crystalline (b) thermoplastics [15]

1.3 Applications of thermoplastic polymers

Thermoplastic polymers have some advantages and disadvantages (Table 3).

Table 3. Advantages and disadvantages of thermoplastic polymers

	Thermoplastics : Advantages/ Disadvantages
Advantages	The softening or melting by heating allows welding and thermoforming
	The processing cycles are very short because of the absence of the chemical reaction of crosslinking
	Processing is easier to monitor, because there is only a physical transformation
	Thermoplastics don't release gases or water vapours if they are correctly dried before processing
	The wastes are partially reusable as virgin matter because of the reversibility of the physical softening or melting
Disadvantages	When the temperature rises, the modulus retention decreases, due to the absence of chemical links between macromolecules
	For the same reason, the creep and relaxation behaviours are not as good as for thermosets
	During a fire, fusibility favours dripping ans annihilates final residual physical cohesion

The Polyamides that are kind of thermoplastics that have huge applications in the automobile industry such as radiator fan, radiator grill, instrument housings, speedometer gears, fuels, oil filter housing, electrical junction box, head/tail lamp housing, front fork bush, steering column bush [16].

The PA/ABS blends (Acetonitrile Butadiene Styrene and Polyamide-based thermoplastic polymer), have a strong impact, abrasion resistance, chemical and heat resistance, low moisture absorption, good processability and surface finish. They are applicable in automotive, chemical, electrical, consumer and sport industries.

The PA/ELASTOMER (EPDM/EPR) blends have a low temperature impact strength and good processability. They are applicable for home appliances, business equipments and consumer products.

The PA/PP blends show good processability, reduced water absorption, low density and paintability improvement. In general, are applicable for automotive, building, furniture and industrial materials [16].

The Polyacetals, called differently as polyoxymethylene (POM), are resins with linear chains derived from the formaldehyde monomer. The structure of the homopolymer and the copolymer in the Figure 10 are shown.

In general, there are some monomers used in copolymerization process as reactive species like Styrene, α-Diphenylethylene, Styrene, Methyl acrylate, indene, stilbene, allyl acetate, vinyl acetate ect [16,17].

$$-CH_2-O-CH_2-O-CH_2-CH_2-$$

Polyacetal homopolymer

$$-CH_2-O-CH_2-CH_2-O-CH_2-$$

Polyacetal Copolymer

Figure 10. The structure of Polyacetal homopolymer and polyacetal copolymer[17]

The Polyacetals have a lot of applications in various industries such as: gears, bearing boxes and bushes, switch relays, terminal blocks, coil formers, blower fans, ventilation fans, pump parts, springs, snap fittings, screw, nuclear engineering applications, clock and watch parts, ect (Figure 11) [16,17].

Figure 11. Screw and coils made from polyacetals[17]

The Polycarbonates represent a linear polyester of carbonic acid in which some of dihydric phenols are lined together through carbonate groups like represented in the Figure 12 [17]. Polycarbonates have a lot of industrial applications due to their optical clarity. To produce polycarbonates industrially the most common method is the phosgenation of bisphenol A and even melt phase polymerization is generating significant interest as solvent free and phosgene-free alternative for polycarbonate synthesis [18] .

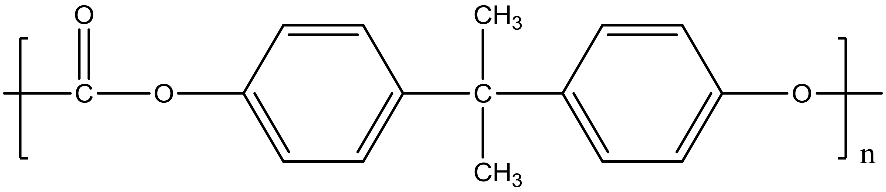


Figure 12. The structure of polycarbonate

The full chemical name of PPO is poly [1,4 – (2, 6-dimethyl phenyl) ether] and the structure is presented in the Figure 13. PPO is widely used as a thermoplastic molding material, especially when is blended with high impact polystyrene. When the PPO or its blends are exposed in the light, they undergo in a photoyellowing and photodegradation processes, occurring mainly in a thin surface layer [19] .

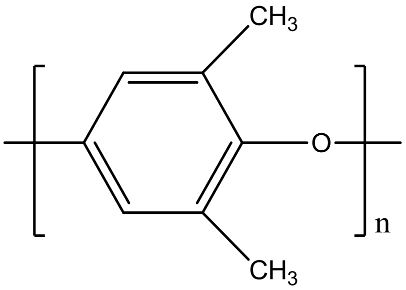


Figure 13**.** The structure of [1,4 – (2, 6-dimethyl phenyl) ether]

They have a lot of applications for fendeers, dash- boards, head lamp systems, instrument and control panels, mud-guards, fuse blocks ect [16].

1.3.1 Packaging

Packaging is an important process that has important functions like: protection from pressure, dropping, shock and vibration, puncture, water or chemical damage. In the specific cases of pharmaceutical products and food it’s necessary the protection from microbial contamination, insect light.

Within the supply chain do exist three different types of packaging: [11]

1. Primary Packaging -> Represent the packaging directly handled by the end user

2. Secondary Packaging -> This kind of packaging, groups individual units together for transportation, display or for multipacks sold to the end user .
3. Tertiary Packaging -> Are pellets, trays, cartons and wrap that are used to assemble together the secondary packs for the ease of transport and handling.

In general, the basic packaging supply chain is illustrated in the Figure 14.

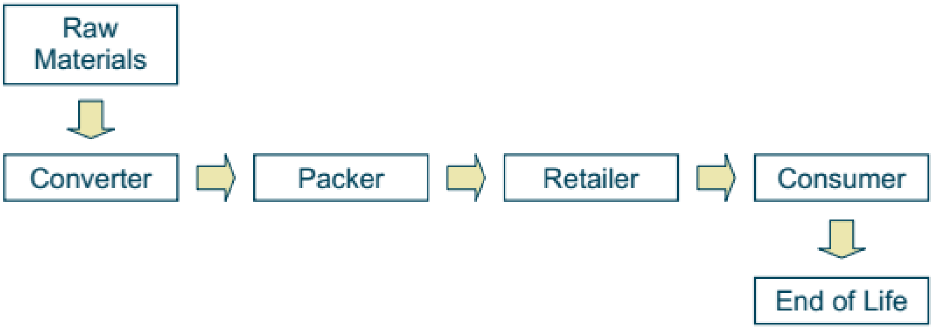


Figure 14. Basic Packaging supply-chain

Depending on the application, maybe there will be integration between different functions in the chain or further sub – division. From the basic roles, (Fig. 14) are[11]:

1. **Raw material supplier** -> This provides the polymers to be converted into packaging. Polymers can be provided in variety forms, from simple pellets to complex laminated films.
2. **Converter** -> The converter is able to produce materials ready-to-use by packer. In this step are produced wide range of products, from single and multi-layer films to blow molded bottles, injection molded containers, closures and thermoformed tubs, pots and trays.
3. **Packer** -> The packer assembles the final product. The packer may be manufacturer of the product or a separate contract packer.
4. **Retailer** -> The retailer displays, sells and increasingly delivers the product to the consumer.
5. **Consumer** -> This step is the end of the product. For the majority of packaging this will be an individual purchasing goods from a retail outlet.
6. **End of life disposal** -> End of life is handled by a complex of commercial organizations and local government bodies providing for reuse, recycling, composting and landfill as appropriate.

1.3.1.1 Polymer Used in Paper Packaging (Food Packaging)

Biopolymers find a huge application in food packaging process and they can be used for wrapping food products. According to Khwaldia et al. (2010), the biopolymers used for paper wrapping provides a lot of functional characteristics and the most important are environment-friendly characteristics. There are lots of biomaterial substances applied as coating biomaterials like: whey protein isolate, soy protein, wheat gluten, corn zein, chitosan, starch and alginate. The use of biopolymeric paper has a lot of advantages and improved the packaging performances in the way of reducing moisture permeability, resisting oil oxidation when the paper is based on whey protein. Further, is necessary that all the biopolymers used for food packaging fulfill all the requirements that are part of the conventional packaging materials:

- Properties of permeability (permeability to water vapor and gases, aroma substances and light)
- Mechanical and optical properties (e.g., transparency)

In Figure 15 is represented some examples of paper bags and cups commercially used.

Figure 15. PLA, PHAs, Cellulose, Chitosan-Lined Paper Bags and Cups

Tetra Pak has launched first plant-based, renewable packaging materials made from 100% bio-low-density-polyethylene (LDPE) and 100% bio-high-density polyethylene (HDPE). All these products were obtained from sugar and laminated certified paperboard by Forest Stewardship Council (FSC™) and this kind of packaging started to be commercially available in 2015 [11].

The table 4 presents an overview of all the biopolymers used in the production of packaging materials.

Table 4 . Properties of biopolymers used in paper coating (Khaoula et al. 2010)

Types of Commercial biopolymers	Main functions/properties	Reference
WPI	Suitable for printing with water- based ink Fat and oil barrier/ resistant	Han and Krochta (1999) Han and Krochta (2001) Chan and Krochta (2001)
NaCAS	Oxygen barrier	Khwaldia (2004)
NaCAS/paraffin wax bilayer	Water vapor barrier	Khwaldia (2010)
Corn zein	Grease barrier Prevention of drying/brittleness	Trezza and Vergano (1994)
Corn zein/paraffin wax bilayer	Water vapor barrier, Grease barrier	Parris et al. (1998)
SPI	Gas and lipid barrier	Park et al. (2000)
SPI with $CaCl_2$ post-treatment	Water vapor barrier	Rhim et al. (2006)
WG	Oxygen barrier	Gallstedt et al. (2005)
Carrageenan	Greasse barrier	Rhim et al. (1998)
HPMC/beeswax	Water vapor barrier	Sothornvit (2009)
Chitosan	Fat barrier Gas barrier	Ham-Pichavant et al. (2005) Kjellgren et al. (2006)
Chitosan / Sodium Alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Chitosan/ carnauba wax bilayer	Gas barrier	Despond et al. (2005)
Chitosan / Sodium alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Paraffin wax	Water vapor barrier	Parris et al. (1998)

The most used polymers for food products packaging are PHAs because their structures can include different kinds of thermoplastic, elastomer, waxes, adhesives, different binders and others because they are most commonly shaped via film extrusion, injection, hollow bodies, ect. The first two commercial PHA products were extrusion coating and cast films and other successive applications are in mulch films, stretch films, different kinds of bag and surfactant soluble packaging .The basic requirement to be used like food packaging material, is that they should not be in direct contact with food because PHAs are natural materials which those life cycle is completely renewable, produced and completely decomposed by microorganisms (Doi et al. 1994; Bugnicourt et al.2014). Some type of PHAs used for food products are shown in the Figure 16 and 17.

Figure 16. Different kinds of PHA bags used in food packaging

Figure 17. PHA thermoformed cups

1.4 Processing Polymeric Techniques

In general, there are some techniques to process the polymers. It is possible to divide the processes in [20] :

1. Standard Processes
    - Compounding
    - Extrusion
    - Injection molding
2. Special Technology
    - IMC (Injection molding compounding)
3. Foam Processing
    - Particle foams / Batch – foaming
    - Foam extrusion
    - Foam injection molding

1.4.1 Extrusion

Extrusion is a continuous process of conversion that transforms the granules (pellets) or even the powder of biodegradable polymers into sheets, profiles, bottles, tubes ect. The term “extrusion” refers to compounding process. The single-screw extrusion is the most important conversion process for biodegradable plastics. The most important element of extrusion is the extruder itself (Figure 18). The thermoplastic materials are introduced into the automatic dosing equipment. The shearing and the mixing of elements is necessary for having a good temperature distribution in the screw channel. The vacuum room is installed to reduce the residual moisture content in the melt. There are some types of polymer designed to run on extruders like: Ecoflex®, PVC, PET, but there are some limitation on using biodegradable polymers like:

- high sensitivity to the moisture, and need to be processed in a predryed form, which extracts volatile components [21].

- high shear forces should be avoided when processing biodegradable polymers such as starch compounds because of their sensitiveness to the thermal degradation [22].

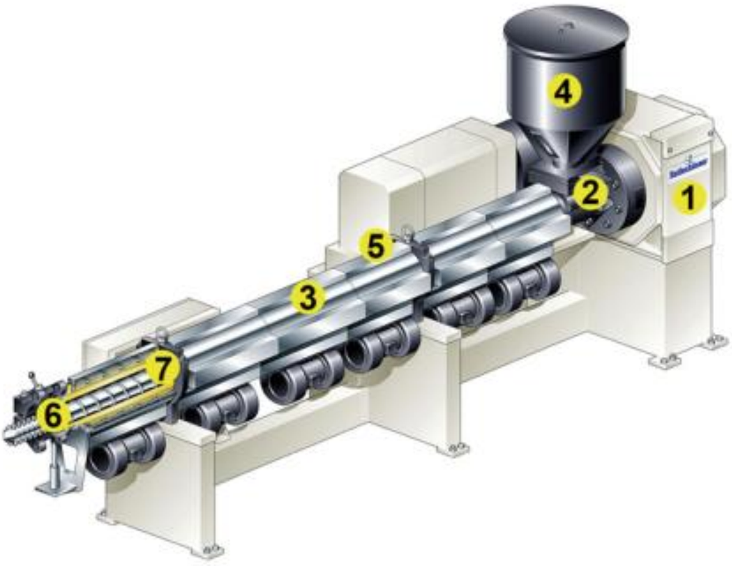


Figure 18. Extruder and Extrussion. 1 Drive unit, 2 barrel inlet, 3 temperature control, 4 feed hopper and dosing unit, 5 vacuum vent, 6 barrel, 7 screw

1.4.1.1 Compounding Extrusion Injection Molding

The compounding Extrusion process is a high volume manufacturing process used to produce items such as pipe/tubing. The equipments are designed to process all polymeric materials and additives in the range of several grams to several kilograms, and the temperature goes up to 400 ℃. To produce innovative polymer compounds, the co-extrusion equipment is combined with compression molding that make possible to produce co-products with classical processing techniques. The processing technique is shown in the Figure 19.

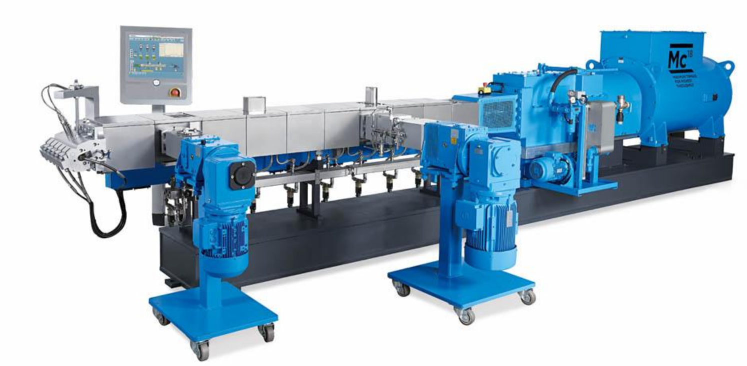


Figure 19. Compounding Extrusion Ejection Molding

1.4.1.2 Blown Film Extrusion

The extraction process is divided in six steps. In Figure 20 is illustrated the blown film extrusion process. The plastic after melting is extruded through an annular slit die, vertically, to form thin walled tube and then the air is introduced in the centre of the die to blow up a tube like a balloon (IBC). The tube then passes through nip rolls where is flattened. The collapsed tube is taken back down the extrusion tower via more idler rollers. On winder the tube or film is wound into rolls.

Figure 20. The blown film process of Bionolle (Starch blend)

In the recent years, the blown film extrusion process has attracted great interest in the polymer processing industry to produce thermoplastic films [23]. The mechanical properties of the polymers are improved by orientation processes [24, 25, 26] and there is a biaxial orientation that films from blown lines exhibit, a high puncture and tear propagation resistance. These blown film lines are designed to produce flexible PE-LD or PE-HD films of 5-200 µm. Ecoflex® is the first processed material by the extruder forming a melt stream with constant melt temperature and output rate. Than the melt is cooled down quickly by the air ring and the internal bubble cooling (Figure 21 -22). To have a good control of the blown film process it’s necessary having a good understanding of the problems of elongational flow. The apparatus of blown film extrusion consist of a 1- Killion extruder, an annular die, an isothermal chamber, nip rolls and a take-up device [23].

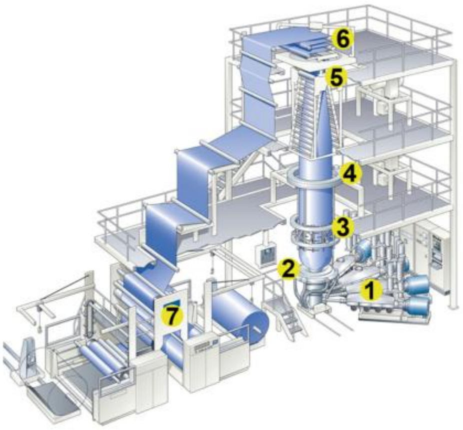


Figure 21. Blown film line for PE-LD. 1. Extruders, 2.Die head with air cooling ring, 3 sizing unit, 4 thickness measuring unit, 5 haul- off unit and collapsing boards, 6 reversing unit, 7 winder .

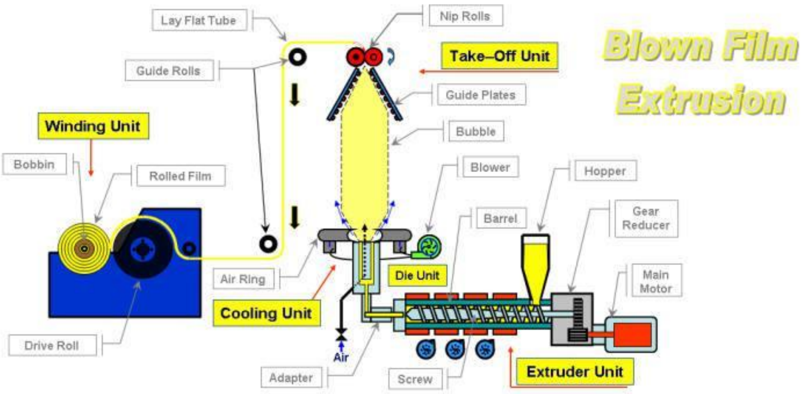


Figure 22. Scheme of the blown film extrusion process.

1.5 Cycle of Life of a plastic material/ Mapping the steps in life cycle of a plastic bag

A recent study used an incremental approach to map steps along a LC (life cycle) of a plastic bag with a specific focus on European production, use and legislation. In order to map the life cycle of a plastic bag a completed survey of the literature between 1990 and 2016 in the database “Web of Science” was used. The literature was reviewed regarding the environmental fate and the behaviour of plastics of each step of LC. Five steps were identified in the LC of a plastic bag: 1) Raw material used in production; 2) Manufacturing process; 3) Use/ reuse; 4) Waste/ Recycle; and 5) Discharge to environment (Fig. 23) [27].

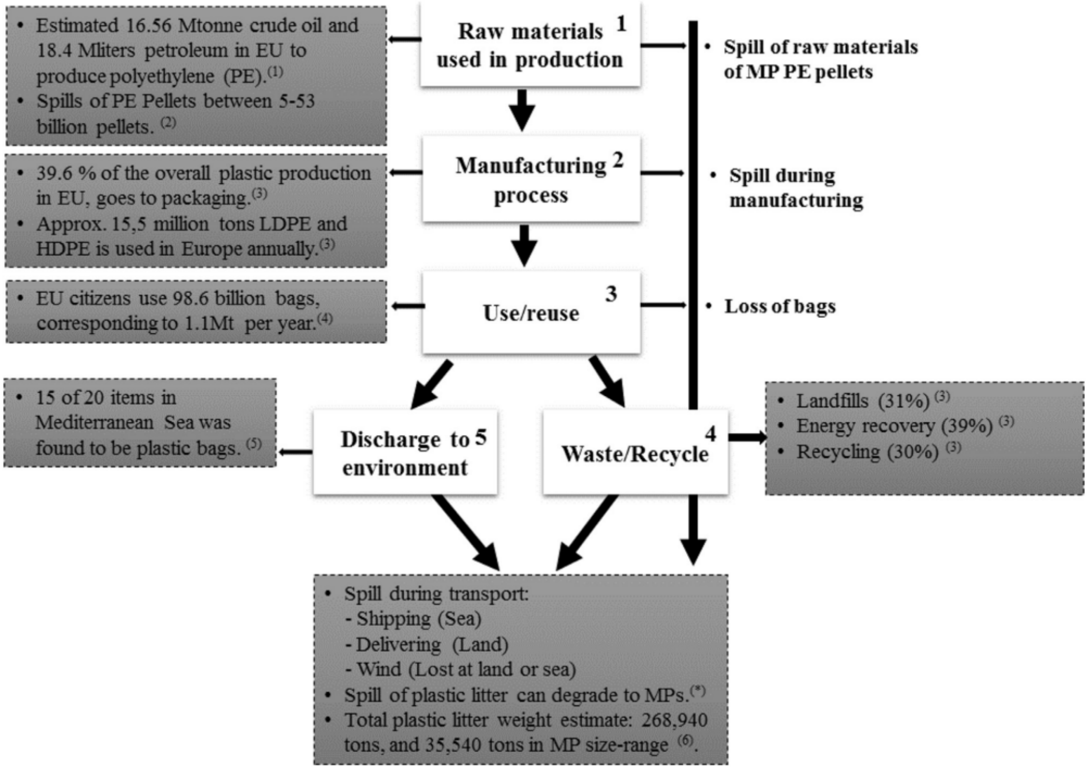


Figure 23. Life Cycle of plastic bags mapping the different steps and elements that influence the fat and behaviour of plastic bags through their life cycle (LC).

1.5.1 Step1: Raw Materials used in production and release of plastic pellets

The first step is related to the raw materials used in the process of manufacturing of the plastic taking into account even the losses of plastic pellets from the production site during the transport[27].

The volunteer-based global monitoring program “International Pellet Watch” aims at monitoring organic pollutants in pellets found as seashores around the world. The data program covers a broad geographical range and illustrates the marine pollution with plastic pellets in global system. A differentiation of plastic pellet types is not yet described.

1.5.2 Step 2: Manufacturing of plastic bags

Plastic bags are often made in PE, which is produced using petrol and crude oil confirming that 4% of global oil production is used for plastic production. In general according to EU rules the lightweight plastic bags are more used than the heavy ones (*European Parliament and the Council*, *2015*) and the plastics are mainly produced from LDPE pellets, as this polymer is very flexible and clear. In EU the total production of LDPE is around 9Mt/yr.

accounting for 17.5 % of the total plastic production and the 39.5% of EU plastic production demand is used for packing (*PlasticsEurope, 2015a*). HDPE is used for producing high-weight plastic bags, which are thicker and reusable because they are more durable compared with LDPE. HDPE production accounts for 12.1% of EU plastic production with a demand of 5.5 Mt/yr[27].

1.5.3 Step 3: Use/ Reuse of plastic bags

Approximately 92% of lightweight bags are single-use, after the usage are disposed as waste or lost in the environment. The use of single and multiple plastic bags vary within different EU member states .

1.5.4 Step 4: Waste/ Recycle of plastic bags

In the end-of-life of the product management, are estimated :

- 69% of collected plastic ends up as a waste;
- 30% recovered through material recycling/39% energy recovery products.

Even all the times industries put a lot of effort to recover plastics, 31% was still disposed in landfills[27].

The technological development now allow plastic waste to be recycled by different methods and they can be grouped in three main categories: (1) Mechanical recycling, (2) Feedstock recycling (monomerization, furnace reducing agent, liquefaction, ect), (3) Thermal recycling. The most used is the mechanical recycling process.

Mechanical Recycling

Mechanical recycling is a way of making new products out of unmodified plastic waste. It is an industrial waste application, and the product after the recycling process is well suited to be used as a raw material for mechanical recycling thanks to the clear separation of different types of resins and plastics and the low impurities available in the process (because before the recycling process is a household manufacture). All the recycled products have a huge number of attractive characteristics: they are durable and easy to process. For example, PET bottles sorted from households are collected, compressed and packed by the municipality for transportation to the plant operating system. First, the waste is sorted to remove impurities and the foreign bodies are removed. Then, all the raw material is converted in granules [28] .

1.5.5 Step 5: Discharge to environment

When the end-of-life of the plastics is not properly managed it is a large potential that all the plastic disposal ends up as marine litter. Marine litter from land-based sources, such as plastic bags, can be transported from land by: run-offs from rivers, discharge in effluents during heavy rain-fall or storm water, ect. It is estimated that 8% of the manufactured plastic bags are littered in the ocean in EU, which correlates as a huge amount of plastic litter in EU with PE as the most abundant polymer[27].

1.5.6 Plastic waste – a global challenge

A life cycle of a plastic material goes through three phases presented in the Figure 24.

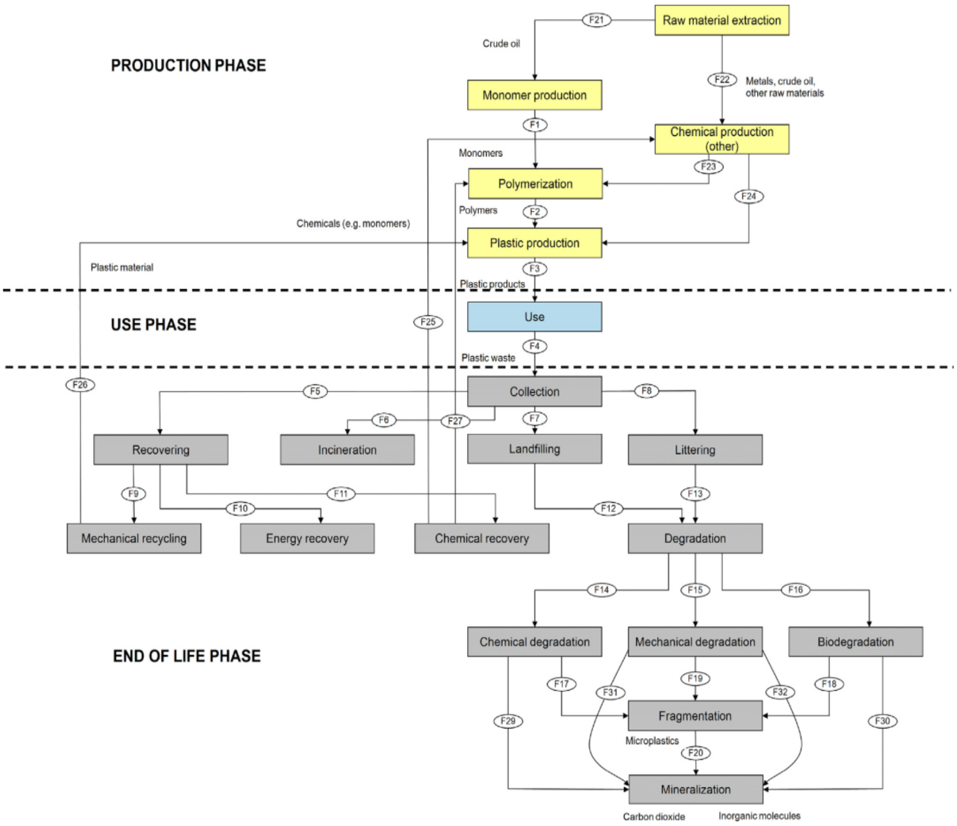


Figure. 24. The life cycle of plastic products (excluding energy input and emissions), created in STAN (substance flow Analysis) Software (redrawn from Source: “F” stands for Flow and the number shown next to corresponds to the particularly flow series (an automatic procedure incorporated in STAN)).

Despite all the worldwide advances in management, treatment and recycling in the last three decades, the largest fraction of plastic waste still possibly ends up in dumpsites or in openly burned, emitting CO and CO_2. Approximately 50% of plastic waste ends up to controlled landfill disposal [3]. Nowadays this is highly debated, and almost unacceptable wastage of resources and promote at least resource recovery via energy form waste (EfW), and others aspire as temporary storage, releasing greenhouse emissions, until landfill mining becomes viable [4].

Landfills are mechanical recycling (primary recycling substituting virgin materials and secondary materials). In most cases plastics are secondary recycling applies, in which used plastics are cascaded into material applications different than original, and often less demanding material specifications (PET bottles into fleece) and could be transported over long distances.

Sometimes the recycling process can be uncontrolled and can also result in the transfer of potentially harmful substances or potentially toxic substances (PoTSs) into plastics for sensitive uses, such as children's toys and food contact materials. Some processes involve innovative uses for plastic waste, with untested potential for dispersion into the environment and associated unknown pollution. As a good example is valuable to mention India, that used recycled plastic into asphalt, as an alternative road material [27].

1.6 Biopolymers

The bio polymers are usually formed by micro or macro organisms, or are extracted from plants or animals and there is a strong interest in biopolymers to replace the oil-based ones. The most important benefits with natural polymers (for example we can mention proteins and polysaccharides) is that they can biodegrade in open atmosphere more easily than oil based polymers [27]. Biopolymers are polymers that occur in nature, and a good example of biopolymers are carbohydrates and proteins. Starch and cellulose are the most abundant biopolymers in the biosphere.

Starch is a natural bio storage material accumulated by plants and is a mixture of linear structure of polysaccharide molecules (amylose) and branched molecules (amylopectin). The Starch is derived from corn, tapioca, potatoes, rice and is an inexpensive renewable polymer with importance in food and non-food fields of application. It's not possible using the native starch as a plastic, but it's possible to use a plasticized form that is called "the thermoplastic starch (TPS)", already used in packaging process and short-time live consumer goods. A recent R&D achievements have been proposed to create more durable materials mostly based on starch as alternatives to oil-based thermoplastics. Cereplast is proposing bio-based Cereplast Hybrid Resins ®, that accounts for more than 50% of the plastic market compared with the oil based plastics. Since these starch blends and PP are design to approach traditional PP characteristics, they can probably replace petrochemical PP. The first product from this family of Bio-polyolefins® is Biopropylene 50™, a 50% starch-based resin exhibiting similar characteristics (HDT, modulus and impact strength) as traditional polypropylene. Biopropylene™ resin can be used in conventional manufacturing processing (i.e., injection molding, profile extrusion, etc) and requires less energy in the production process by using lower process temperatures. Moreover, the price per pound of Cereplast Hybrid Resins® products is similar to the price of traditional polyolefin [29, 30, 31].

1.6.1 Starch

Starch is the most abundant polymer derived from potatoes, corn and crops. It is composed from amylase (the most linear polymer) and amylopectin (Figure 25). From thermoplastic starch, traditional plastic goods can be obtained by blending or mixing starch with synthetic polymers. The properties and morphology of these blends can be adjusted easily and efficiently. The first company that took the advantage of this phenomenon was Novamont that produced Mater-Bi® materials that are mainly formed into films and sheets which found application in agriculture, waste management, packaging, personal care & hygiene ect.

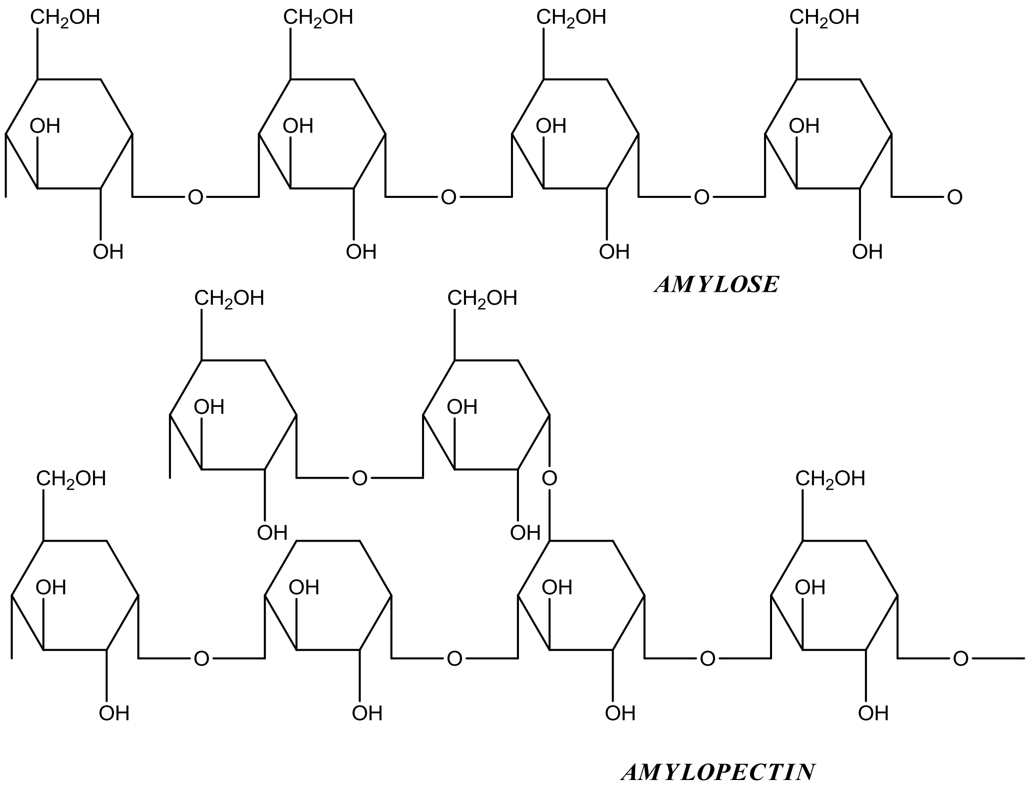


Figure 25. Amilose and Amilopectine Structures

According to Novamont Company, TPS (thermoplastic starch) can be blended with different synthetic polymers to create three families :

- TPS blends with synthetic copolymers and hydrophobic groups (polyester – urethanes, ethylene – acrylic acid copolymers, ect).
- TPS blended with incompatible or slightly compatible synthetic polymers.

Under Mater- Bi® trademark four classes of biodegradable materials based on thermoplastic starch:

- Class Z – Made from TPS and poly (capralactone).
- Class Y –Made from TPS in dispersed form and cellulose derivates.
- Class V – Made with content of TPS more than 85% and biodegradation time even shorter than Z class.
- Class A – made of starch and ethylene vinyl-alcohol copolymer. This polymer is biodegradable within 2 years in a stimulated environment.

Although the basic chemistry of starches is the same in all plants, of course that do exsist differences between them. For example: potato starch contains about 21% of amylase at a number – average molecular weight (Mn) of 4900, corn starch contains about 29% of amylase at a much lower Mn of about 900 [32] .

1.6.2 BASF's Biodegradable Polymers, Ecoflex® and Ecovio®

The biodegradable polymers are good and sustainable alternatives to standard plastics in applications where the principal property of biodegradability is an advantage. Ecoflex® is a brand name produced by BASF of completely biodegradable aliphatic-aromatic polyester. These kind of renewable raw materials can be used either like Ecoflex® itself, but either by blending it with other biodegradable polymers like poly(lactic acid) (PLA), starch to enhance and obtain desired properties. All the compounds containing Ecoflex® and PLA are been commercialized by BASF under the brand name Ecovio®, Ecoflex® and Ecovio® combine very good mechanical properties and completely biodegradable, so are drop-in substitutes for standard plastics like polyethylene or polystyrene and the application range is very huge: organic waste bags, shopping bags, coating paper board [33].

Ecoflex® is designed for processing on regular equipments for standard polymers like PE. These biodegradable polymers mostly are used to produce organic waste plastic bags, because what is with a major interest in this case is the composting process. From e technical point of view, compost bags have to be biodegradable according to EN 13432. The temperature resistance should allow to transport and storage these plastic bags even at 60 °C. Another advantage using these polymers are the low barrier properties for gases and water. Ecoflex® and Ecovio® fulfill these basic requirements for compost bags even at low moisture levels below 50% relative humidity, the mechanical stability stays intact. Ecoflex®/ Starch compounds are very versatile regarding their biodegradation method (They fulfill the composting standard EN 13432. Ecoflex® acts as an enabler for starch, providing good processing on blown film lines. On its own, without Ecoflex® , starch would form only water sensitive, brittle sheets without flexibility. Ecoflex®/ Starch compounds can enhance the temperature stability to 60 °C and they can provide good storage stability (for example they do not become brittle even if the humidity level drops considerably)[33].

1.6.2.1 Shopping (Carrier) Bags

Based on higher sensitivity for environmental issues, changing consumer behavior have an increasing of interest of retailers to go toward using biodegradable shopping bags. After shopping, these bags can be applied for disposal of organic waste, resulting in the double use of the material. Thin biodegradable carrier bags have a property profile that is similar to compost bags:

- Good mechanical properties for loads of about 1,000 times their own weight
- Good puncture resistance, e.g., for liquid beverage cartons
- Down-gauging to 10–20 mm
- Good printability (eight color flexo printing) for superior presentation
- Good welding performance for high speed bag-making
- Usefulness as compost bags after several services as a carrier bag

Because of the higher prices the paper bags are often more used than the compost ones, but paper bags with high quality printing and coatings are generally not biodegradable because of the coating materials applied.

1.6.3 Biodegradability

Biodegradability is a property typically of naturally occurring materials because our everyday experiences are formed by natural circle of biomass generation and degradation. On the other hand, it is known that the plastics in general are made up from materials that are persistent, but the biodegradability is not depending on the origin of the raw materials, but only on its chemical structure. While the term “bio-based” is used to describe the origin of the polymer (raw material), the term bio-degradable is associated to the end of life of the product. So, in other terms a polymer can be bio-based, but not necessarily bio-degradable. The biodegradable polymers find lots of uses in industrial scale since 1990s when BASF launched Ecoflex®. a totally biodegradable polymer (Figure 26) [34] .

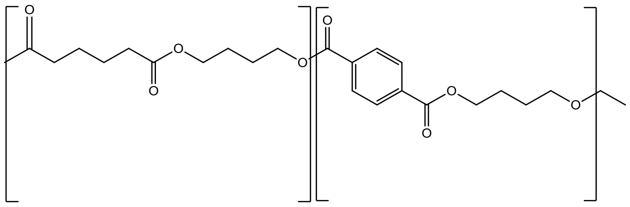


Figure 26. Ecoflex Chemical Structure

The process of biodegradation is specific and depends on the type of microrganism chosen. The microorganisms have to be able to take up the substance and metabolize it within their cells. A requirement is that the molecules have to be water-soluble in order to allow them to pass through the cell walls and membranes of the microorganisms [34].

In the first step of biodegradation has to be dissolved the secondary part structure e.g, crystalline part and the temporary flexible chain is formed. After this process the polymer needs to be broken down into small fragments by microorganisms that cleavage the chemical bonds. This can be considered an enzimatic cleavage reaction that needs functional sites. In most cases, the chemical reaction that is catalysed by exo-enzymes is a hydrolysis process that converts all the polymer chain into small fragments for example, oligomers or monomers. At a third step, all the oligomers and monomers formed need to be small enough and water-soluble to pass through the cell walls and membranes of the microorganisms and finally within the microorganisms all the small fragments are converted into water, gaseous products (CO_2 or methane), biomass and energy. Usually since is difficult to diffuse degradation into the bulk polymeric material , biodegradation is an erosion process that takes place at the surface of the polymeric material [35].

1.6.4 Crystallization of Biodegradable Polymers

The crystallization can occur during the polymerization, where the formation of macroscopic single polymer crystal occur (Figure 27) [36].

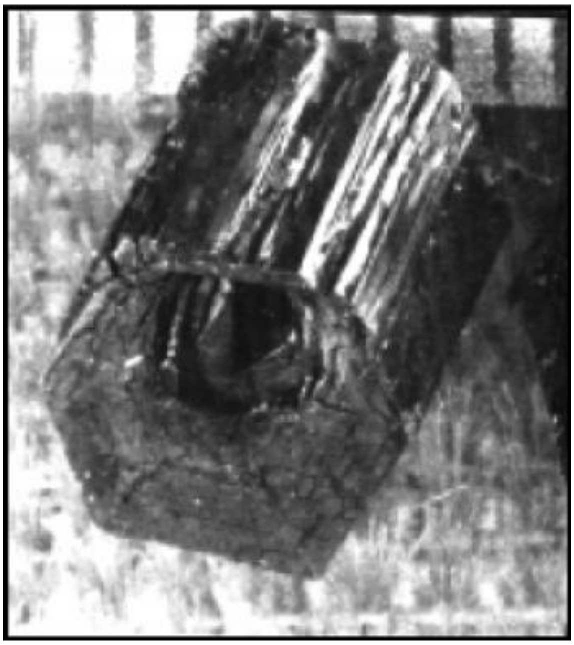


Figure 27. Macroscopic single crystal

During the process of crystallization, the monomers can be joined into chains by solid state polymerization. Than the final crystal is obtained from chemical reactions at gas/solid or liquid/solid interface and not just as a consequence of the change in physical state of material [37] .The mechanism of the process is shown in the Figure 28.

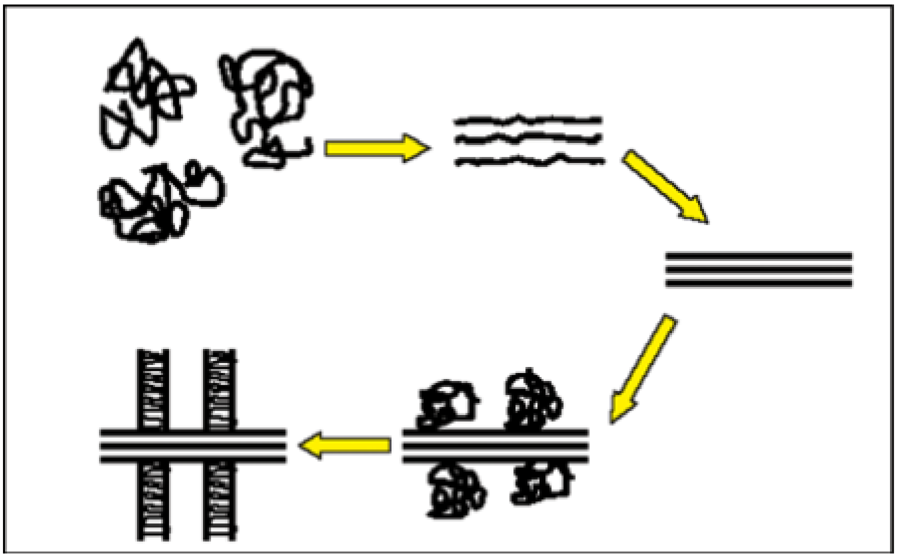


Figure 28. Schematic of orientation induced by crystallization. (The first drawing illustrate the orientation and crystallization of random coils and the second show the growth of folded chain kebab around the central shish.)

This mechanism of this process have 2 types :

- The simultaneous polymerization and crystallization;
- The successive polymerization and crystallization ;

During the crystallization from melt, the nucleation growth of crystalline regions characteristics are directly linked to the understanding of the morphological details of these crystalline regions. The morphology of the crystals can be classified into two broad classes :

- Fringed micelle
- Lamellar type

The fringed micelle model was constructed in 1930 by Hermann, Gerngross and Abitz [38] in order to explain the structure of gelatins and then was extended by Flory [39]. In this model a part of polymer chain align themselves to form bundled crystalline regions (Figure 27) [37]

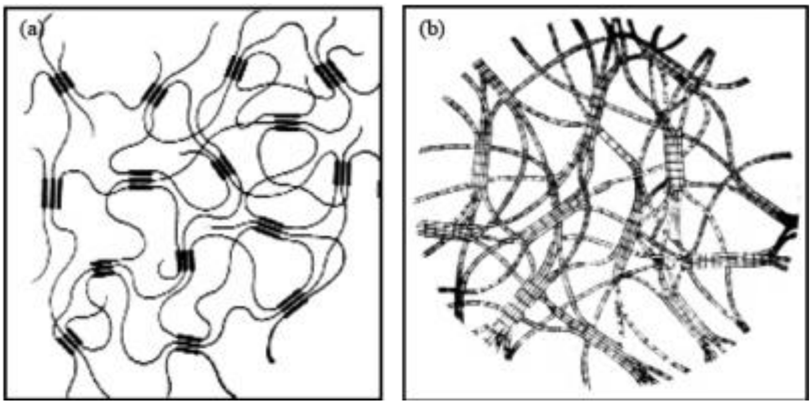


Figure 29 (a) Keller model for crystallization; (b) Hermann & Gerngross model [41]

2. THE OBJECT OF THESIS

The sustainability is focused to meet the needs of the present without compromising the new generations to meet their needs. When we talk about sustainable polymers we refer to a plastic material that addresses the needs of the consumers without damaging our environment, health and economy. In the recent years, it is observed that the sustainability of plastic materials plays an important role to have materials with excellent quality. While sustainability can be addressed in a number of ways, every possible effort is welcome in improving the impact of the plastics in terms of environmental friendliness. While the obvious way would be to substitute common oil-based plastics with bio-based biodegradable ones, this is not always possible owing, among other parameters, to the lack of availability and high cost of such alternatives. In this frame, the most susceptible market is the one of packaging and single-use items. Hence, every effort undertaken by companies to address the environmental impact of such materials is important.

Hence, during my internship I worked in order to increase the competency of a local company that is now dealing with single-use plastic shoppers. Since the use of alternative sustainable plastics is a high cost process, that cannot always be positively accepted by the final users, the company is presently trying to evaluate the production of biodegradable bags, while contemporary evaluating the possibility of using recycled oil based plastics from the traditional process. In this frame I thus evaluated the properties of both raw materials obtained from an internal recycling process, as well as possible sustainable alternatives. Hence in this work we present the characterization of some internally recycled materials, such as Rig. Neutro and Rig. Bianco, as well as commercially available polymeric blends pellets like Biocomp, Biotech, Basf Ecovio The characterization is based on Thermogravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC), and FT-IR/ATR. Moreover, in order for the company to set a standard reference for the production of disposable bio-based plastic bags, as alternative to the oil based traditional ones, the characterization of commercial bags available in the market like: Esselunga, Coop, Carrefour, Pam , BioF3 ect has been carried out.

3. RESULTS AND DISCUSSIONS

Related to the valuation of the product and to the process used to produce the plastic bags like blown film extrusion realized from a local company, were characterized all the raw materials of common utilization with the objective to have a key reference point and to compare them with commercial products. In this contest the raw materials that was characterized are defined like:

Company	**Product Family**	**Product Grade**	**Composition**	**Description & Notes**
Biotec®	Bioplast®	GF 106/02	Starch + other biodegradable polymers*	Starch is from GMO–free potatoes. 30%wt of the raw material is renewable based. 23% of carbon is biobased according to ASTM D6866.
BASF®	ecovio®	F23B1	PLA + biodegradable polyesters	ecovio® is a blend of ecoflex® F (another product of BASF, composed by biodegradable polyesters) and a small amount of PLA. Ok for food contact application.
Microtec	BioComp®	BF7210S	PLA + other biodegradable polymers*	This grade of compostable polymer blend has 43% (±3) of biobased carbon. No starch. Pending certification for food contact application.
Local Company	Rig. BIO	–	Mix of biodegradable polymers	Mix of biodegradable/compostable polymer scraps recovered by the company at different stages of the production. These scraps are grinded, fed to the hopper of an extruder and re–granulated in form of recycled pellets.
	Rig. NEUTRO	–	Mix of LDPE	Mix of LDPE scraps recovered by the company at different stages of the production, of the same base colour (white in this case). These scraps are grinded, fed to the hopper of an extruder and re–granulated

				in form of recycled pellets.
	Rig. Bianco		Mix of LDPE + white masterbatch	Mix of LDPE scraps recovered by the company at different stages of the production, of the same base colour (white in this case). These scraps are grinded, fed to the hopper of an extruder and re–granulated in form of recycled pellets.

To define the characteristics of the raw materials was performed Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry and Infrared Spectroscopy in (AT-IR/ATR). The TGA permits to evaluate the minimum of the temperature that a product can be used and all the weight losses referred to the organic part of the material. In addition, it is possible to see the inorganic residue present in the sample. From the other hand, DSC gives the opportunity to evaluate all the fusion enthalpy temperatures, the phase transformations, the crystallization temperature useful to deeply understand the thermic story of the material. The FT-IR/ATR analysis is necessary for the chemical characterization of the material.

3.1 Characterization of raw materials

3.1.1 Attenuated Total Reflectance

The FT-IR/ATR was performed using a Bruker Alpha spectrometer equipped with ATR (Attenuated Total Reflectrance) with a diamond crystal. The chemical characterization for all raw materials are shown below (Figure 30-35). The Attenuated Total Reflectance (ATR) accessory used represents critical conditions for data acquisition, due to the difficulties in obtaining good sample/ crystal contact and the effectiveness of the sample contact will dramatically affect the quality of the final result. The identification of the polymer, the presence of co-monomers and oxidation products are possible with this technique. In particular was performed a comparison with the database spectra to see the analogy.

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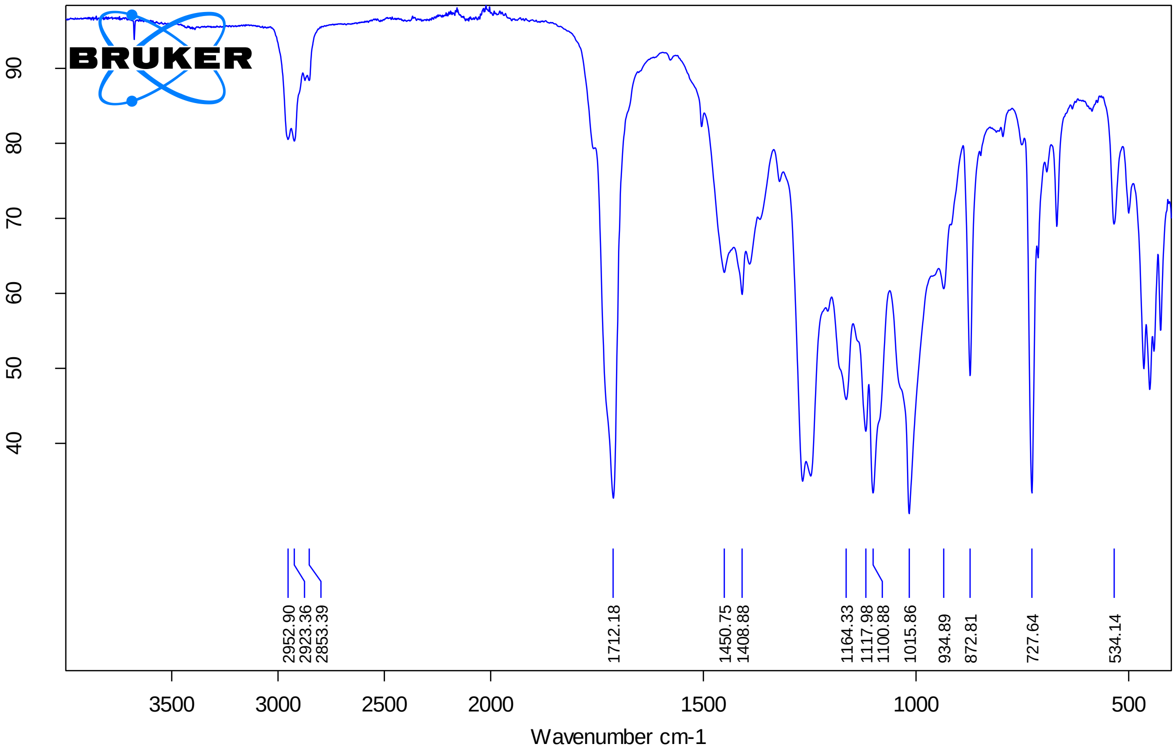
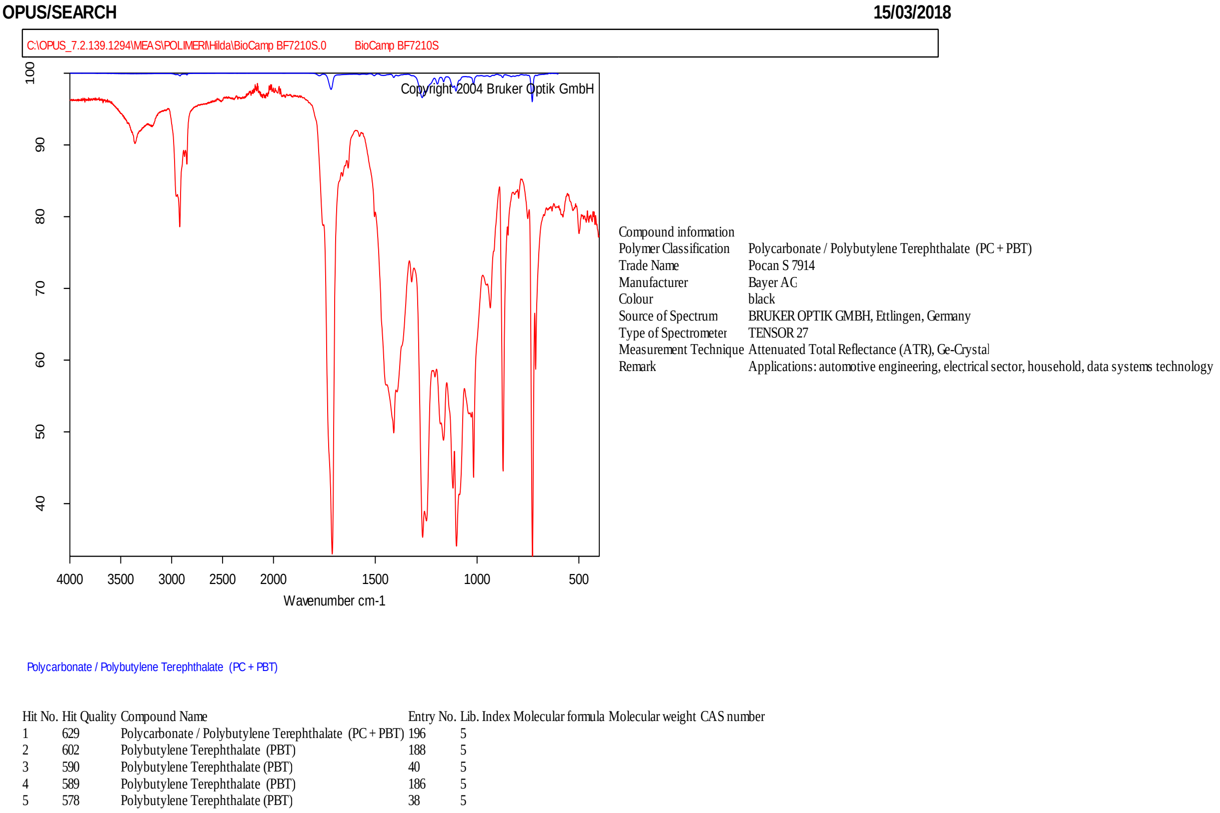


Figure 30-FT-IR/ATR spectra of Basf Ecovio F23B1 raw material

From the comparison of FT-IR /ATR spectra of Basf EcovioF23B1 with database furnished by Bruker, was possible to have an analogy with the spectra of Polylactic acid like shown in the figure 30. The region of 3600 -3000 cm $^{-1}$ corresponds to the O-H stretch and these bands became more pronounced, broader and shifted to slightly lower wave numbers when the free hydroxyl groups get engaged in hydrogen bonding with other additives[42]. It is able to characterize some important bands like 2953 cm^{-1} – corresponding to an asymmetric Stretching of CH_3, 1712 cm^{-1} – Bending of C=O and a symmetric Stretching of COC pointed at 1100 cm^{-1}. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material[42] .



OPUS/SEARCH **15/03/2018**

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Compound information

Polymer Classification	Polycarbonate / Polybutylene Terephthalate (PC + PBT)
Trade Name	Pocan S 7914
Manufacturer	Bayer AG
Colour	black
Source of Spectrum	BRUKER OPTIK GMBH, Ettlingen, Germany
Type of Spectrometer	TENSOR 27
Measurement Technique	Attenuated Total Reflectance (ATR), Ge-Crystal
Remark	Applications: automotive engineering, electrical sector, household, data systems technology

Polycarbonate / Polybutylene Terephthalate (PC + PBT)

Hit No.	Hit Quality	Compound Name	Entry No.	Lib. Index	Molecular formula	Molecular weight	CAS number
1	629	Polycarbonate / Polybutylene Terephthalate (PC + PBT)	196	5			
2	602	Polybutylene Terephthalate (PBT)	188	5			
3	590	Polybutylene Terephthalate (PBT)	40	5			
4	589	Polybutylene Terephthalate (PBT)	186	5			
5	578	Polybutylene Terephthalate (PBT)	38	5			

Figure 31- FT-IR/ATR spectra of Biocomp raw material

From the comparison of FT-IR /ATR spectra of Biocomp with database furnished by Bruker, was possible to have an analogy with the spectra of Polylactic acid (PLA) like shown in the figure 31. The region of 3600 -3000 cm $^{-1}$ corresponds to the O-H stretch and these bands became more pronounced, broader and shifted t slightly lower wave numbers when the free hydroxyl groups get engaged in hydrogen bonding with other additives. From the spectra it is possible to understand that it is a polymeric blend (not only PLA) because the region 3600 – 3000 is broader than in Basf Ecovio sample that mostly accounts for PLA. It is known that in Biocomp polymers are made up PLA and some other biodegradable polymers suitable for food packaging applications. Moreover, it is able to characterize some important bands like: 2920 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1267 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible identify some other bands ascribed at the inorganic fraction of the raw material.

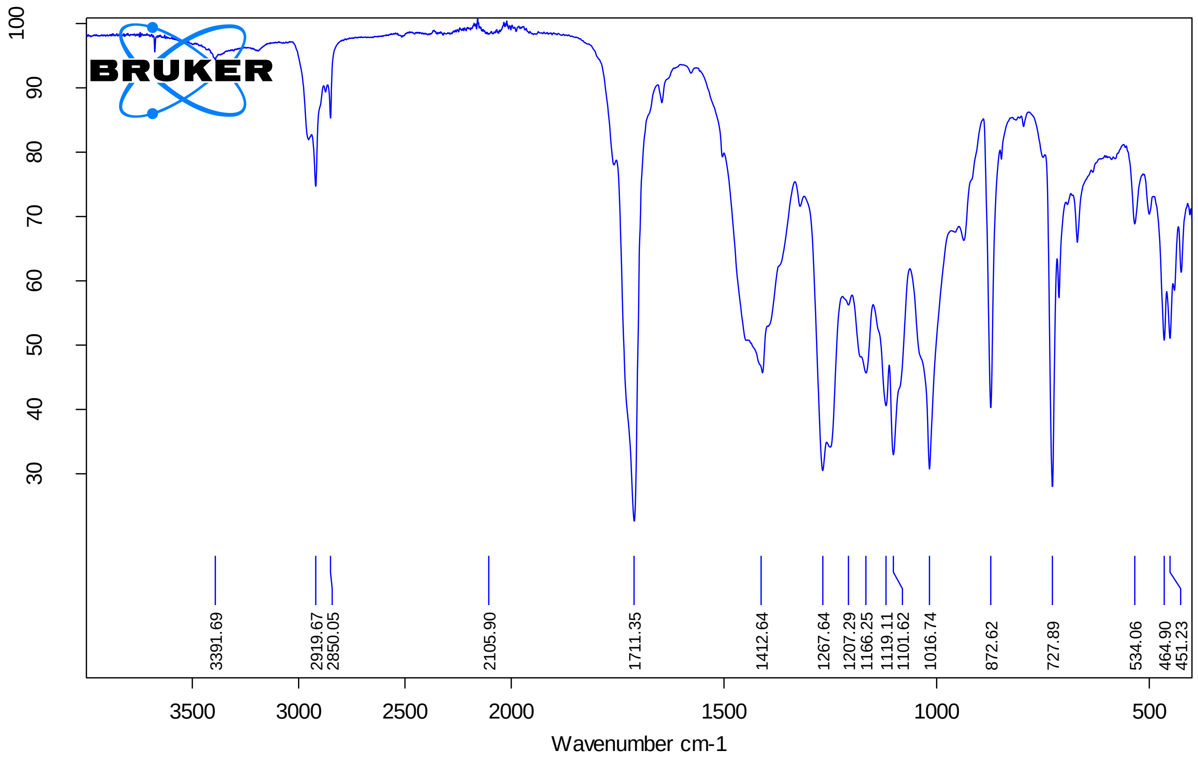


Figure 32- FT-IR/ATR spectra of BioTech raw material

From the comparison of FT-IR /ATR spectra of Biotech with database furnished by Bruker, was possible to have an analogy with the spectra of Polylactic acid (PLA) like shown in the figure 32. The region of 3600 -3000 cm $^{-1}$ corresponds to the O-H stretch and these bands became more pronounced, broader and shifted t slightly lower wave numbers when the free hydroxyl groups get engaged in hydrogen bonding with other additives. It is able to characterize some important bands like: 2920 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1711 cm^{-1} corresponding to a C=O Stretching, 1268 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

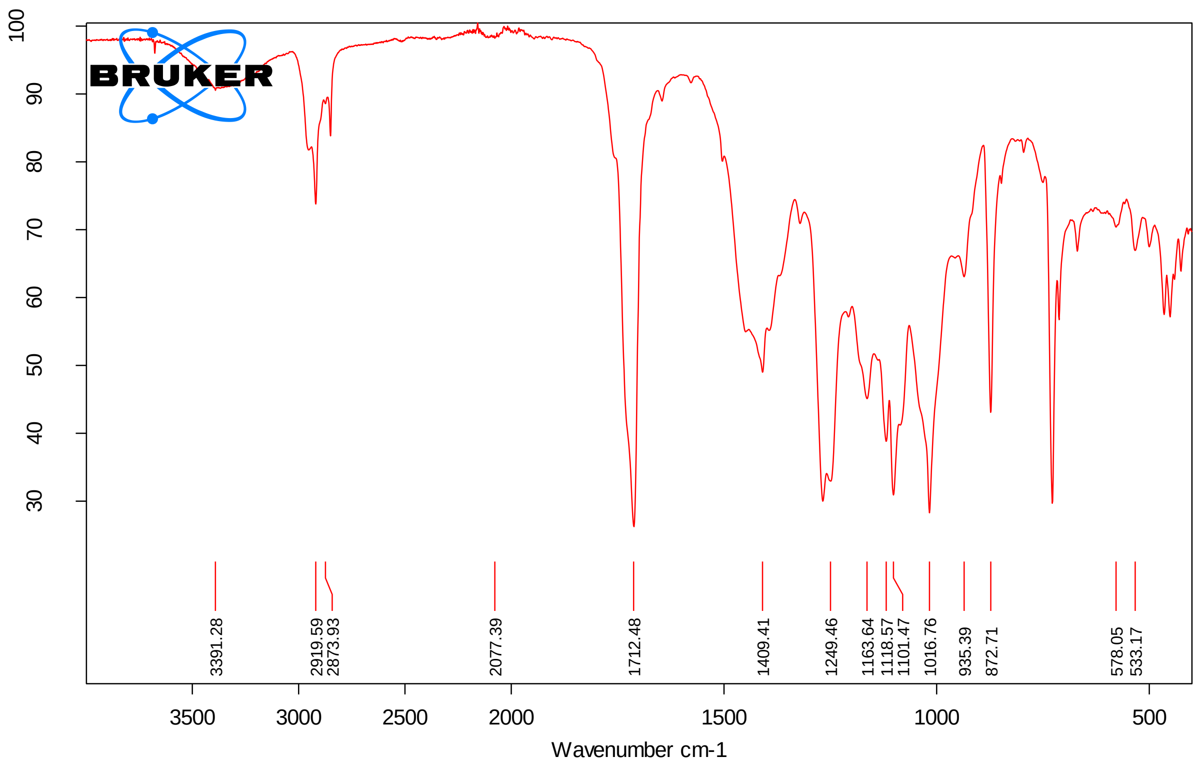
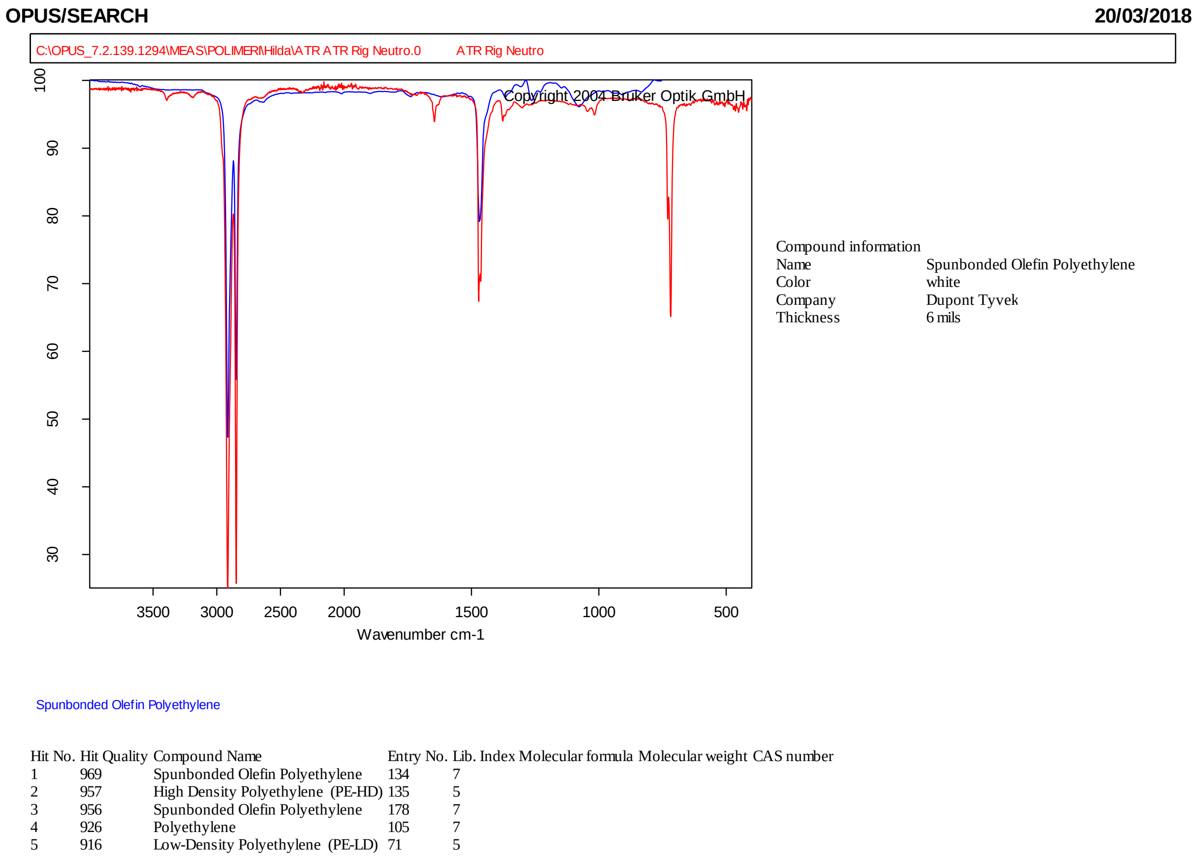


Figure 33- FT-IR/ATR spectra of BioRig raw material

From the comparison of FT-IR /ATR spectra of BioRig with database furnished by Bruker, was possible to have an analogy with the spectra of Polylactic acid (PLA) like shown in the figure 33. The region of 3600 -3000 cm $^{-1}$ corresponds to the O-H stretch and these bands became more pronounced, broader and shifted t slightly lower wave numbers when the free hydroxyl groups get engaged in hydrogen bonding with other additives. It is able to characterize some important bands like: 2920 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1712 cm^{-1} corresponding to a C=O Stretching, 1249 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.



OPUS/SEARCH **20/03/2018**

C:\OPUS_7.2.139.1294\MEAS\POLIMER\Hilda\ATR ATR Rig Neutro.0 ATR Rig Neutro

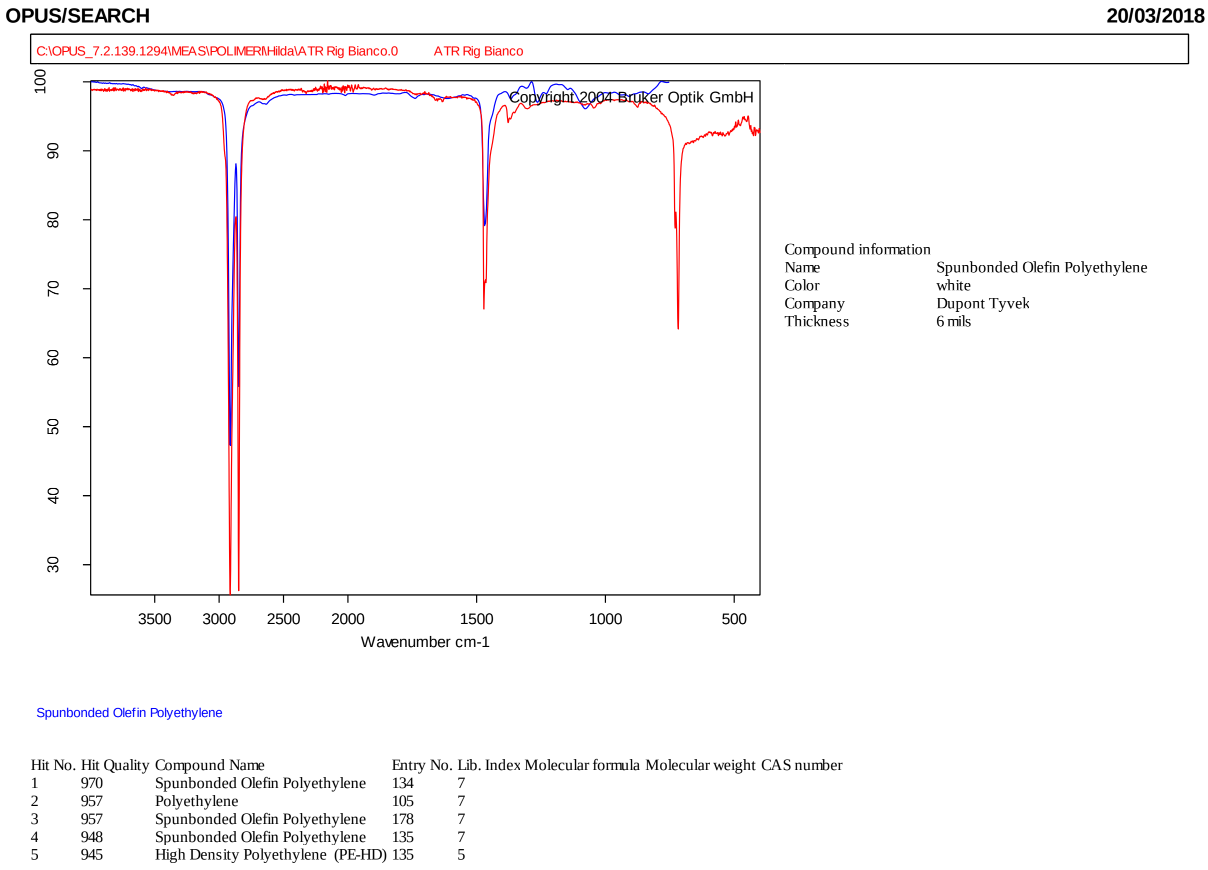
Compound information	
Name	Spunbonded Olefin Polyethylene
Color	white
Company	Dupont Tyvek
Thickness	6 mils

Spunbonded Olefin Polyethylene

Hit No.	Hit Quality	Compound Name	Entry No.	Lib. Index	Molecular formula	Molecular weight	CAS number
1	969	Spunbonded Olefin Polyethylene	134	7			
2	957	High Density Polyethylene (PE-HD)	135	5			
3	956	Spunbonded Olefin Polyethylene	178	7			
4	926	Polyethylene	105	7			
5	916	Low-Density Polyethylene (PE-LD)	71	5			

Figure 34- FT-IR/ATR spectra of Rig Neutro raw material

From the comparison of FT-IR /ATR spectra of Rig Neutro with database furnished by Bruker, was possible to have an analogy with the spectra of low density polyethylene (LDPE) like shown in the figure 34. It is able to characterize some important bands like: 2914 cm^{-1} – corresponding to an asymmetric Stretching of CH_2 and strong bending deformations at 1472 cm $^{-1}$. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.



OPUS/SEARCH **20/03/2018**

C:\OPUS_7.2.139.1294\MEAS\POLIMERI\Hilda\ATR Rig Bianco.0 ATR Rig Bianco

Compound information

Name	Spunbonded Olefin Polyethylene
Color	white
Company	Dupont Tyvek
Thickness	6 mils

Spunbonded Olefin Polyethylene

Hit No.	Hit Quality	Compound Name	Entry No.	Lib. Index	Molecular formula	Molecular weight	CAS number
1	970	Spunbonded Olefin Polyethylene	134	7			
2	957	Polyethylene	105	7			
3	957	Spunbonded Olefin Polyethylene	178	7			
4	948	Spunbonded Olefin Polyethylene	135	7			
5	945	High Density Polyethylene (PE-HD)	135	5			

Figure 35- FT-IR/ATR spectra of Rig Bianco raw material

From the comparison of FT-IR /ATR spectra of Rig Bianco with database furnished by Bruker, was possible to have an analogy with the spectra of low density polyethylene (LDPE) like shown in the figure 35. It is able to characterize some important bands like: 2914 cm^{-1} – corresponding to an asymmetric Stretching of CH_2 and strong bending deformations at 1471 cm $^{-1}$. In the region of 1700 cm^{-1}it is possible to identify a small peak that is due to the oxidation processes. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material related mostly to the content of $CaCO_3$ in the material.

Because the inorganic fraction has an important relevance in the performances of the final product, the residues obtained from the TGA were analyzed with FT-IR/ATR.

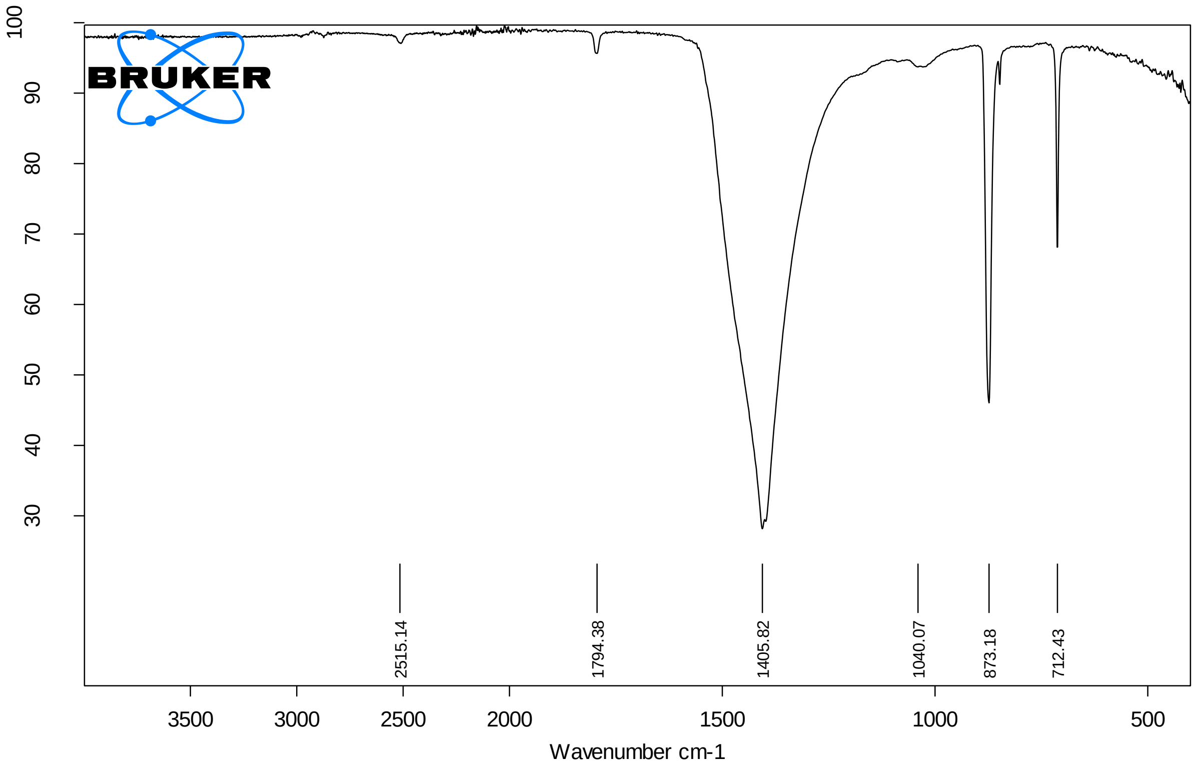


Figure 36- FT-IR/ATR spectrum of the residue of BioComp raw material

The spectra of the residues are very similar and as example the spectrum of the residue of Biocomp is shown (Figure 36). From the FT-IR/ATR the bands of $CaCO_3$ are identified. It is evident that $CaCO_3$ is present in a form of calcite and the band at 873 cm^{-1} shows a special interference due to the strong absorption at this wavelength. This interference can be corrected by applying the proposed absorbances correction method. This method can be applied whenever the interferent component has an absorption peak at a wavelength free of interferences (called auxiliary frequency). The peak at 1794 cm^{-1} corresponds to a symmetric stretching of C-O followed by an in plane bending of O-C-O. The peak in this region is not to sharp and followed by a noisy signal coming from some interferences related to the environment background. At 1405 cm^{-1} is noticeable an asymmetric stretching of C-O and at 873 cm^{-1} an out of plane deformation of CO_3 .

The Infrared Analysis performed in these pellets presents some differences between Rig Neutro and Rig. Bianco. In Rig. Neutro it is possible to see an oxidation peak that is not evident in Rig. Bianco. This can happen due to the aliphatic stretching C-H at 2914 cm^{-1}.

3.1.2 Thermogravimetric analysis

The thermogravimetric analysis (TGA) permit to evaluate the presence of volatile additives, the limits of utilization of the raw materials, the temperature of the weight losses and the presence of inorganic residues. All TGA analysis represent more or less the same weight losses, apart Rigenerato Neutro that has not an inorganic residue an composed only from LDPE . From the TGA results was possible to say that Rigenerato Neutro was used to produce the transparent plastic bag, but from ATR analysis they didn’t match.

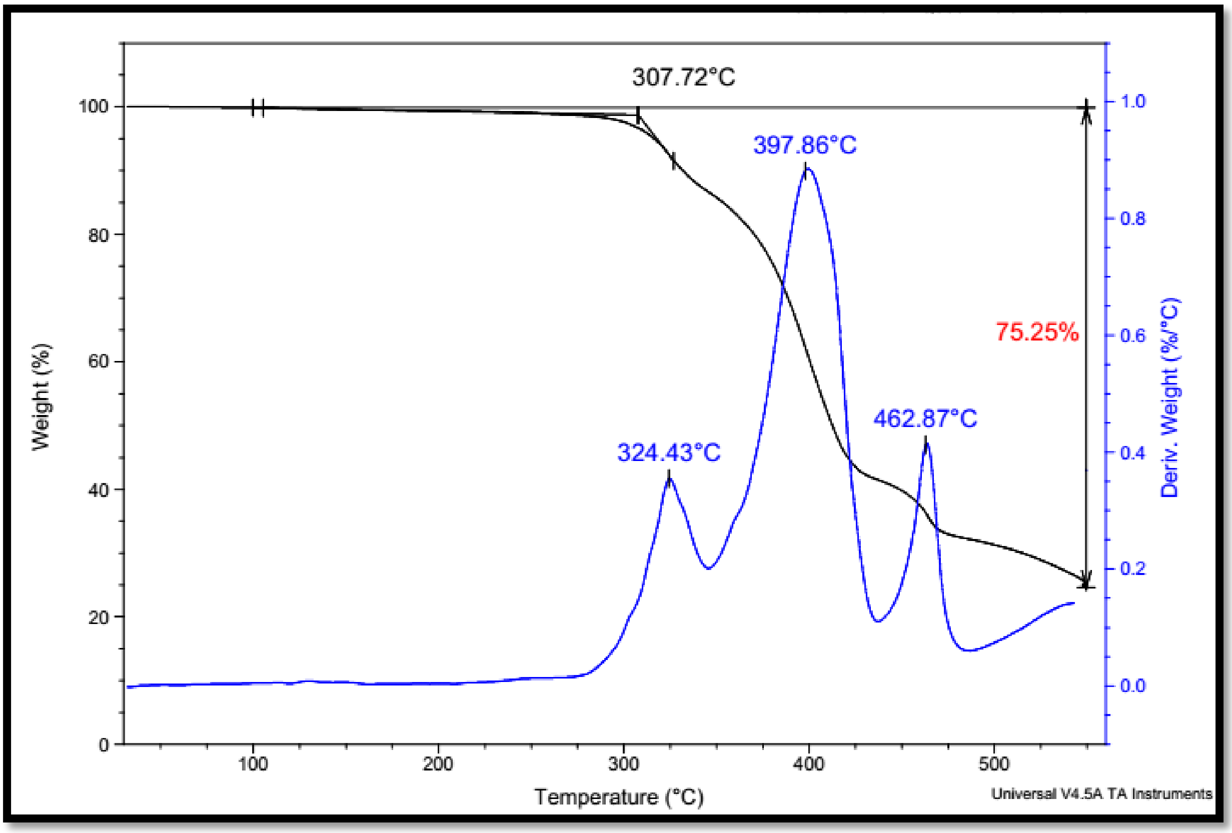


Figure 37- Results of the TGA of BioCamp Sample in oxidant atmosphere (air)

From TGA analysis, represented in Figure 37 with the derivative of the loss weight, is possible to see three weight loss about 75 % that goes from 275 °C to 550 ºC with onset at 308 ºC and degradation maximum peaks of 324, 398 and 463 ºC with a final residue of 25% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

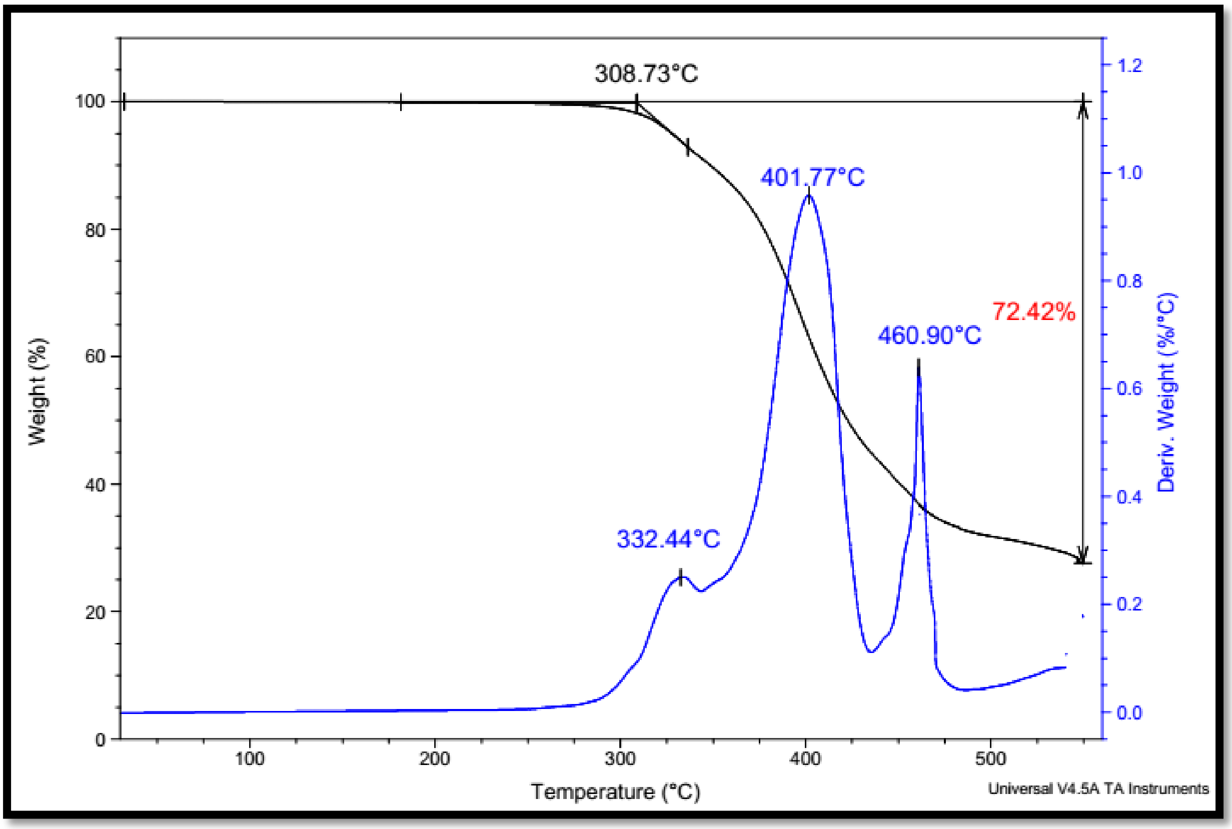


Figure 38- Results of TGA of BioTech in oxidant atmosphere (air)

From TGA analysis, represented in Figure 38 with the derivative of the loss weight, is possible to see three weight loss about 72% that goes from 275 °C to 550 ºC with onset at 309 ºC and degradation maximum peaks of 332, 402 and 461 ºC with a final residue of 28% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

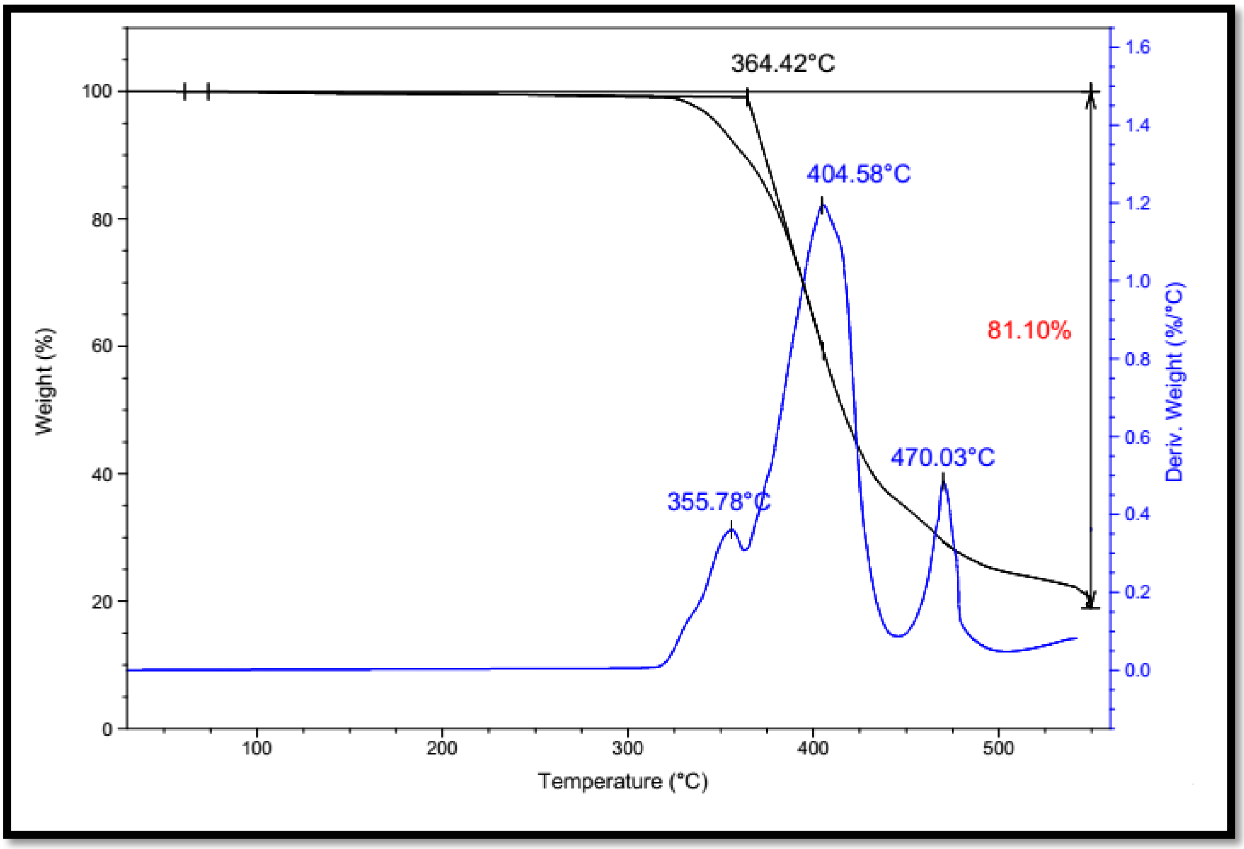


Figure 39- Results of the TGA of Basf Ecovio in oxidant atmosphere (air)

From TGA analysis, represented in Figure 39 with the derivative of the loss weight, is possible to see three weight loss about 81% that goes from 300 °C to 550 ºC with onset at 364 ºC and degradation maximum peaks of 405 and 470 ºC with a final residue of 19% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

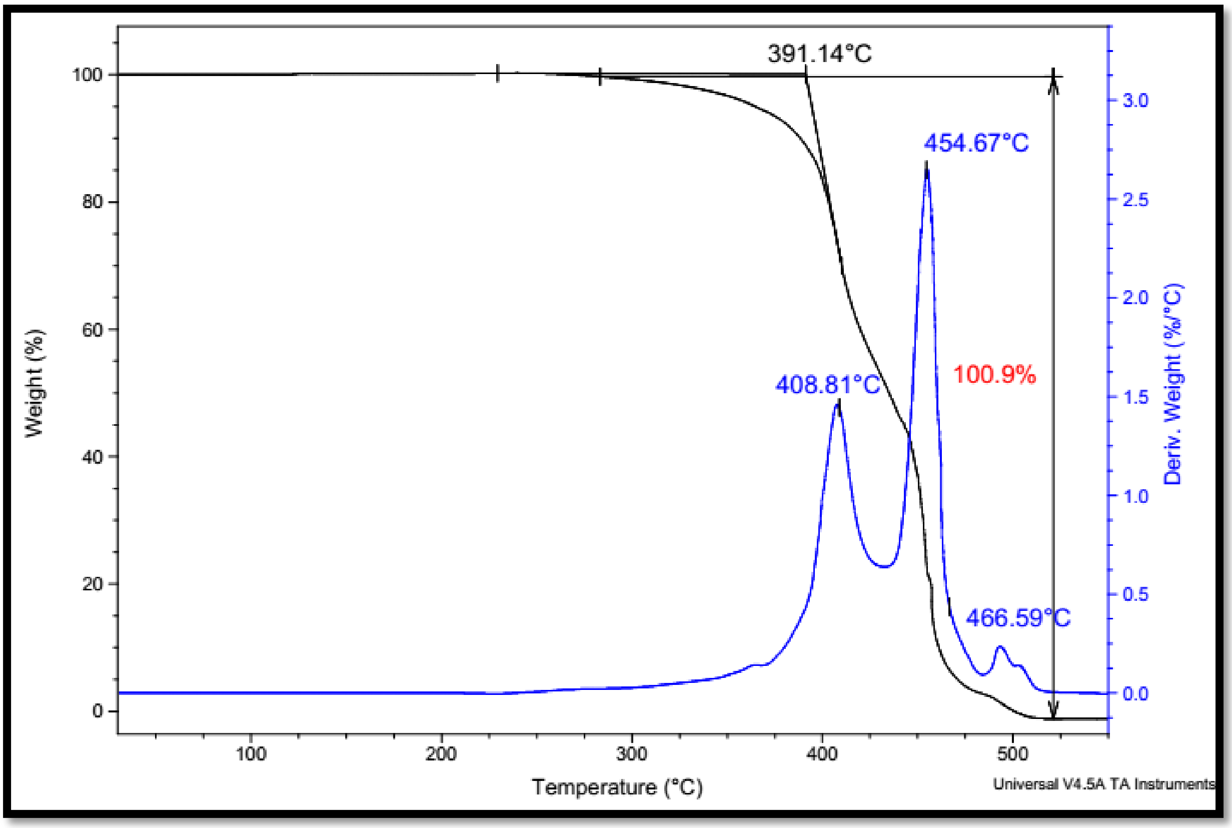


Figure 40- Results of the TGA analysis of Rigenerato Neutro in oxidant atmosphere (air)

From TGA analysis, represented in Figure 40 with the derivative of the loss weight, is possible to see three weight that goes from 250 °C to 510 ºC with onset at 391 ºC and degradation maximum peaks of 409, 455 and 467 ºC with no final residue during the isotherm step in air at 550 ºC.

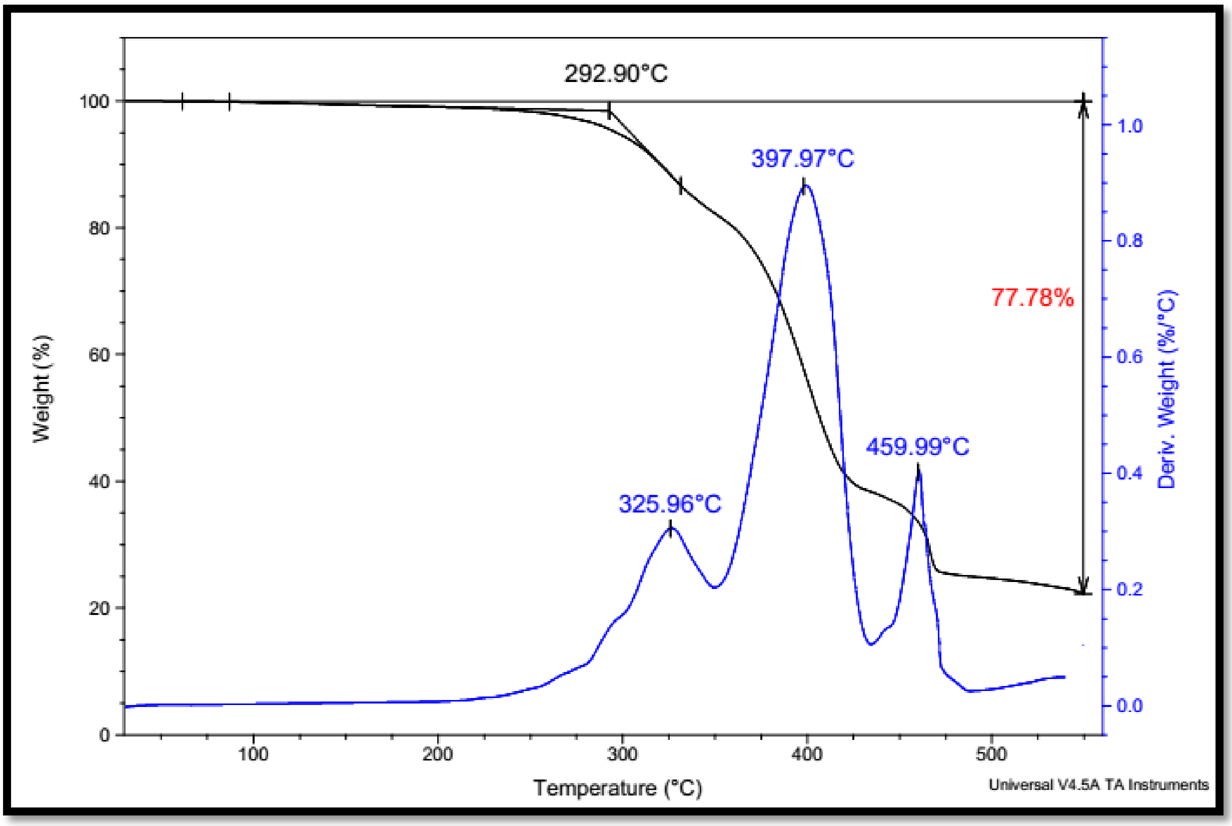


Figure 41- Results of the TGA of Rigenerato Bio in oxidant atmosphere (air)

From TGA analysis, represented in Figure 41 with the derivative of the loss weight, is possible to see three weight loss about 78 % that goes from 200 °C to 550 ºC with onset at 293 ºC and degradation maximum peaks of 326, 398 and 460 ºC with a final residue of 22% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

3.1.3 Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) permits to evaluate the glass transition temperature (T_g), the melting point and melting enthalpy necessary to quantify the crystalline phase useful for the realization of the characteristics of the raw material. In particular, for the raw material, the DSC is important to know the working temperatures in extruder. For a better evaluation of the characteristics of the material is necessary considering the second cycle of heating. During the second scan the thermic story of the material is canceled and the Tg of the material is lower. This is due to some stretching of the polymeric chains during the endothermic reaction and the Tg in the second scan have a higher transition scale.

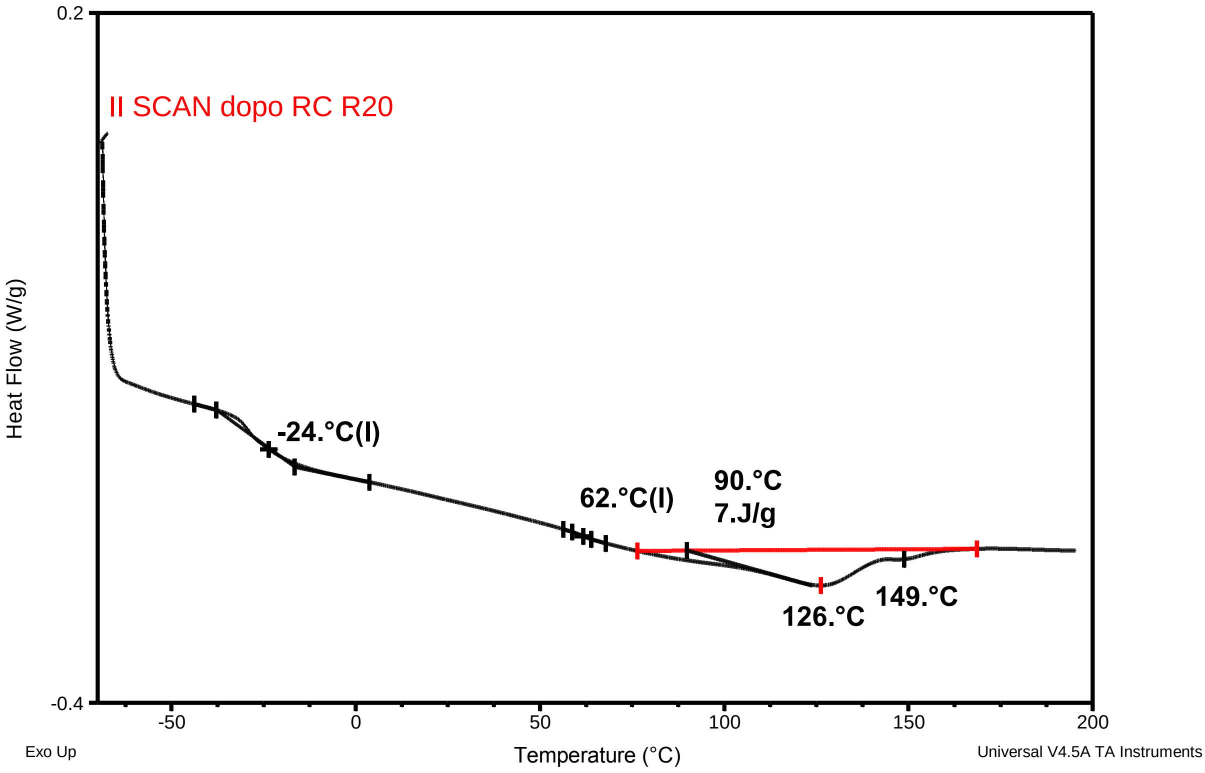


Figure 42- Thermogram of the Second heating DSC at 20°C/min of Basf Ecovio

From Differential Scaning Calorimetry (DSC), can be observed two step transitions at -24 and 62 °C ascribed to the T_g of the two components of the blend and two endothermic peaks at 124 and 149 °C, attributed to the melting of crystalline part of the material.

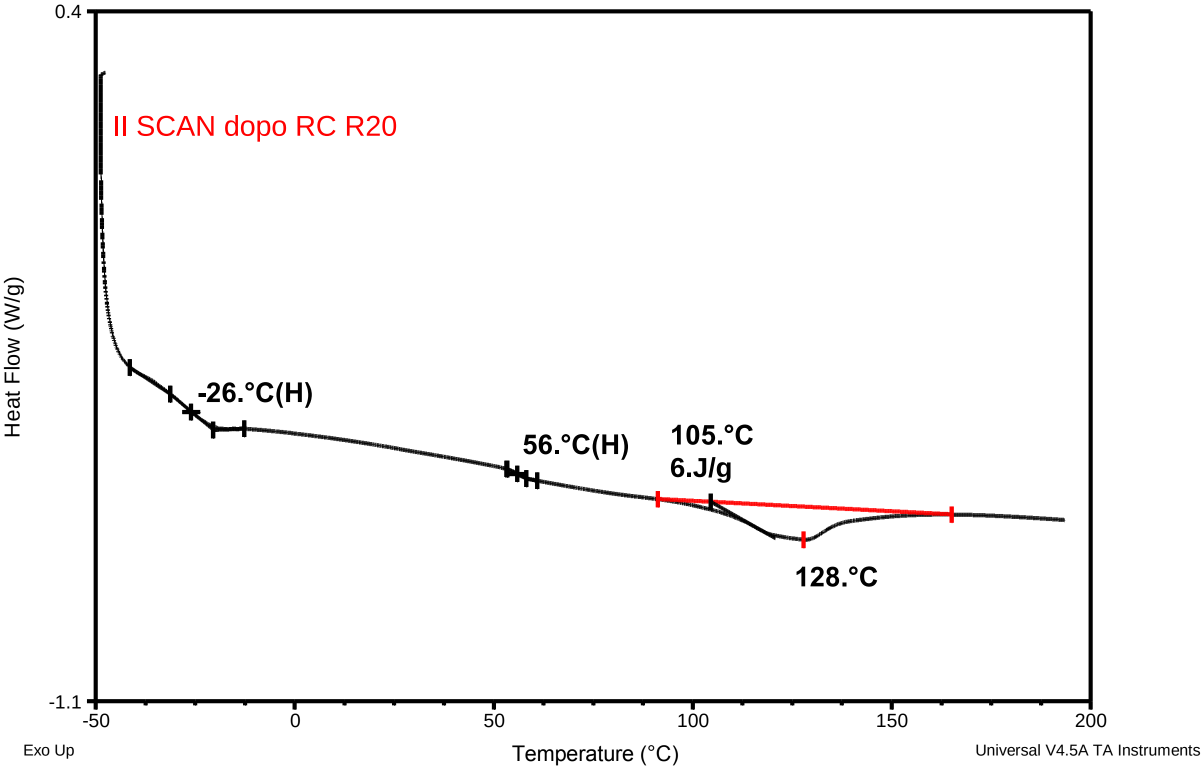


Figure 43 - Thermogram of the Second heating DSC at 20°C/min of BioCamp

From Differential Scaning Calorimetry (DSC), can be observed two step transitions at -26 and 56 °C ascribed to the T_g of the two components of the blend and an endothermic peaks at 128°C attributed to the melting of crystalline part of the material.

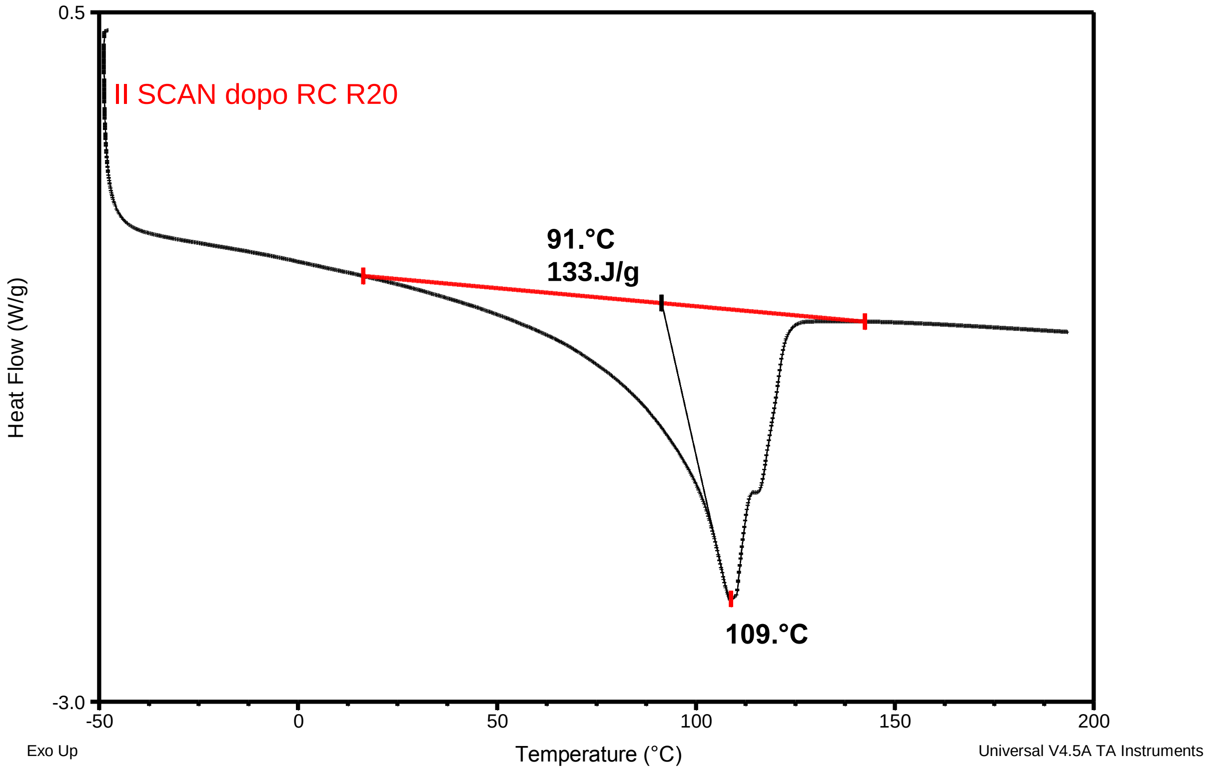


Figure 44 - Thermogram of the Second heating DSC at 20°C/min of Rig:Bianco

From Differential Scaning Calorimetry (DSC), can be observed an endothermic peaks at 109°C attributed to the melting of crystalline part of LDPE . The melting temperature is proper of the LDPE like in FT-IR/ATR is shown.

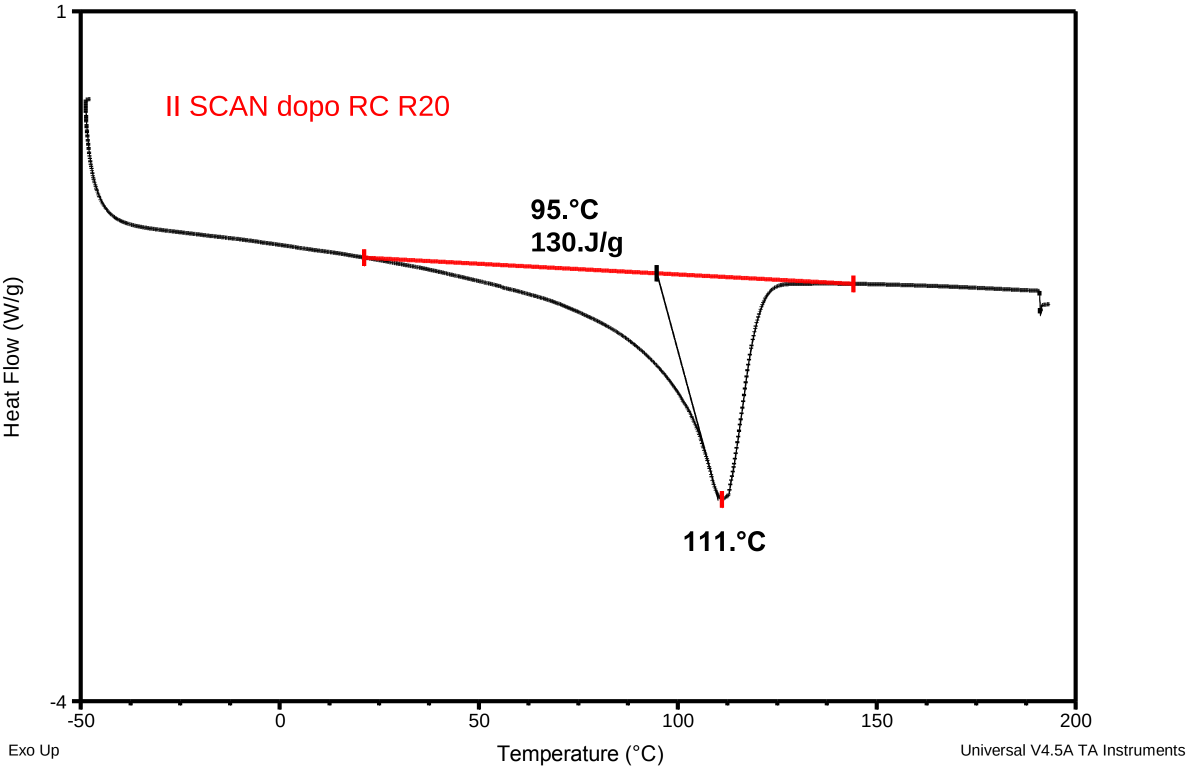


Figure 45- Thermogram of the Second heating DSC at 20°C/min of Rig:Neutro

From Differential Scaning Calorimetry (DSC), can be observed an endothermic peaks at 111°C attributed to the melting of crystalline part of the material. The melting temperature is proper of the LDPE like in FT-IR/ATR is shown.

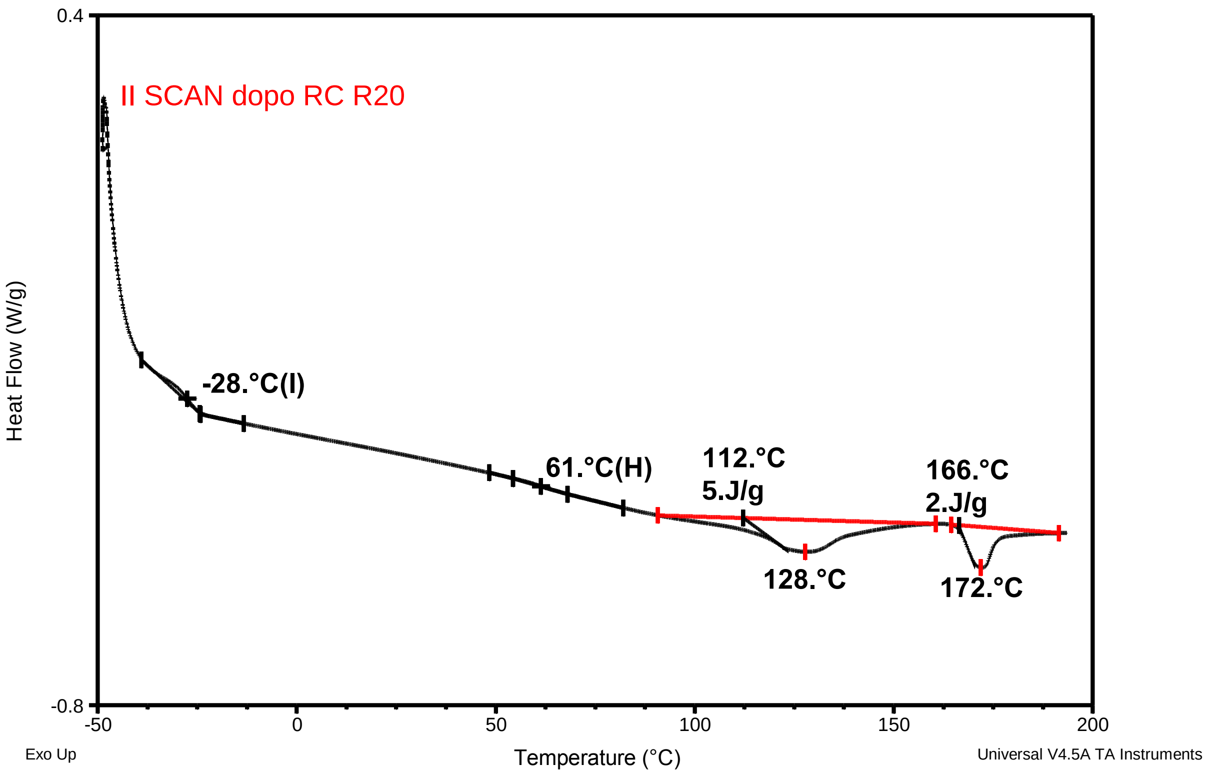


Figure 46 - Thermogram of the Second heating DSC at 20°C/min of BioTech

From Differential Scaning Calorimetry (DSC), can be observed two step transitions at -28 and 61 °C ascribed to the T_g of the two components of the blend and two endothermic peaks at 128 and 172 °C, attributed to the melting of crystalline part of the material.

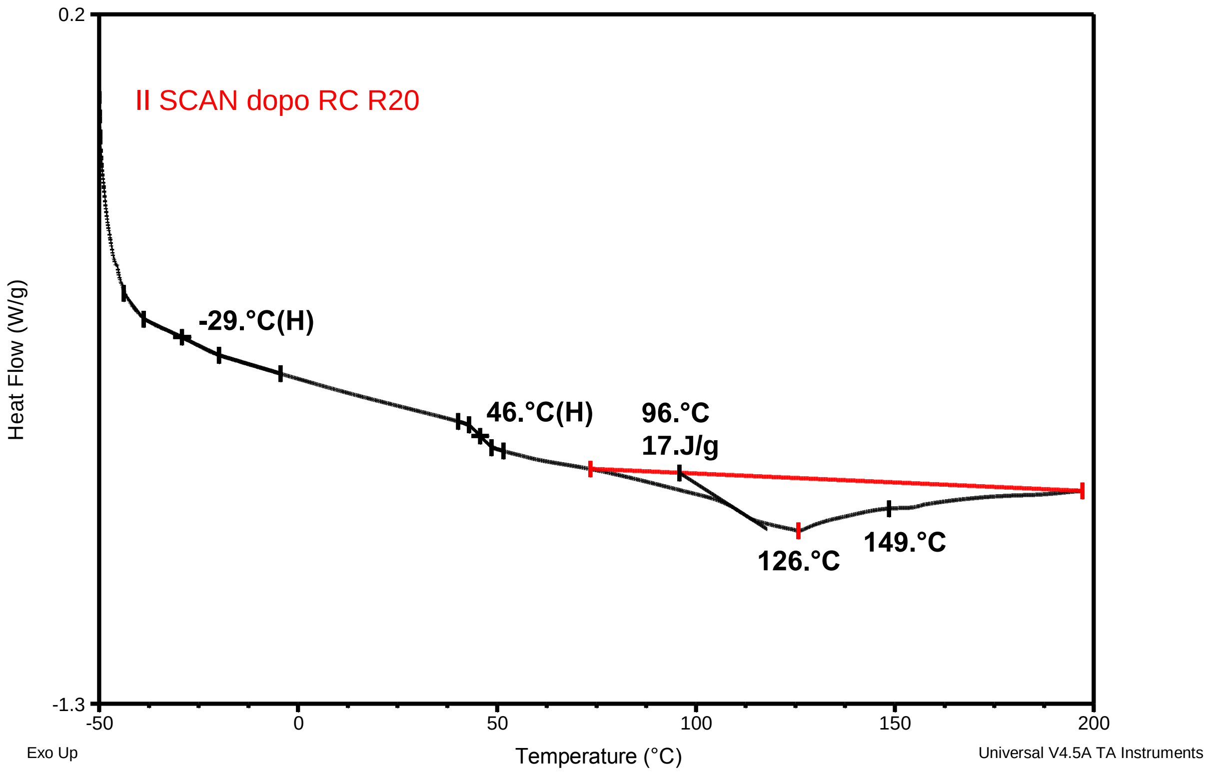


Figure 47 - Thermogram of the Second heating DSC at 20°C/min of RigBio

From Differential Scaning Calorimetry (DSC), can be observed two step transitions at -29 and 46 °C ascribed to the T_g of the two components of the blend and two endothermic peaks at 126 and 149 °C, attributed to the melting of crystalline part of the material.

3.2 Characterization of plastic bags

3.2.1 Attenuated Total Reflectance

For all ATR analysis done for the commercial plastic bags no spectral differences were observed. The only one difference is related to the inorganic fraction residue represented in the fingerprint region.

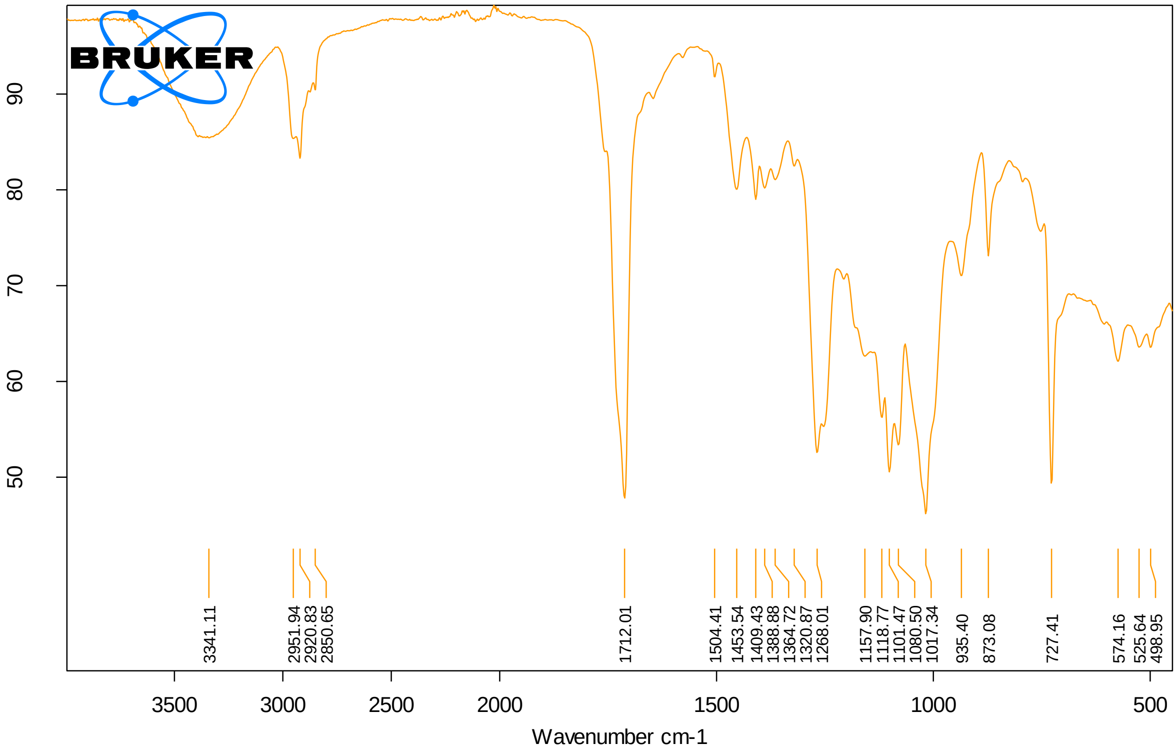


Figure 48 - FT-IR/ATR of INS Bag

From the comparison of FT-IR /ATR spectra of IN'S plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 48. It is able to determine some important bands like: 3041 cm^{-1} – corresponding to a symmetric Stretching of CH$_3$, 1712 cm^{-1} corresponding to a C=O Stretching, 1268 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

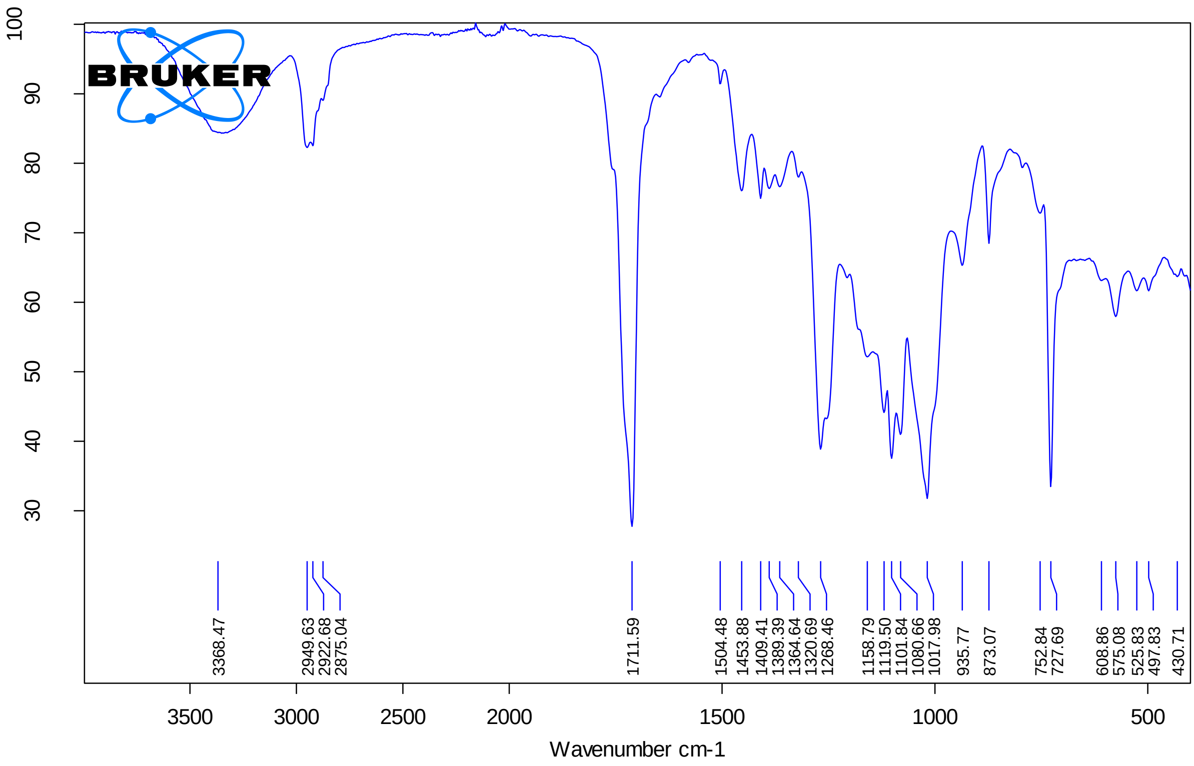


Figure 49 - FT-IR/ATR of Carrefour Bag

From the comparison of FT-IR /ATR spectra of Carrefour plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 49. It is able to determine some important bands like: 2049 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1711 cm^{-1} corresponding to a C=O Stretching, 1268 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

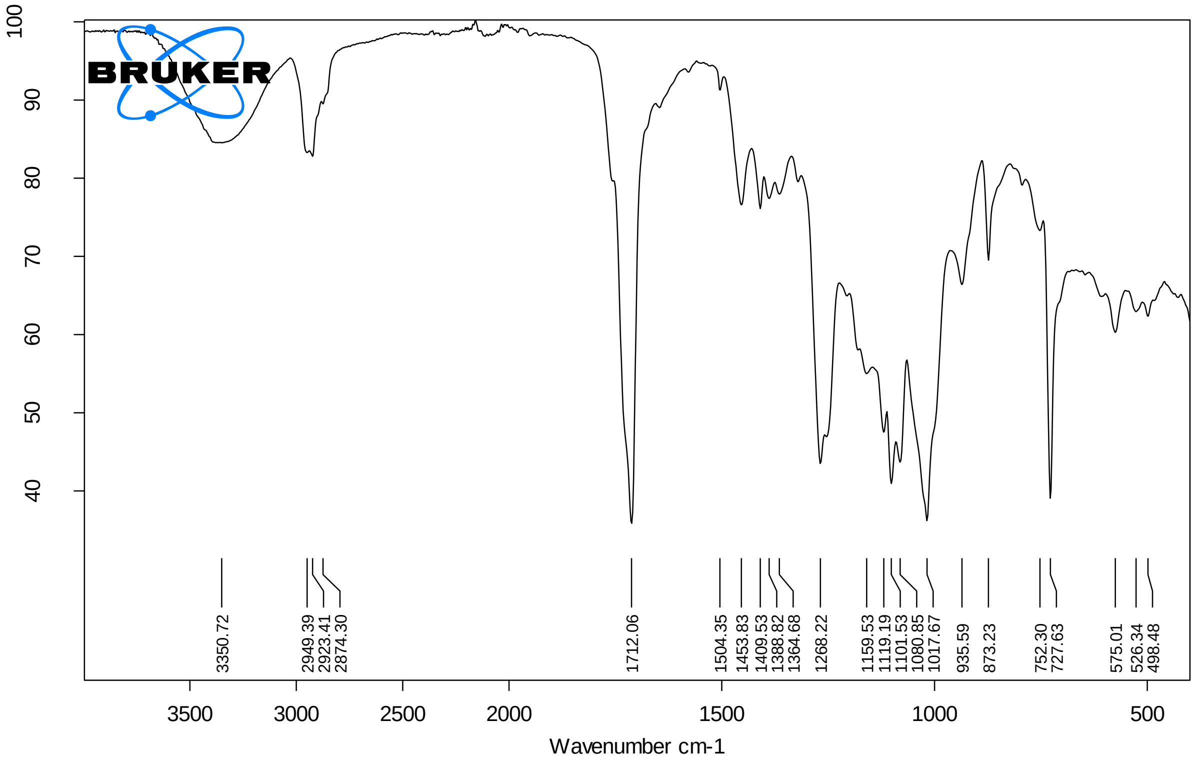


Figure 50 - FT-IR/ATR of Esselunga Bag

From the comparison of FT-IR /ATR spectra of Esselunga plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 50. It is able to determine some important bands like: 2949 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1712 cm^{-1} corresponding to a C=O Stretching, 1269 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

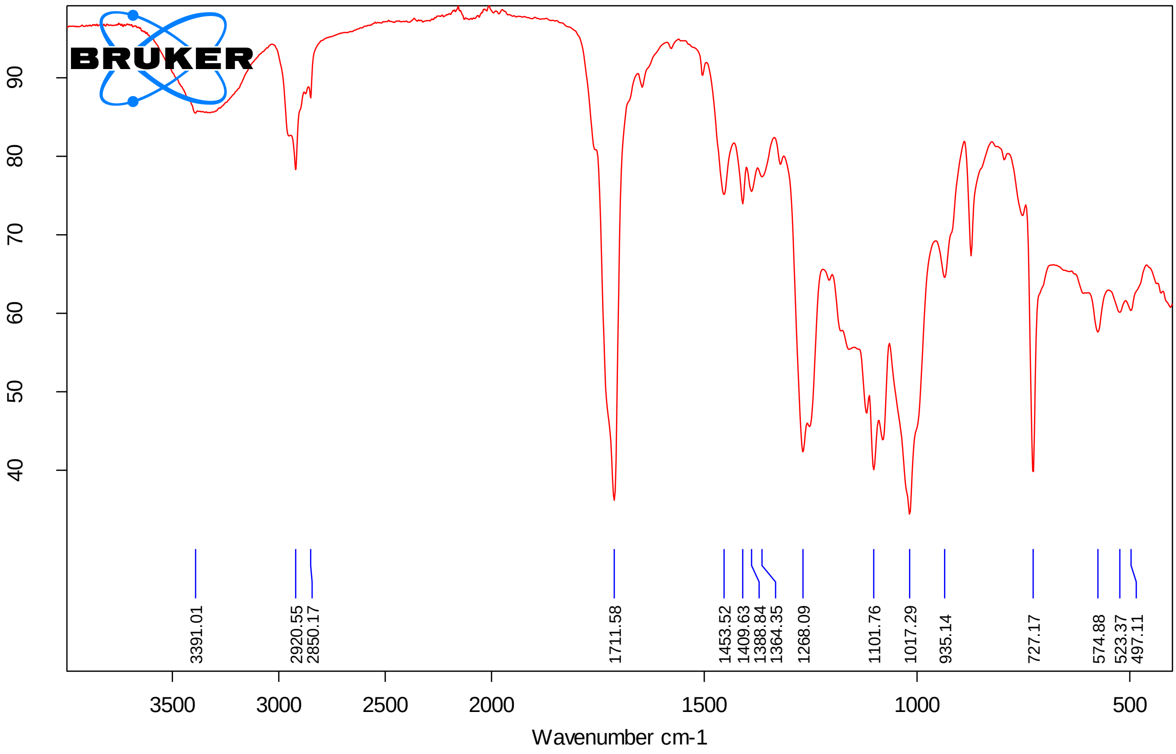


Figure 51 - FT-IR/ATR of COOP Bag

From the comparison of FT-IR /ATR spectra of COOP plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 51. It is able to determine some important bands like: 2921 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1712 cm^{-1} corresponding to a C=O Stretching, 1288 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

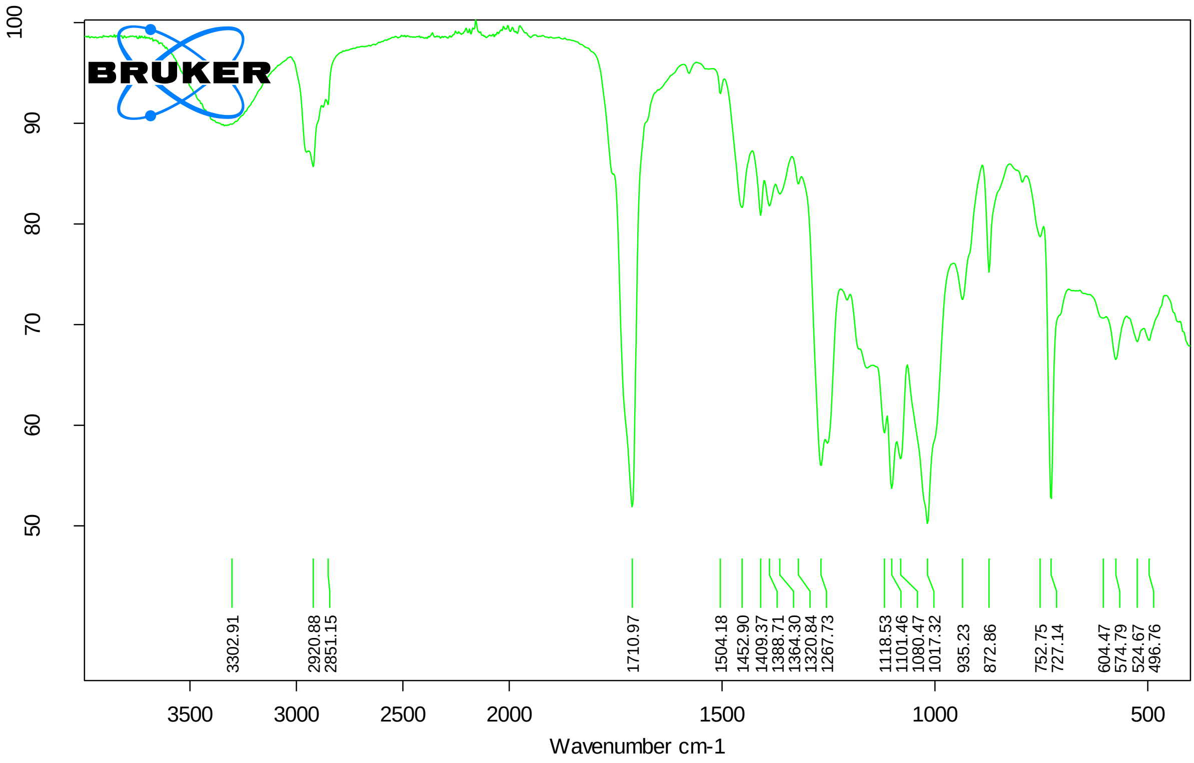


Figure 52 - FT-IR/ATR of BioF3 Bag

From the comparison of FT-IR /ATR spectra of BioF3 plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 52. It is able to determine some important bands like: 2921 cm^{-1} – corresponding to a symmetric Stretching of CH$_3$, 1711 cm^{-1} corresponding to a C=O Stretching, 1288 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material.

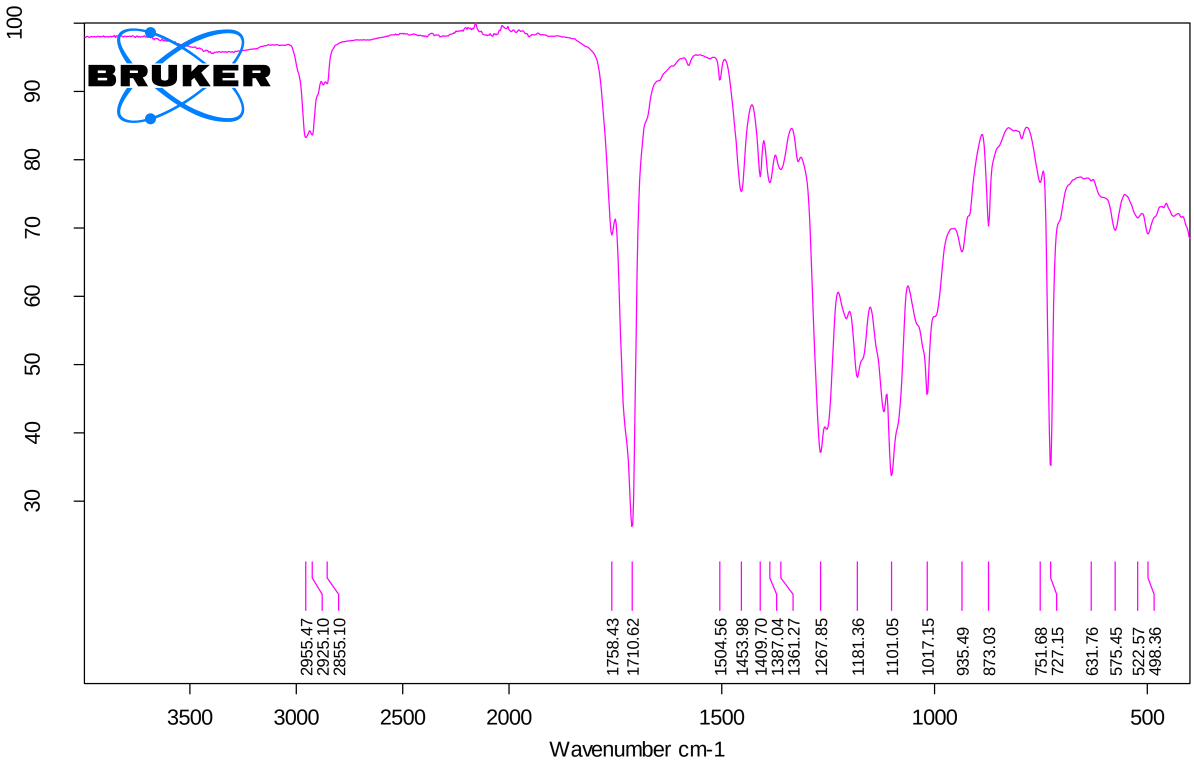


Figure 53 - FT-IR/ATR of Transparent Bag

From the comparison of FT-IR /ATR spectra of Transparent plastic bag with database furnished by Bruker, was identified the spectra of Polylactic acid (PLA) like shown in the figure 53. It is able to determine some important bands like: 2966 cm^{-1} – corresponding to a symmetric Stretching of CH_3, 1711 cm^{-1} corresponding to a C=O Stretching, 1268 cm^{-1} corresponding to a symmetric Stretching of COC. From the fingerprint bands (1500 – 500 cm^{-1}) is possible to identify the bands ascribed to the inorganic fraction of the raw material. From the fingerprint bands is possible to say that this sample do not have an inorganic residue.

3.2.2 Thermogravimetric analysis

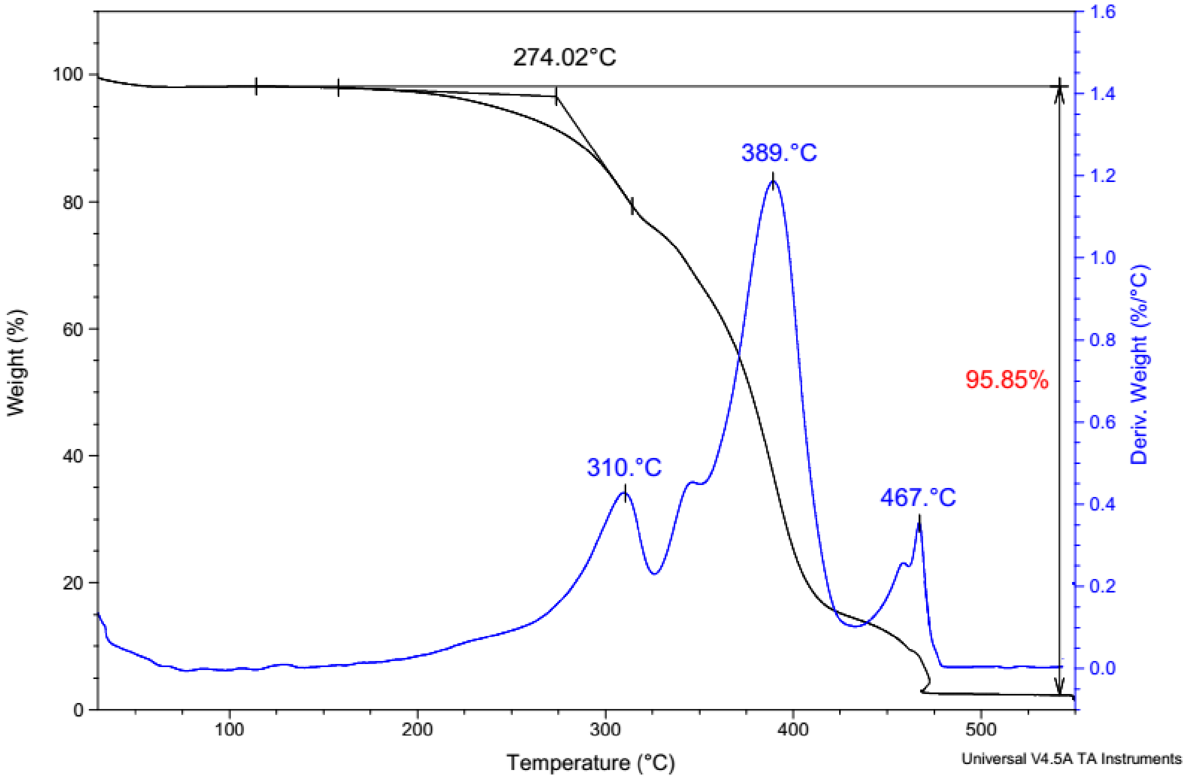


Figure 54 - Results of the TGA of Coop Bag in oxidant atmosphere (air)

For Coop plastic bag, from TGA analysis, represented in Figure 54 with the derivative of the loss weight, is possible to see three weight loss from 190 °C to 470 ºC with onset at 274 ºC and degradation maximum peaks of 310, 389 and 467 ºC with a final residue of 4% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

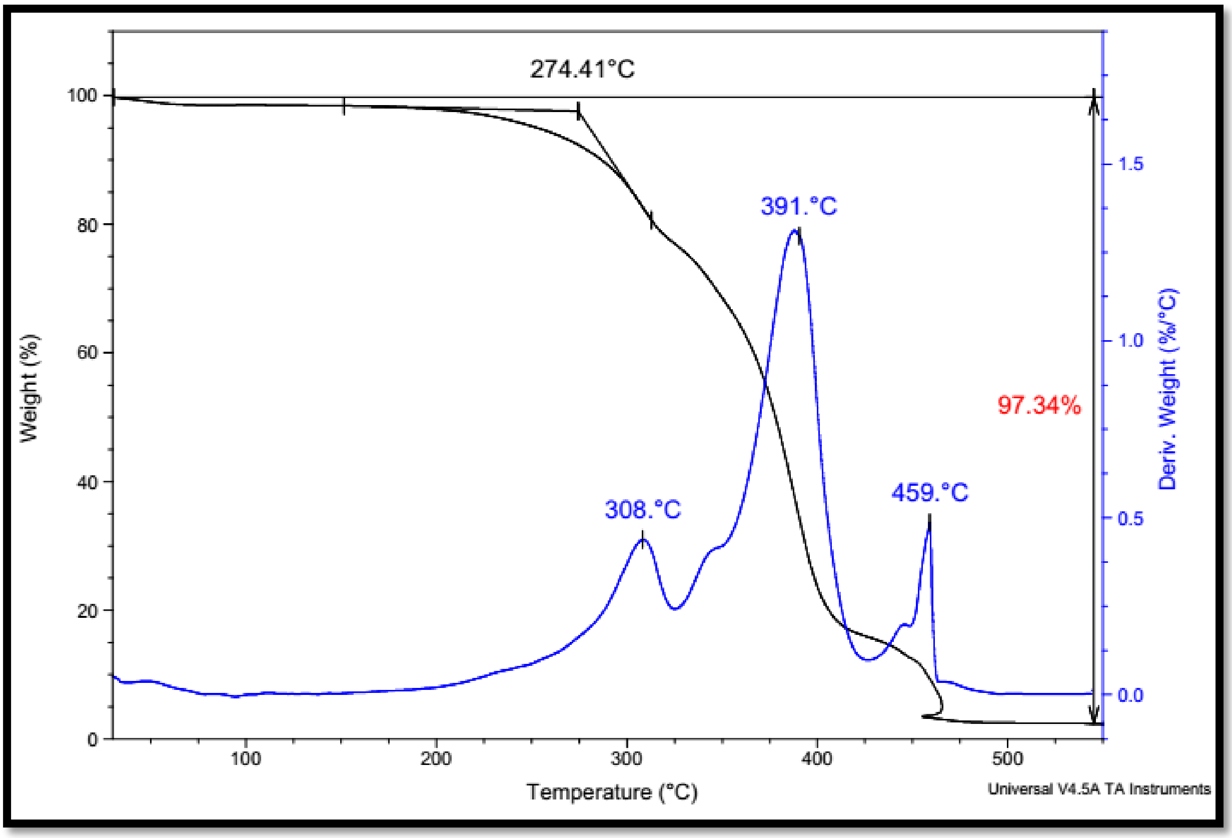


Figure 55- Results of the TGA of INS Bag in oxidant atmosphere (air)

From TGA analysis, represented in Figure 55 with the derivative of the loss weight, is possible to see three weight losses from 200 °C to 490 ºC with onset at 274 ºC and degradation maximum peaks of 308, 391 and 459 ºC with a final residue of 3% that doesn't degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

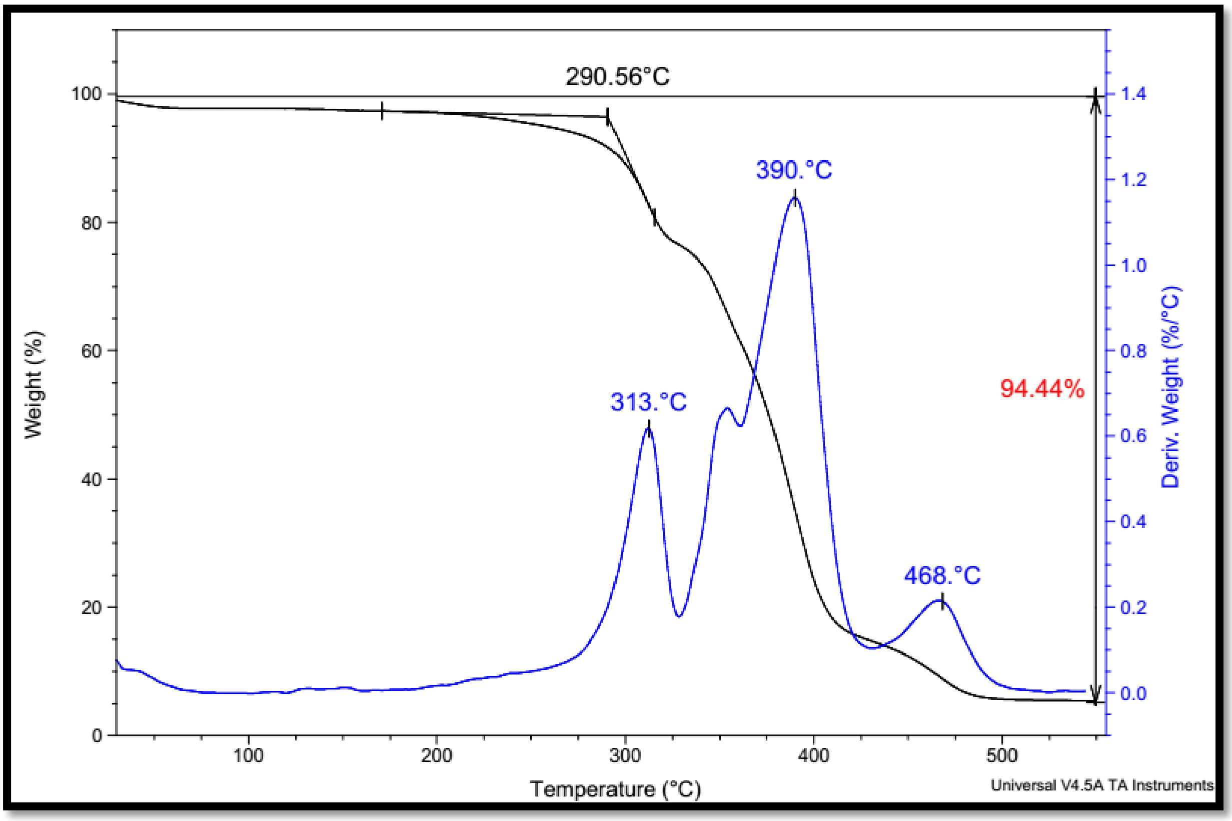


Figure 56 - Results of the TGA of Esselunga Bag in oxidant atmosphere (air)

From TGA analysis, represented in Figure 56 with the derivative of the loss weight, is possible to see three weight losses from 200 °C to 495 ºC with onset at 291 ºC and degradation maximum peaks of 313, 390 and 468 ºC with a final residue of 6% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

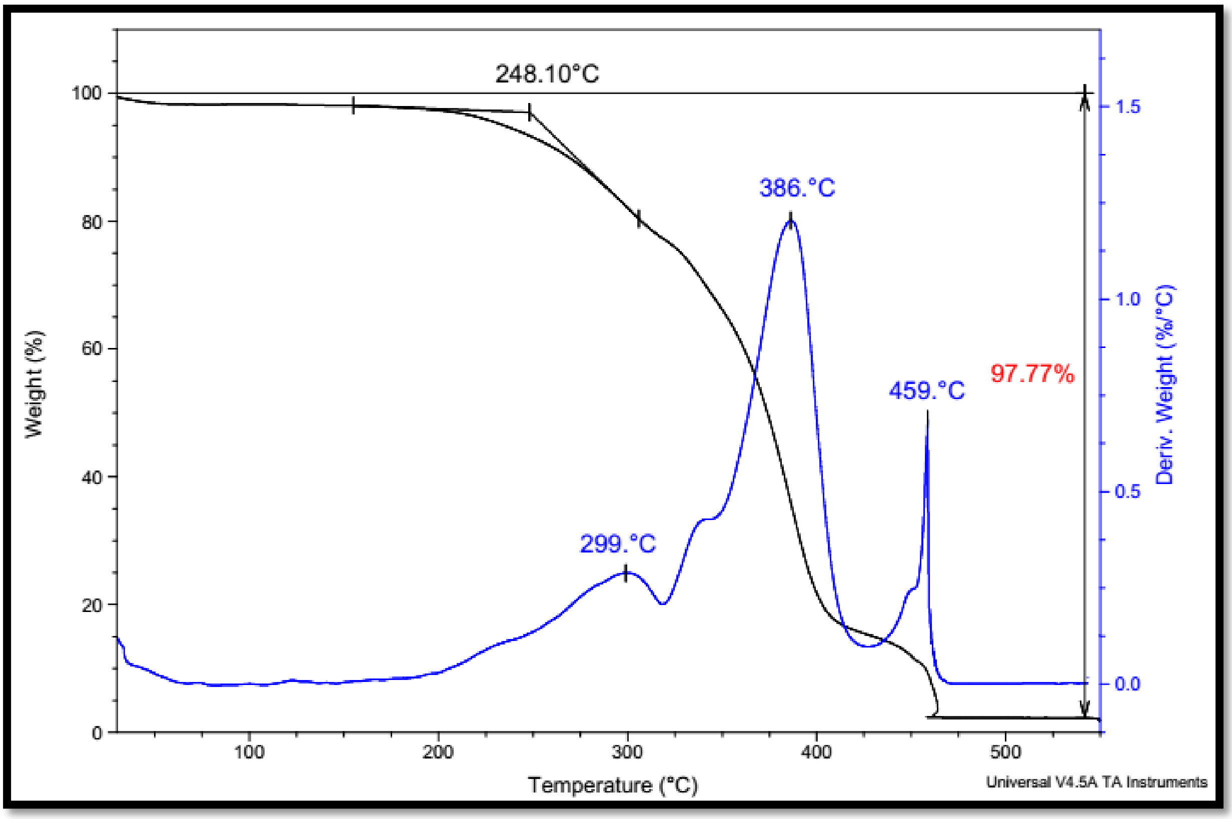


Figure 57 - Results of the TGA of BioF3 Bag in oxidant atmosphere (air)

From TGA analysis, represented in Figure 57 with the derivative of the loss weight, is possible to see three weight losses from 200 °C to 460 ºC with onset at 248 ºC and degradation maximum peaks of 299, 386 and 459 ºC with a final residue of 2% that doesn't degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

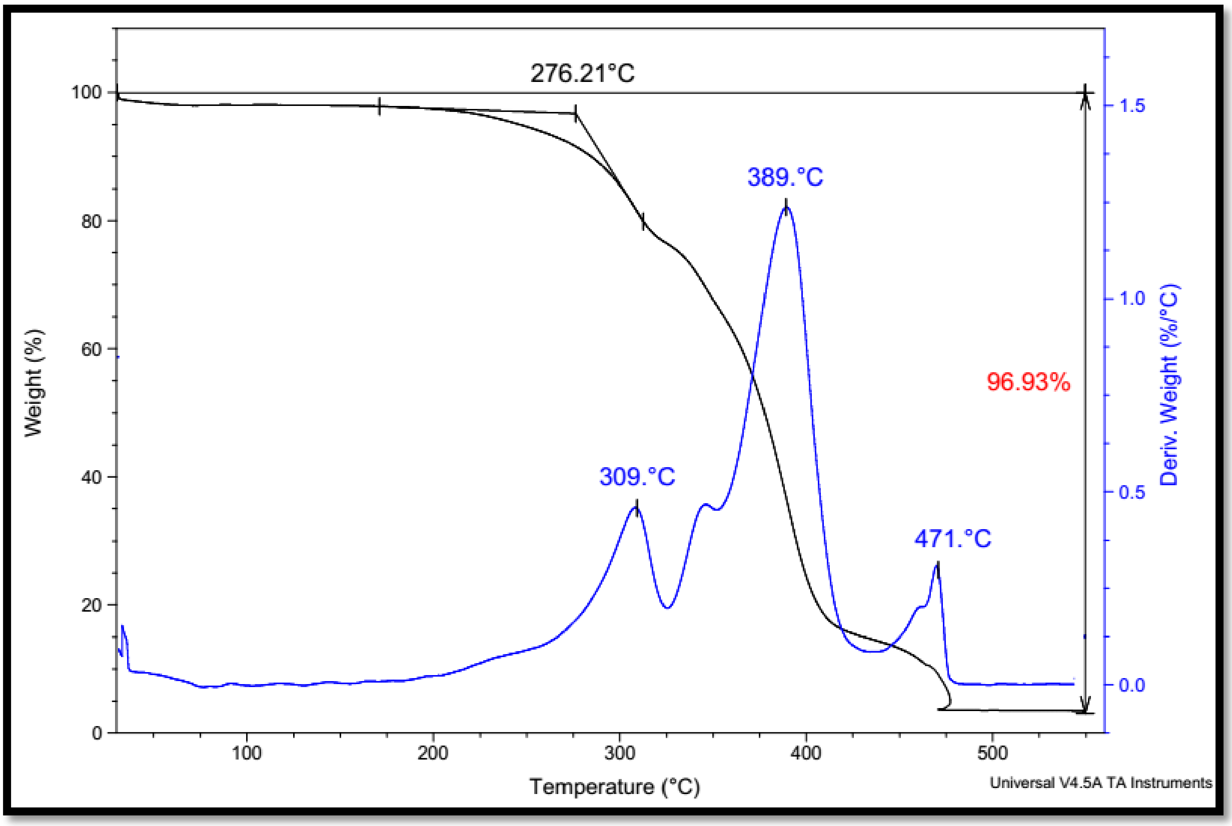


Figure 58 - Results of the TGA of Carrefour Bag in oxidant atmosphere (air)

From TGA analysis, represented in Figure 58 with the derivative of the loss weight, is possible to see three weight losses from 200 °C to 490 ºC with onset at 276 ºC and degradation maximum peaks of 309, 389 and 471 ºC with a final residue of 3% that doesn’t degrade during the isotherm step in air at 550 ºC, index of the inorganic fraction in the material.

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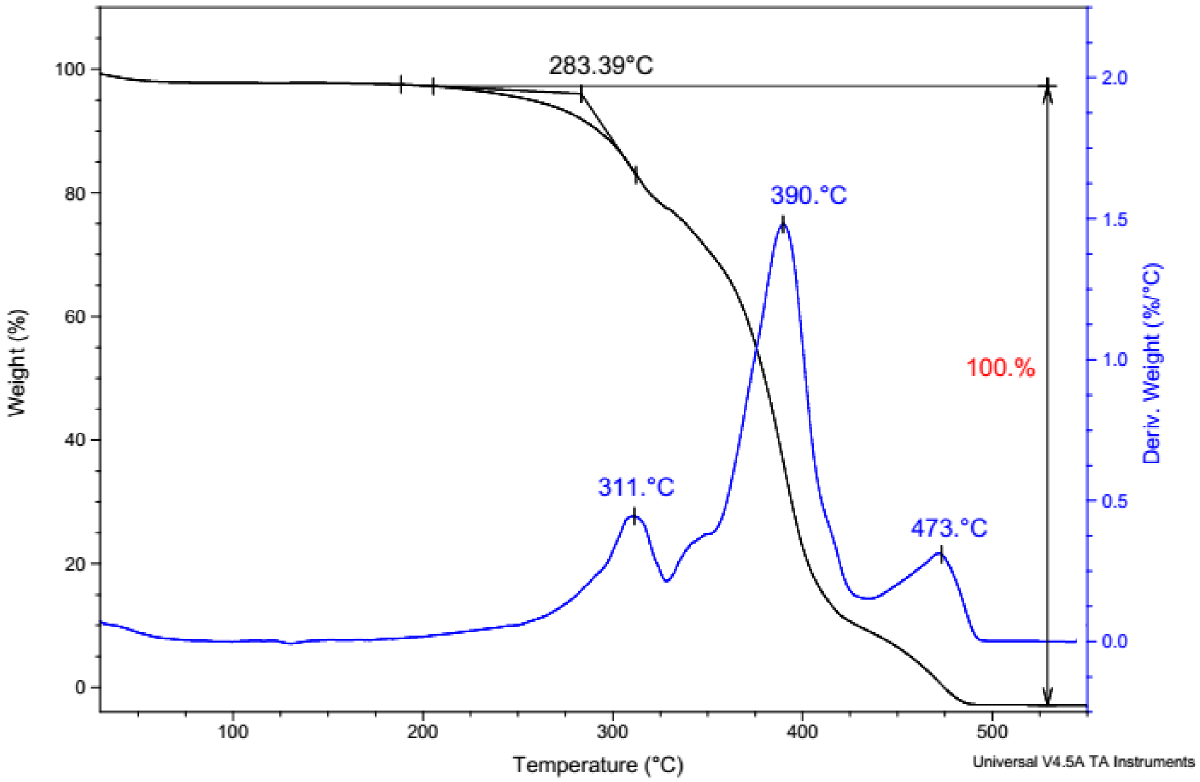


Figure 59 - Results of the TGA of Transparent Bag in oxidant atmosphere (air)

From TGA analysis, represented in Figure 59 with the derivative of the loss weight, is possible to see three weight losses from 200 °C to 490 ºC with onset at 284 ºC and degradation maximum peaks of 311, 390 and 473 ºC with no final residue during the isotherm step in air at 550 ºC. The presence of three weight losses indicates that the material is decomposed from a polymeric blend. In particular the bag show a higher thermal stability (onset 383°C) than commercial bags without inorganic residue. From the company was reported that one of the raw material pellets was used to produce the transparent plastic bag, but no one of the raw materials match with the transparent plastic bag spectra. From TGA was verified that Biocomp, Biotech, Basf Ecovio and Rig Bio have an inorganic residue that is not present in the transparent plastic bag. The only one that doesn’t have inorganic residue is the sample Rig. Neutro, but from the ATR analysis was not possible to find a matching spectra with that of the transparent plastic bag.

To verify the fraction of inorganic residue determined from TGA analysis, the plastic bags were calcinated in muffle furnace for two hours at 550 ºC like are presented below. To determine the weight loss was performed another measurement in crucibles weighting the amount of the sample before and after the muffle furnace (Table 5).

Table 5. Weight losses of all the bags treated in muffle furnace at 550 ºC

		% Residue
Carrefour Bag	Exp 1	1.92
	Exp 2	1.94
	Exp 3	2.05
BIOF3 Bag	Exp 1	3.21
	Exp 2	3.79
	Exp 3	3.64
INS Bag	Exp 1	4.14
	Exp 2	4.13
	Exp 3	4.12
COOP Bag	Exp 1	4.19
	Exp 2	4.15
	Exp 3	4.27
Esselunga Bag	Exp 1	1.60
	Exp 2	1.83
	Exp 3	1.84
Transparent Bag	Exp 1	/
	Exp 2	/
	Exp 3	/

3.2.3 Humidity content

For all bags a humidity measurement was performed to know the amount of moisture adsorbed in the surface of the plastic. The samples were measured before and after exposure at 70ºC for 24 hours like shown in Table 6 .

Table 6. Humidity Loss measurements post furnace at 70º C

Esselunga Bag	**Exp 1**	%
	Humidity Loss	3
	Exp 2	
	Humidity Loss	2
Carrefour Bag	**Exp 1**	
	Humidity Loss	3
	Exp 2	
	Humidity Loss	2
IN'S Bag	**Exp 1**	
	Humidity Loss	2
	Exp 2	
	Humidity Loss	2
BioF3 Bag	**Exp 1**	
	Humidity Loss	3
	Exp 2	
	Humidity Loss	3
COOP Bag	**Exp 1**	
	Humidity Loss	2
	Exp 2	
	Humidity Loss	2
Transparent Bag	**Exp 1**	
	Humidity Loss	2
	Exp 2	
	Humidity Loss	2

3.2.4 Differential Scaning Calorimetry (DSC)

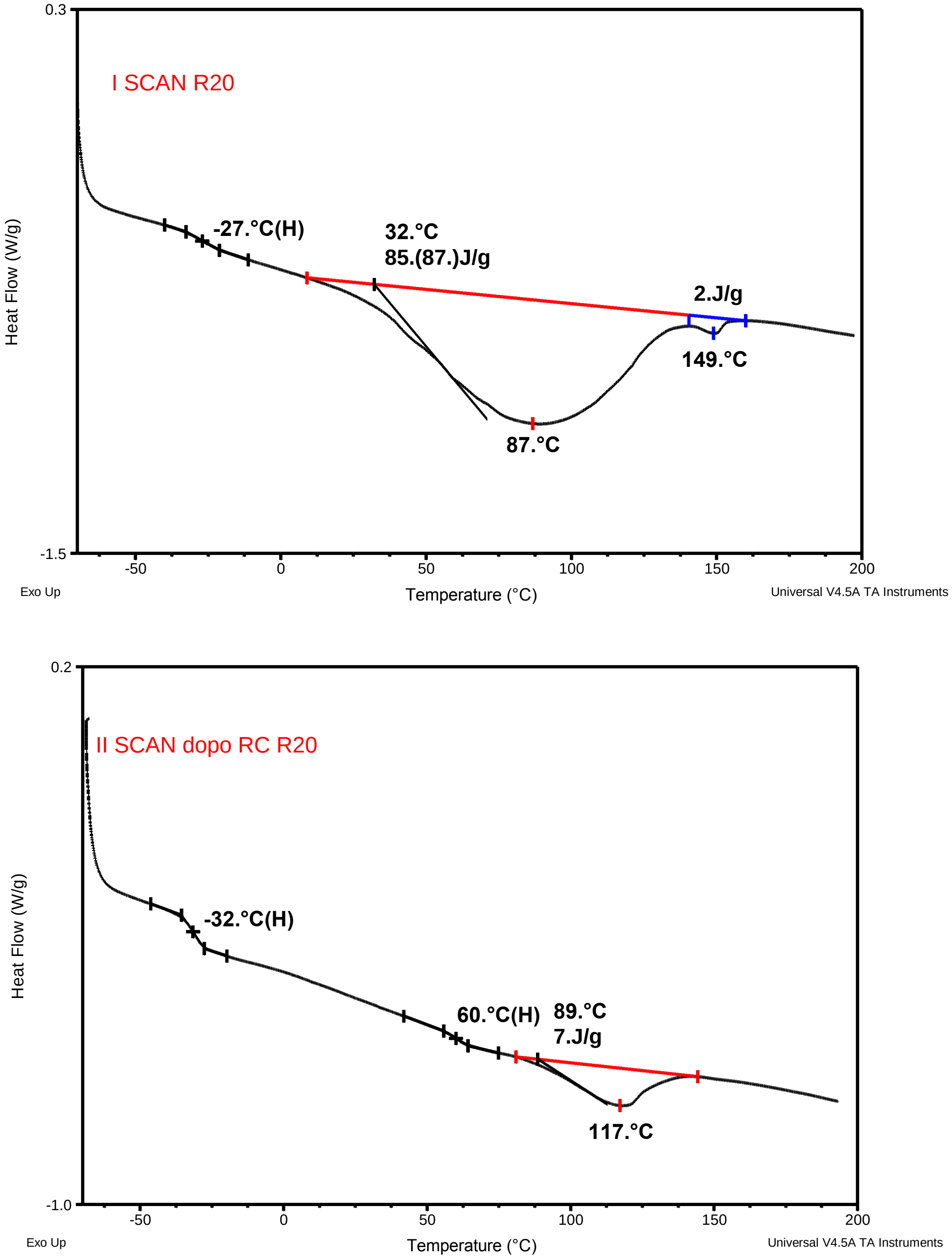
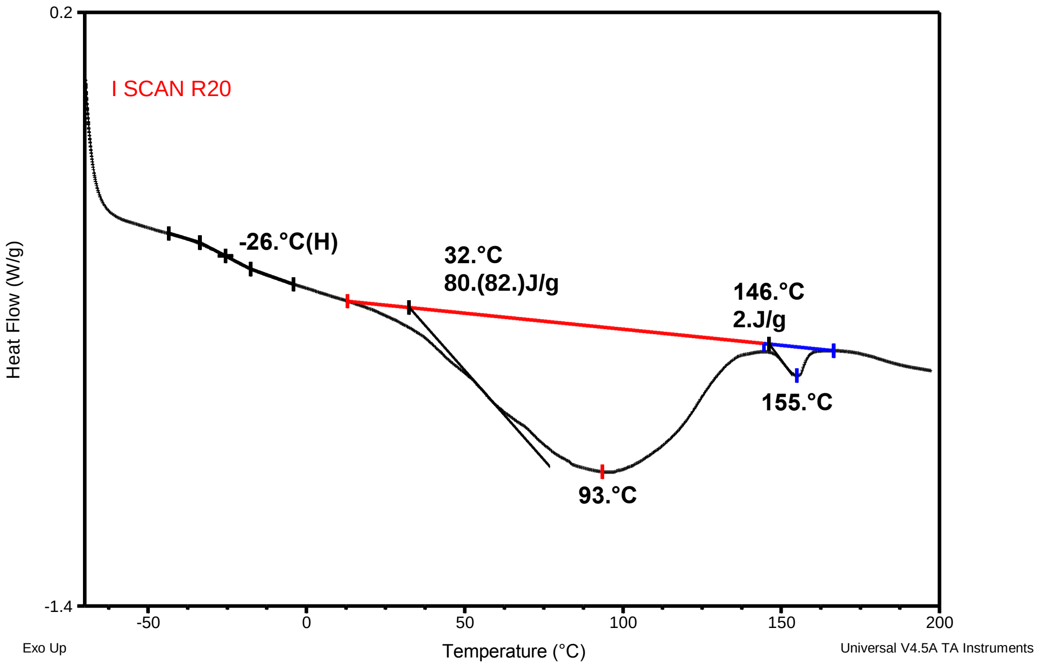


Figure 60 -First and second heating at 20°C/min of the INS bag

In the first heating can be observed a step transition at -27°C followed from an endothermic broad peak from 10 to 135°C, attributed to the molecular rearrangement and to the humidity loss and finally a second peak at 149°C ascribed to the melting of the crystalline phase. In the second heating there are two step transitions at -32 and 60°C ascribed at the glass transition followed from an endothermic peak at 117°C for the melting of the crystalline part.



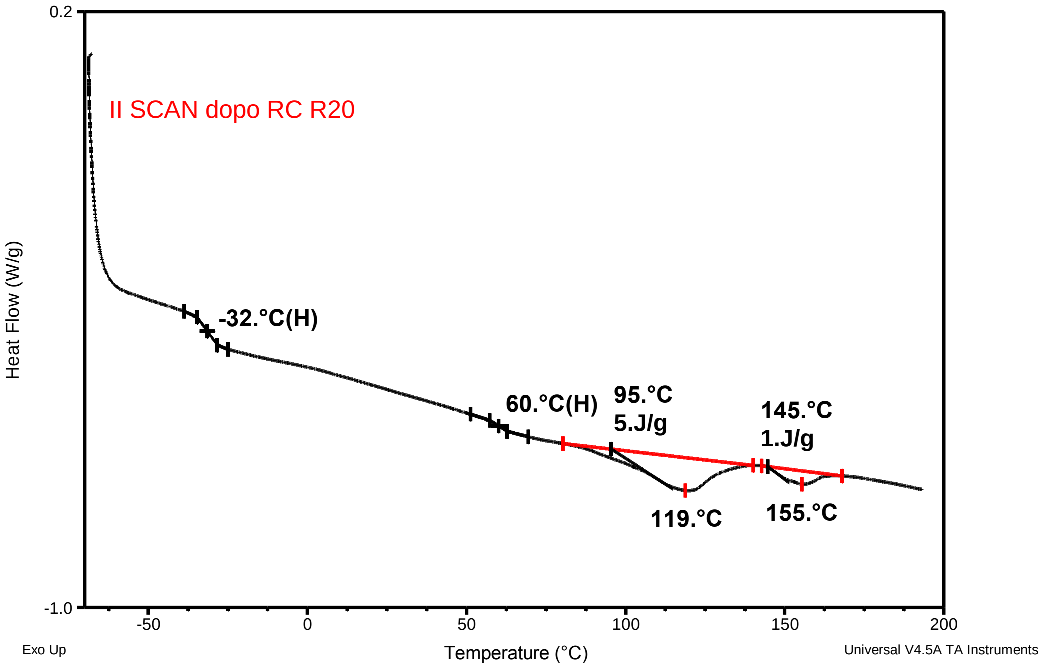
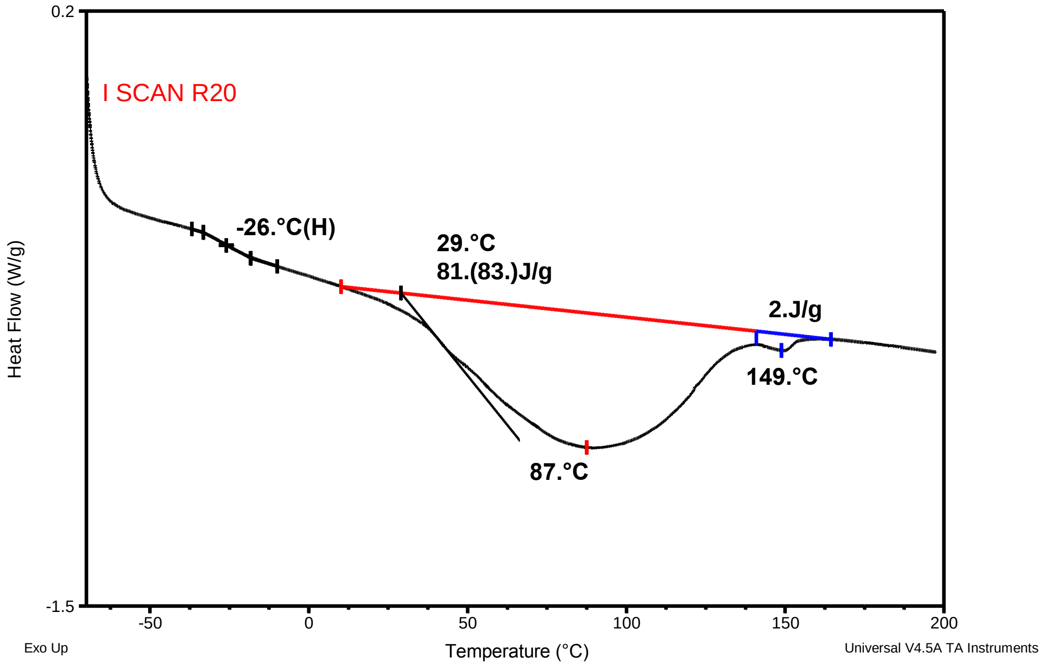


Figure 61-First and second heating at 20°C/min of the Esselunga bag

In the first heating can be observed a step transition at -26°C followed from an endothermic broad peak at from 10 to 135°C, attributed to the molecular rearrangement and the humidity loss and finally a second peak at 155°C ascribed to the melting of the crystalline phase. In the second heating there are two step transitions at -32 and 60°C ascribed at the glass transition followed from two endothermic peaks at 119 and 155°C for the melting of the crystalline part. During the first scan we have a rearrangement of molecular chains in order to let the plastic bag material obtain the original structure. In this case the Tg value do not change too much, but it appears to be more broader in scale. After the first scan the thermic story of the material is cancelled and the Tg have a proper scale transition due to the orientation of the molecular chains.



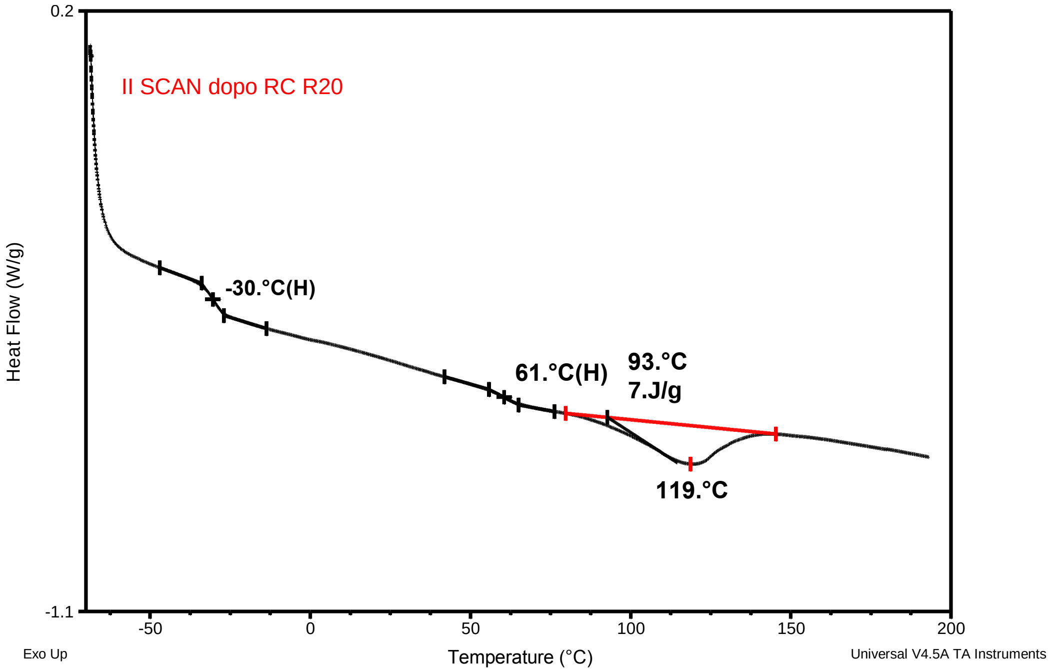
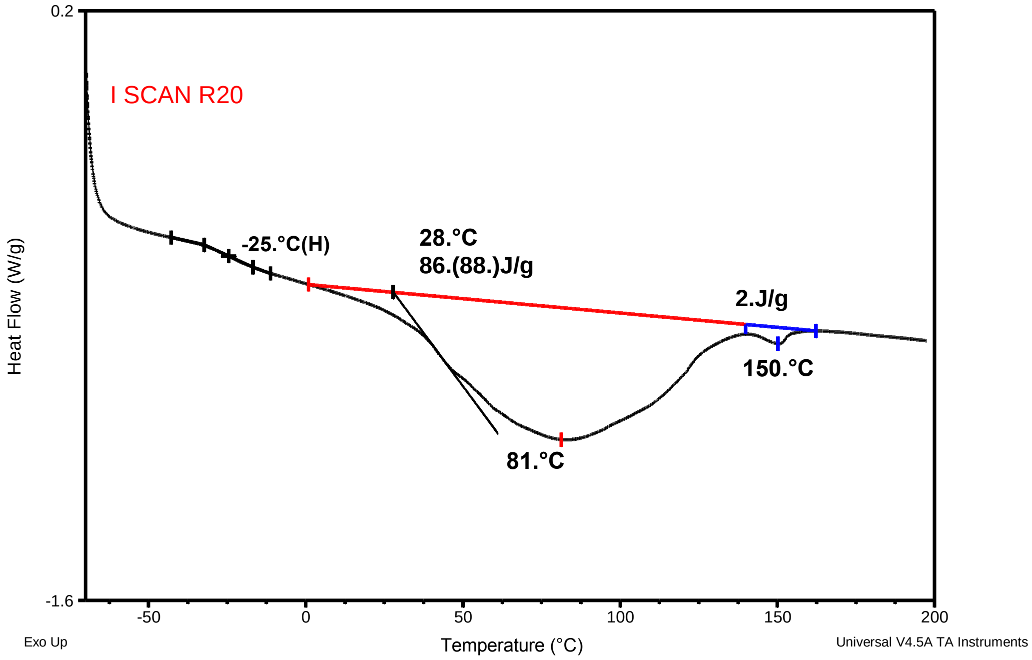


Figure 62 - First and second heating at 20°C/min of the Carrefour bag

In the first heating can be observed a step transition at -26°C followed from an endothermic broad peak at from 10 to 135°C, attributed to the molecular rearrangement and the humidity loss and finally a second peak at 149°C ascribed to the melting of the crystalline phase. In the second heating there are two step transitions at -30 and 61°C ascribed at the glass transition followed from an endothermic peak at 119°C for the melting of the crystalline part.



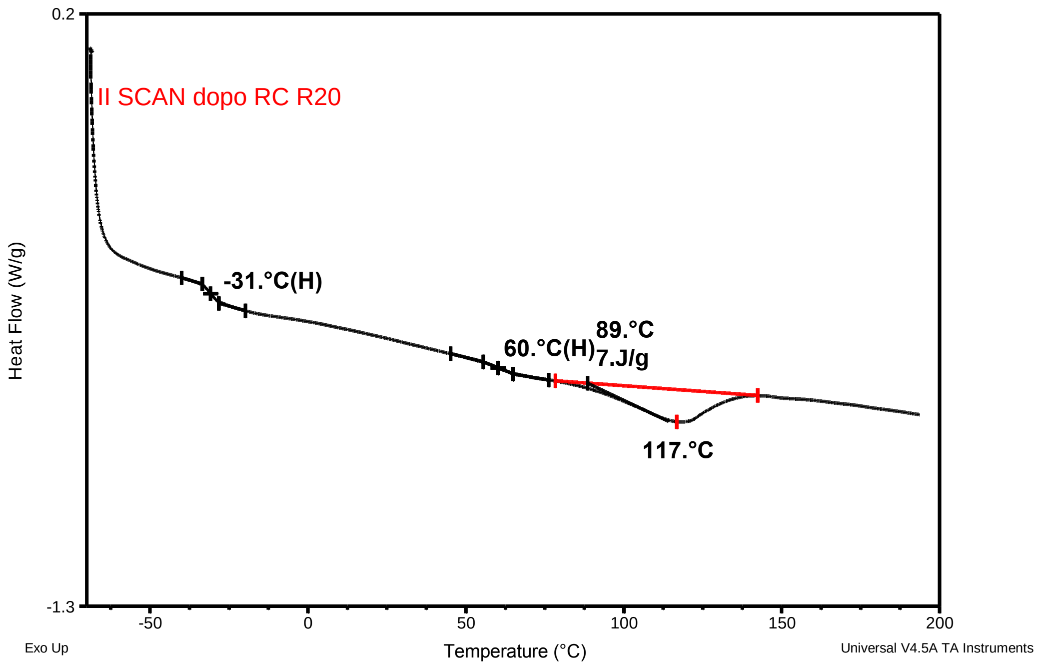
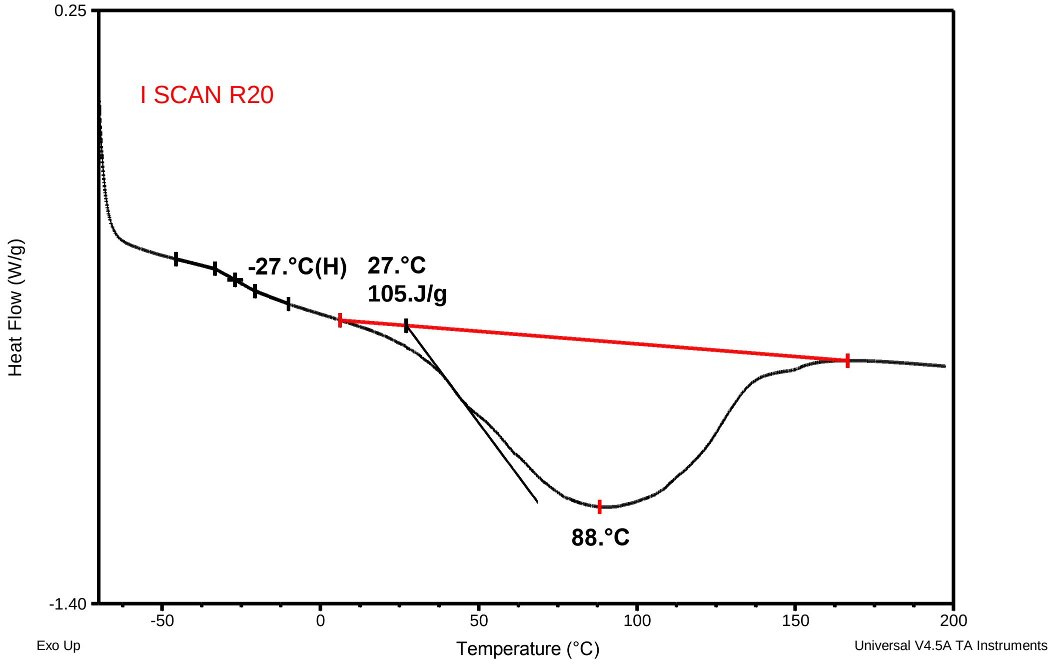


Figure 63- First and second heating at 20°C/min of the Coop bag

In the first heating can be observed a step transition at -25°C followed from an endothermic broad peak at from 10 to 135°C, attributed to the molecular rearrangement and the humidity loss and finally a second peak at 150°C ascribed to the melting of the crystalline phase. In the second heating there are two step transitions at -31 and 60°C ascribed at the glass transition followed from an endothermic peak at 117°C for the melting of the crystalline part.



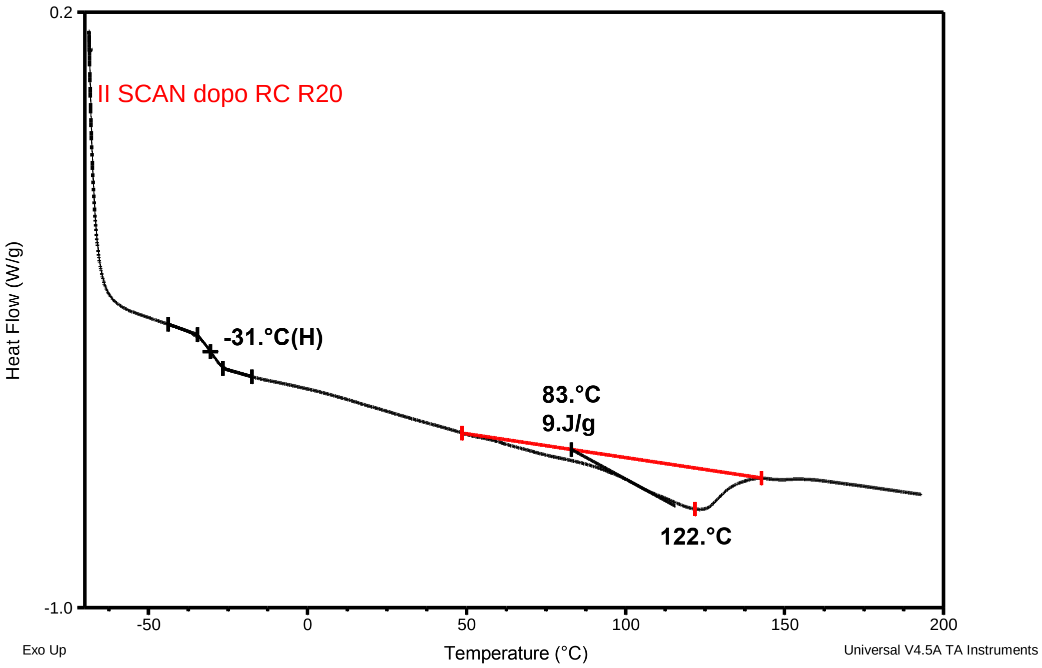


Figure 64- First and second heating at 20°C/min of the BioF3 bag

In the first heating can be observed a step transition at -27°C followed from an endothermic broad peak at from 10 to 135°C, attributed to the molecular rearrangement and the humidity loss and finally a second peak at 150°C ascribed to the melting of the crystalline phase. In the second heating there is a step transitions at -31 ascribed at the glass transition followed from an endothermic peak at 122°C for the melting of the crystalline part.

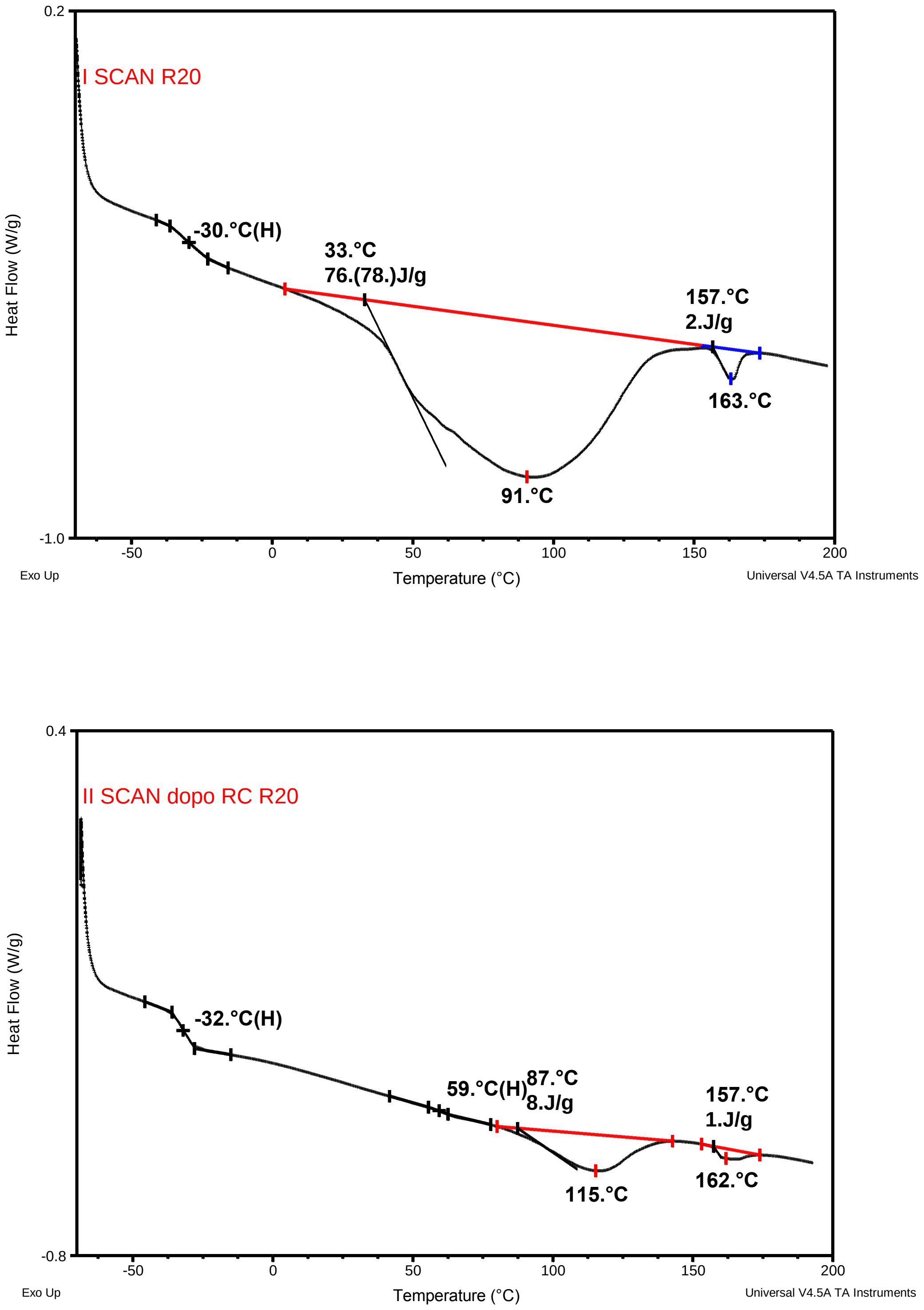


Figure 65- First and second heating at 20°C/min of the Transparent bag

In the first heating can be observed a step transition at -30°C followed from an endothermic broad peak at from 10 to 135°C, attributed to the molecular rearrangement and the humidity loss and finally a second peak at 150°C ascribed to the melting of the crystalline phase. In the second heating there are two step transitions at -32 and 59°C ascribed at the glass transition followed from two endothermic peaks at 115 and 162 °C for the melting of the crystalline part.

3.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a technique that allows to apply a stress or strain to a sample in order to analyze the response to obtain phase angle and deformation data. All these data allows the calculation of the damping or tan delta (δ) as well as complex modulus and viscosity data . These technique is very sensitive to all motions of the polymer chains and a tool to measure all the transitions in polymers. In DMA is applied a sinusoidally deformation like is shown in the figure 66. This will be reproducible only if the material is deformed within its linear viscoelastic region [43] .

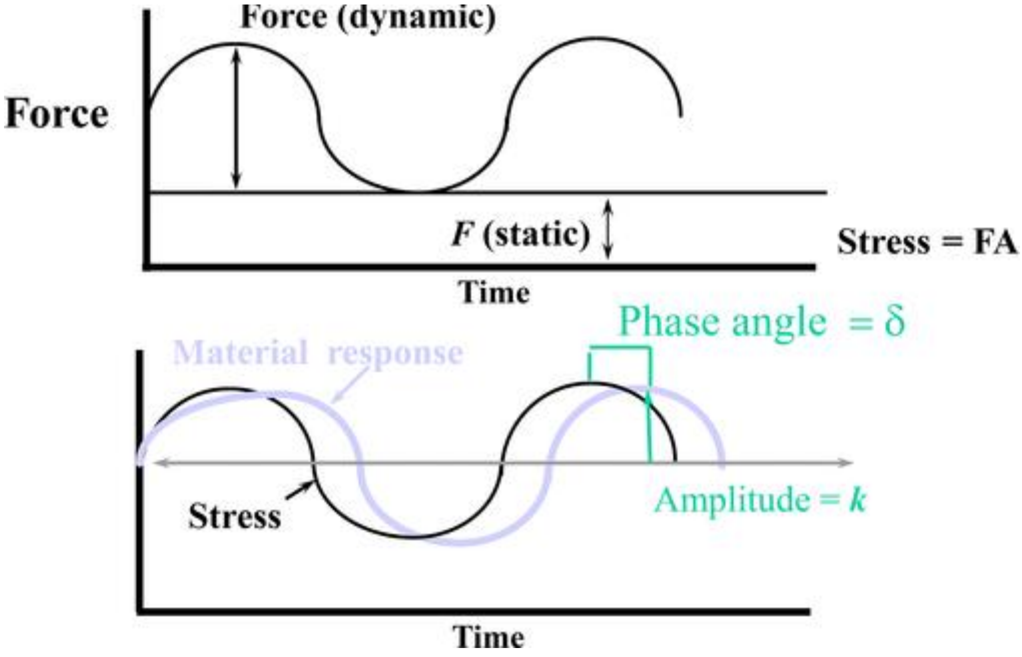


Figure 66. Oscillation stress applied to a sample

DMA measures the viscoelastic properties of the material applying an oscillation stress as was explained above dependent by a temperature variation. From this analysis is possible to determine the Tg, Young Modulus and antistress factor depending by a temperature variation. So, applying a temperature interval near the interval utilization it is possible to see how the vary the material and how it can be used.

In the graphic represented in the Figure 67 is reported the elastic modulus with the tan d curve (in the light blue curve is E’ and in the black curve is tan d) . We see a rapid decrease of the elastic modulus ascribed in the range -40 ° C – (-10 ° C) for the T_g of the amorphous part with a peak of tan d of (-24 ° C) and after the glass transition temperature a constant decrease of the elastic modulus.

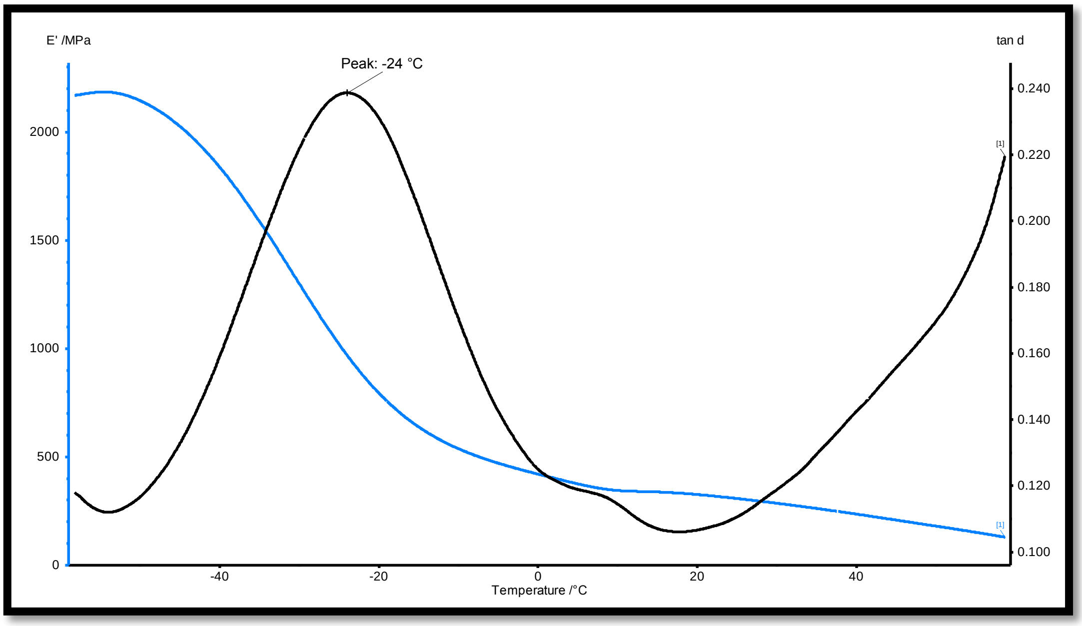


Figure 67-The Elastic Modulus of the Carrefour Bag from -55 ° to 60°C

The values of Elastic modulus the T_g values are reported at 0 and 20 ° C like in Figures 68 and 69 is shown.

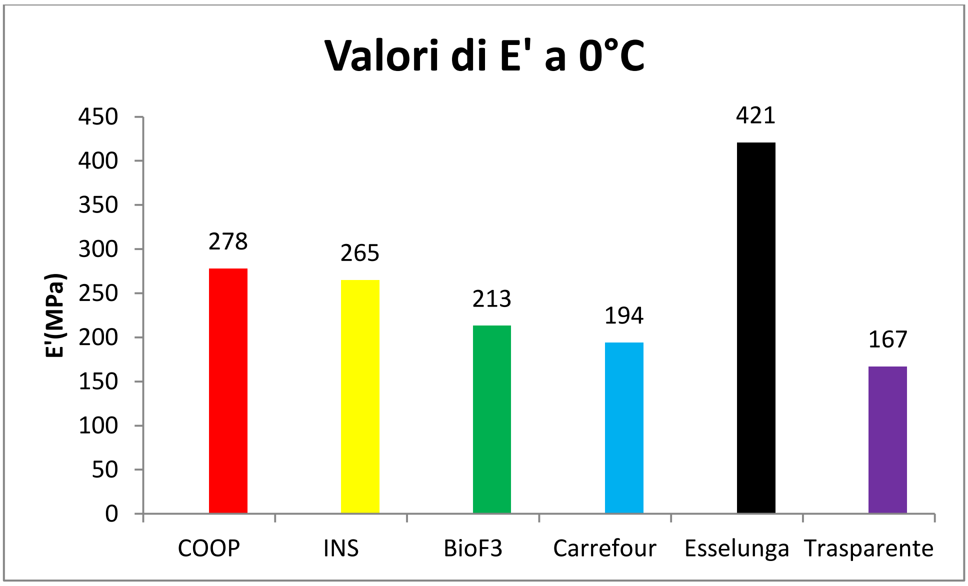


Figure 68-Values of the elastic modulus at 0°C

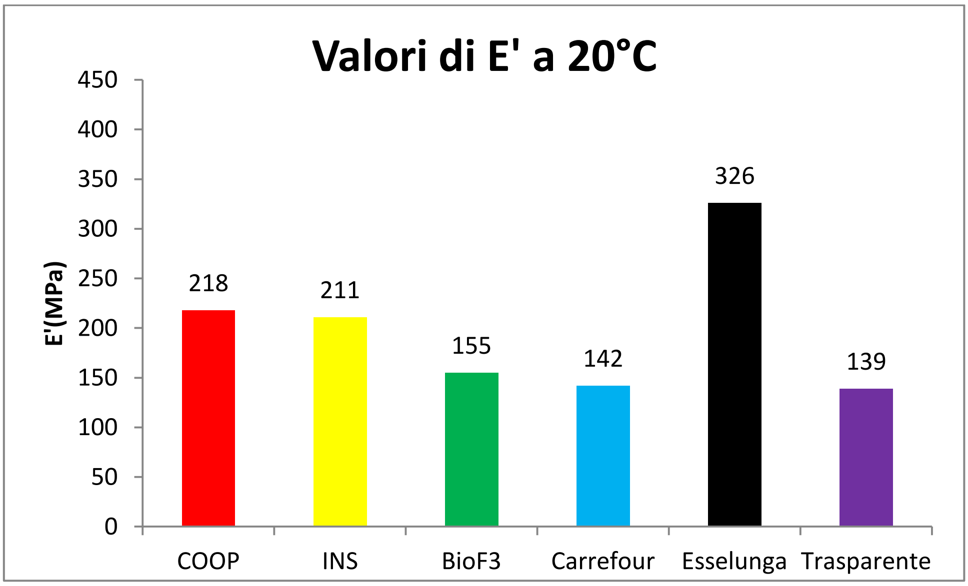


Figure 69- Values of the elastic modulus at 20°C

The difference of Elastic Modulus E’ (MPa) is attributed to the inorganic continent in each sample. The trend of Elastic modulus follows the content of inorganic fraction in the plastic bag. The only exception is represented in the Esselunga plastic bag ascribing at a major orientation of the macromolecules during the production phase.

3.4 CONCLUSIONS

The characterization of some raw materials obtained from internal recycling process was carried out using different spectroscopic techniques such as TGA, DSC and ATR. The aim of the company is to increase the competency of single-use plastic shoppers. We proved that the blown film extrussion technique is a good alternative to produce biodegradable single-use plastic shoppers evaluating the possibility to have the same quality after the recycling process. In addition, we verified that the single-use plastic shoppers provided by the company had a lack on the residue fraction that was present in all raw material like Biocomp, Biotech, Basf Ecovio and Rig. Bianco. The only one that was without a residue fraction was Rig. Neutro, but from the ATR analysis we had a negative result. All the results were compared with commercial bags in the market like Esselunga, Coop, Carrefour, Pam , BioF3 in order to set a standard reference for the disposal of the plastic bags.

4. EXPERIMENTAL PART

4.1 REAGENTS AND MATERIALS

The pellets and the bags used as sample for this study were supplied by a Local Company, whose name cannot be made public due to the presence of a Non-Disclosure Agreement.

4.2 METHODOLOGY AND INSTRUMENTS

Thermogravimetric Analysis (TGA) were performed with a TA instrument model SDT-Q600. The measurements were performed in platinum crucibles with an amount of sample at most 30 mg. The sample was heated at 20 °C / min from room temperature to 550 °C and held at 550°C for 15 minutes. The purging gas was air. The flux of air was set to 100 ml/min.

Thermal properties were performed with a differential scanning calorimeter equipment **(DSC)** modulated TA Instruments Q2000 connected with a cooling system RCS-90. The instrument is calibrated using an indium temperature calibration reference material (Perkin Elmer 0319-0053), whose melting temperature is 156.60 °C. All the measurements were performed in aluminum pans. The mass of the samples ranged from 2.50 to 5.00 mg. The purging gas was nitrogen. The flux of nitrogen was set to 50 mL/min. The sample was scanned at heating rate of 20°C/min from -50 to 200 °C, then cooled down to -50°C at 20°C/min and finally reheated to 200°C at 20°C/min.

FT-IR/ATR Analysis were performed with a Bruker Alpha Spectrometer with diamond clamp for the attenuated total reflectance measurements (ATR).

Dynamical Mechanical Analysis were performed with NETZSCH 242 E Artemis in tension with strain control at 25 µm from -30 to 60°C and heating rate 2°C/min.

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