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Master of Science Thesis

Polybutylene Succinate thermal and hydrolytic aging

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Candidato

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R: I’ve been looking out of a window for eighteen years, dreaming about what I might feel like
when those lights rise in the sky. What if it’s not everything I dreamed it would be?
F: It will be.
R: And what if it is? What do I do then?
F: Well, that’s the good part I guess. You get to go find a new dream.

Tangled

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Abbreviations

PBS: polybutylene succinate
PLA: Poly lactic acid
TPS: Thermoplastic starch
PBAT: Polybutirrate
PET: polyethylene terephthalate
PP: polypropylene
PE: polyethylene
THF: tetrahydrofuran
MFR: Melt flow rate
TGA: Thermal Gravimetric Analysis
DSC: Differential scanning calorimetry
SEM: Secondary electron microscopy

Aim of the work

Polybutylene succinate has been synthesized as a biodegradable polyester many years ago but the low molecular weight blocked further development and applications for the polymer matrix. Recently, thanks to the work of many researcher, they succeeded to obtain a product that can be used in packaging industrial applications. In 2015 Succipack european project brought new ideas in this field, investigated how PBS can be used today in food packaging application, considering also the entire life cycle of packaging from raw material production to the end of life (http://www.succipack.eu). Additional work is needed to study the many possibilities brought by this new material that can be both biodegradable and biobased.

This study focuses on thermal and hydrolytic stabilization of various PBS matrices with different acidity grade, produced with reactor melt synthesis. Firstly a screening process was carried out, extruding PBS with different stabilizers and studying how they behaved during the aging process in terms of mechanical properties. This was necessary to spot the most efficient and compatible additive among the wide industrial choice on our disposal.

During the second phase PBS with different properties were synthesized, in particular with different additives for hydrolytic stabilization or thermal stabilization added directly into the melt. The aging process of the different matrixes was studied afterward, with different conditions of temperature and humidity.

Hydrolysis resistance was also considered and investigated with various combinations of additives and clay, in fact one of the most promising solutions to the weaknesses of the polyester could be the use of nano composites.

In Chapter 1 an overview of the state of the art about Polybutylene Succinate is presented, properties, applications and major drawbacks are analyzed. The second Chapter focuses on Reactor synthesis, analyzing and commenting the procedures used and presenting the first experimental results. Different matrices were synthesized and characterized in Novamont laboratories, in order to vary the polymer's properties. Chapter 3 presents the state of the art for PBS thermal aging and the experimental results obtained from PBS and different additives with three conditions of thermal aging. Initially an additive screening procedure was necessary, in order to determine which one was the most efficient: Irganox 1010, 1425, 1330, MD 1024 and 1076 were tested. PBS aging was also studied at room temperature and different RH values, at 60°C and 80°C at fixed RH. Thus was possible to analyze how temperature, humidity and the polymer properties influenced the process. Hydrolysis resistance is analyzed in Chapter 4, an initial overview is presented, followed by the experimental results. An initial screening of different nano fillers was conducted, in order to determine the most compatible one. Then the water absorption experiments were conducted on a nano composite and samples were an anti-hydrolysis additive was added. Chapter 5 summarizes the most significant results obtained and highlights the subsequent steps.

Chapter 1 - Polybutylene Succinate

1.1 Introduction

In this era of high life quality where plastic surrounds the consumer in every step of his day, waste management is one of the main concerns, to solve the problems related to plastic end of life lot of effort has been made. It is mind-blowing if we try to imagine how our lives would look like if we eliminate plastic completely; packaging, wraps, computers, cutlery, electronic devices, utensils, cosmetics products, hygiene products, medical kits. Every object around us has been in contact with plastic at a certain point of its life; during transportation, production, raw material extraction or disposal. Two thirds of the total waste produced in the so called developed countries is made of plastic packaging; the problem is real and must be solved.

As is well-known plastic recycling is not the complete solution to our problems with plastic waste management. Surely it helps to create new lives for the unwanted products, but in most cases every time a polymeric material undergoes the usual recycling routes its properties are degraded under a certain extent. Few cases exists where plastic is completely recyclable otherwise, usually, Young modulus and elongation at break decrease with the number of recycling cycles. The recycled plastic is used for less demanding applications than the initial one.

Three “R”s can get to rescue; Reduce, Reuse and Recycle, with this slogan, proposed by the United States Environmental Protection Agency a path toward a more sustainable plastic consuming is indicated. The priority of the three actions that have to be taken by the consumers is the one displayed: firstly reduce the amount of packaging and plastic items, in particular the disposable ones, do we really need all the wrapping used today in processed food? Reuse is the second step, non biodegradable plastic lasts hundreds of years in the environment: on average we use it for short percentages of its possible life. Very common examples are: plastic bottles, food containers, plastic boxes. Just in the end recycling becomes the recommended option. Beside this three ways another end of life has grown in importance for food packaging applications from the beginning of the 21st century: biodegradation and composting. This is the best alternative for food packaging in the vision of circular economy where what comes from the Earth to that returns, polymers act as a nutrition source for microorganisms that transform food scrap in fertile soil.

In the recent years the interest in new polymer matrixes has aroused, in particular toward those bio-sourced and biodegradable. One of the main problem of modern society is related to waste management, the huge quantity of plastic packaging produced every day in our cities has become an interesting challenge for every plastic engineer. Thus the importance of having alternative routes for the end of life of polymer packaging is considered one of the main field for improvements and research. In this scenario was developed Polybutylene succinate, its story starts in

Fig.1.1: The three "R"s slogan, proposed by EPA in the united states (1)

the beginning of the 20th century, but it has been taken into account as a polymer of industrial interest just in last few decades, thanks to the work of Takiyama (2) and Fujimaki (3).

Poly(butylene succinate) (PBS) and its copolymers are a family of soft semicrystalline polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties. PBS properties are comparable to polypropylene. It can be fossil based or bio-sourced via bacterial fermentation and can be used in a wide range of applications between -20 and 100°C. The crystallinity and semi polar structure confer a good rigidity to the polyester, the fast crystallization rate allows high cooling rates that can be of use for the polymer's industrialization. PBS is considered a middle oxygen barrier and a poor water barrier.
It can be processed following the usual routes; injection molding, extrusion and film blowing using. Therefore, they are considered to be potential alternatives to petrochemical polyolefin.

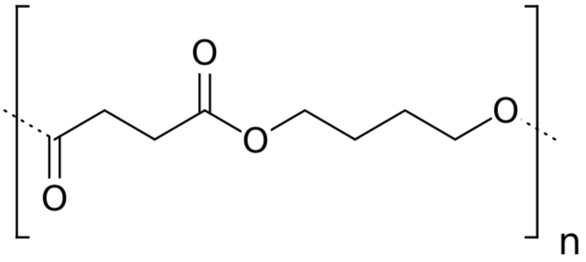


Fig.1.2 Polybutylene succinate chemical structure (2).

At first, about 70 years ago, the main problem related to the synthesis of PBS was related to the molecular weight; referring to Carothers et al. work (4), it could not be increased above 5000. The resulting products were brittle and not suitable for processing. Luckily Takiyama et al, during the early 90s succeeded to overcome this issue using new catalysts and were able to control the number average molecular weight in a range of 20000-200000.

Here following in Tab 1.1 some interesting properties of PBS and PBSA compared with some commodity plastics like PLA, PP and HDPE (5);

Tab 1.1 Comparison of PBS properties with PBSA, PP, HDPE and PLA (5).

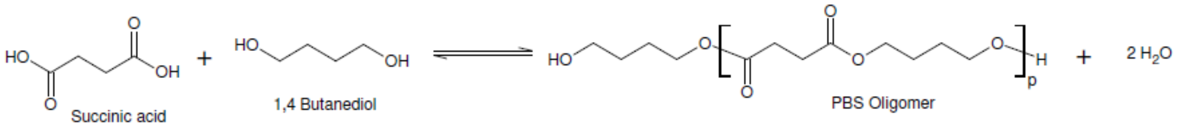
	PBS (Bionolle #1000)	PBSA (Bionolle #3000)	PP	HDPE	PLA
Glass Transition Temperature (°C)	-32	-45	-5	-120	55
Melting point (°C)	114	96	163	129	170-180
Heat distortion Temperature (°C)	97	69	110	82	55
Tensile Strength (MPa)	34	19	33	28	66
Elongation at break (%)	560	807	415	700	4
Izod impact strength (J/m)	300	>400	20	40	29
Degree of crystallinity (%)	35-45	20-30	56	69	-

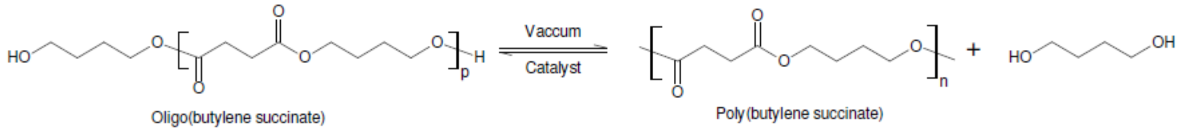
1.2 Synthesis and Polymerization

Polybutylene succinate is one of the most important biodegradable polyesters synthesized by polycondensation between succinic acid and 1,4-butanediol. PBS properties are often modified via copolymerization with other dicarboxylic acids or diols, for example PBSA with adipic acid.

The reaction proceeds in two steps. At first esterification occurs between the diacid and the diol, and then polycondensation takes place under high temperature to form high molecular weight PBS. Showa Highpolymer (Japan) synthesized various aliphatic copolyesters (PBS and PBSA) based on succinate, adipate, ethylene glycol, and 1,4-butanediol, which were synthesized and commercialized under the trade name “Bionolle” (3).

The two monomers can be derived from fossil-based or renewable resources. The direct esterification of succinic acid with 1,4-butanediol is the most common way to produce PBS. Here schematized the first condensation step (6):





Polyesters follow a step polymerization with a condensation mechanism and elimination of water (6).
For further informations about PBS synthesis refer to Chapter 2.

1.3 Pioneering PBS: Bionolle

With Bionolle trade name, 1000 series, the Japanese company Showa Highpolymers intended PBS (3) since the very first years of polybutylene production. These first grades could be processed on polyolefin processing machines at temperature of 160-200°C in various products such as injected, extruded or blown ones.

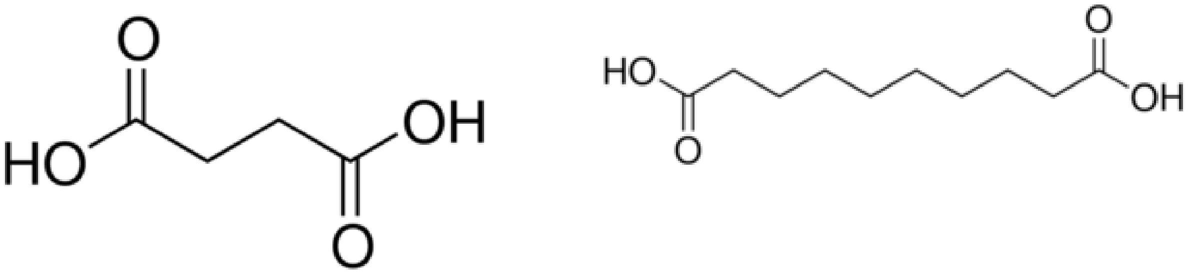
Fig.1.3 Biodegradation of PBS bottle Bionolle in 6 weeks in compost (7).

From that first production technical progress was made, Showa was among the pioneers that produced this bio-polyester, unfortunately the production was ended in December 2016. The MFR can be designed varying Mw and Mn to make it suitable for different production techniques, in this case MFR was measured at 190°C and the grades were produced for melt blowing, injection moulding, film extrusion and blow molding. PBS films with 40 and 70um thickness have excellent heat seal strength, which are superior to that of PE and PP. Stretched blown bottles of BIONOLLE #3000 (poly- butylene succinate adipate copolymer) can be processed either by cold parison or hot parison. The permeability values of these bottles to water and alcohol are somewhat high in comparison with PET bottles.

Bionolle grades become degradable in compost, wet soil, fresh water, seawater and activated sludge where microorganisms are present (7), it has earned the “OK Compost” label from AIB-Vincotte.

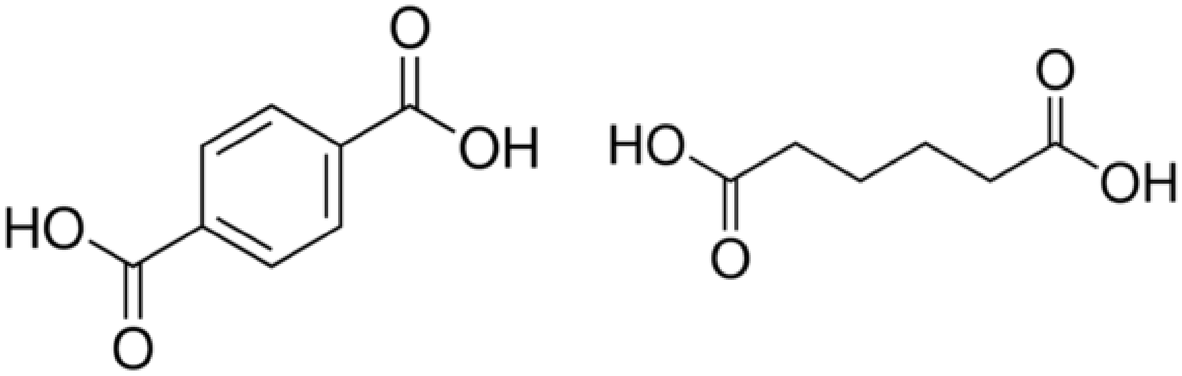
1.4 Copolymers

In order to tailor PBS properties one of the main routes followed is co-polymerization; random copolymers were produces, using 1,4 butanediol and different dicarboxylic acids like: adipic acid (PBA), terephtalic acid (PBT), sebacic acid, 1,3-propanediol or other substituted glycols (8). Some compounds are displayed in Fig.1.4, usually copolymerization lowers crystallinity because the macromolecules have a less regular structure, lowers thermal properties, improves elongation and has variable effects on degradability.



Sebacic Acid

Succinic Acid



Terephthalic Acid

Adipic Acid

Fig 1.4, Structure of the main dicarboxylic acids used for copolymerization with PBS (9).

Polybutylene succinate-co-butylene fumarate is in this case an exception, the melting point results constant up to 20% molar of butylene fumarate (5). To avoid excessive lowering usually comonomer content is maintained below 15%.

Considering PBSA, with increasing content of BA up to 20 mol% crystallinity grows from 40% to 47%, because butylene adipate co-crystallized in PBS crystal lattice, thus resulting in better mechanical performances. The biodegradation in activated sludge is also enhanced with increasing content of BA, but lowers the susceptibility to hydrolysis.

Terephthalic acid can be used for copolymerization with succinic acid, in this case an aliphatic-aromatic polyester is obtained. For PBST the properties don't change linearly, the lowest point in crystallinity, thermal and mechanical properties is at 30-40 mol% of butylene terephthalate. The degradation rate is lower than PBSA, meanwhile, compared with PBS it shows faster degradation rate at the beginning and later it slows down (5).

1.5 Crystalline Structure

PBS is a semicrystalline polyester, its mechanical, optic and thermal properties depend upon the degree of crystallinity.

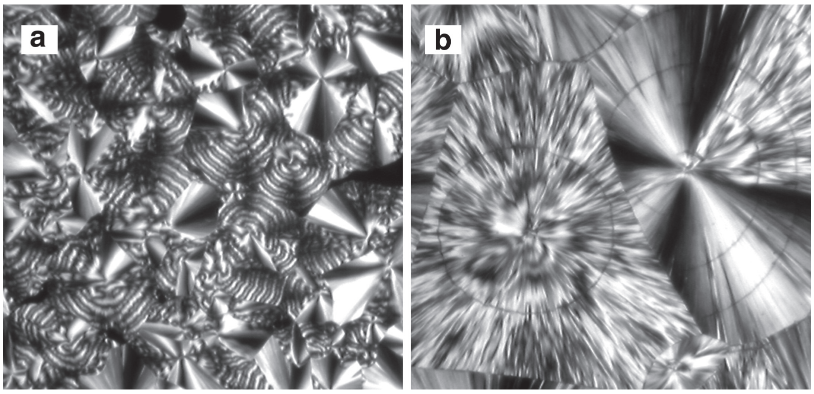


Fig 1.5. Different spherulites obtained at 70°C (a) and 90°C (b) as crystallization temperature (8).

PBS forms spherulites that can be observed using polarized optical microscopy, their size and morphology depends greatly upon the crystallization temperature as shown in Fig 1.5 (8). The spherulites consist of lamellar crystals arranged in radial order. PBS crystallization behavior is similar to PE, the thickness of the lamellae depends greatly upon the temperature, higher temperatures bring to thicker lamellae; on the other hand the total degree of crystallinity doesn't vary with temperature.

Polybutylene succinate has two crystalline forms, alfa and beta, the first appears within a quiescent melt, the second one when the melt undergoes mechanical stress. The transition between the two forms is reversible and appears under the application or the release of strain.

1.6 Mechanical properties

PBS may be used for various flexible or rigid packaging applications (10), it displays properties similar to those of polyolefin such as PP and HDPE:

- Young's modulus of about 0.9 GPa
- Flexural modulus of about 0.6 GPa
- Stress at yield of about 40 MPa
- Elongation at yield of about 10%
- Elongation at break of about 560%
- Crystallinity usually between 50% and 60%

PBS is tougher than PLA but has lower rigidity and Young's modulus. Mechanical properties of PBS can however be modified with blending and additives or via copolymerization. The presence of co-monomers modifies thermal and mechanical properties, but also the morphological structure, with a content higher than 30% the copolymer obtained has not the structure of PBS anymore (8).

1.7 Thermal properties

Thermal parameters such as: melting point, glass transition temperature, heat distortion temperature, thermal degradation are fundamental properties that affect application and processing of the polymer.

For thermal properties Succipack project is one of the most reliable references (10), which highlighted that the melting points (T_m) ranged from 109 to 115°C, with the lowest values documented in the case of bio-based PBS grades (bPBS). The melting point varies with the thermal history, in particular with the crystallization temperature, with DSC analysis cold crystallization has been highlighted in most of PBS samples between 60°C and 90°C (11). It is a rubbery polymer at room temperature, the glass transition can be individuated at T_g=-30°C, heat distortion temperature is of about 97°C.

Fossil-based PBS grades (fPBS) proved to be more homogenous compared to bPBS grades, as indicated by their sharper melting endotherms. Further investigation in order to develop PBS grades with more homogeneous properties are needed before polymer application and commercialization.

PBS undergoes thermal degradation above 300°C, weight loss reaches 5% at 325°C and grows up to 90% at 424°C, thus permits a wide range of temperature for its applications. During processing PBS undergoes degradation because of high temperatures and high shear forces also at 200°C. As shown in Fig 1.6 the difference between air and nitrogen condition is light regarding the degradation temperature. As highlighted by the TGA curve in air there is a carbonaceous residue thus indicating the presence of charring mechanisms in the oxidative environment. Nikolic et al. (12) studied also the influence of the presence of fumaric acid as a copolymer, in this case this brought to lower thermal degradation temperature and higher percentage of char.

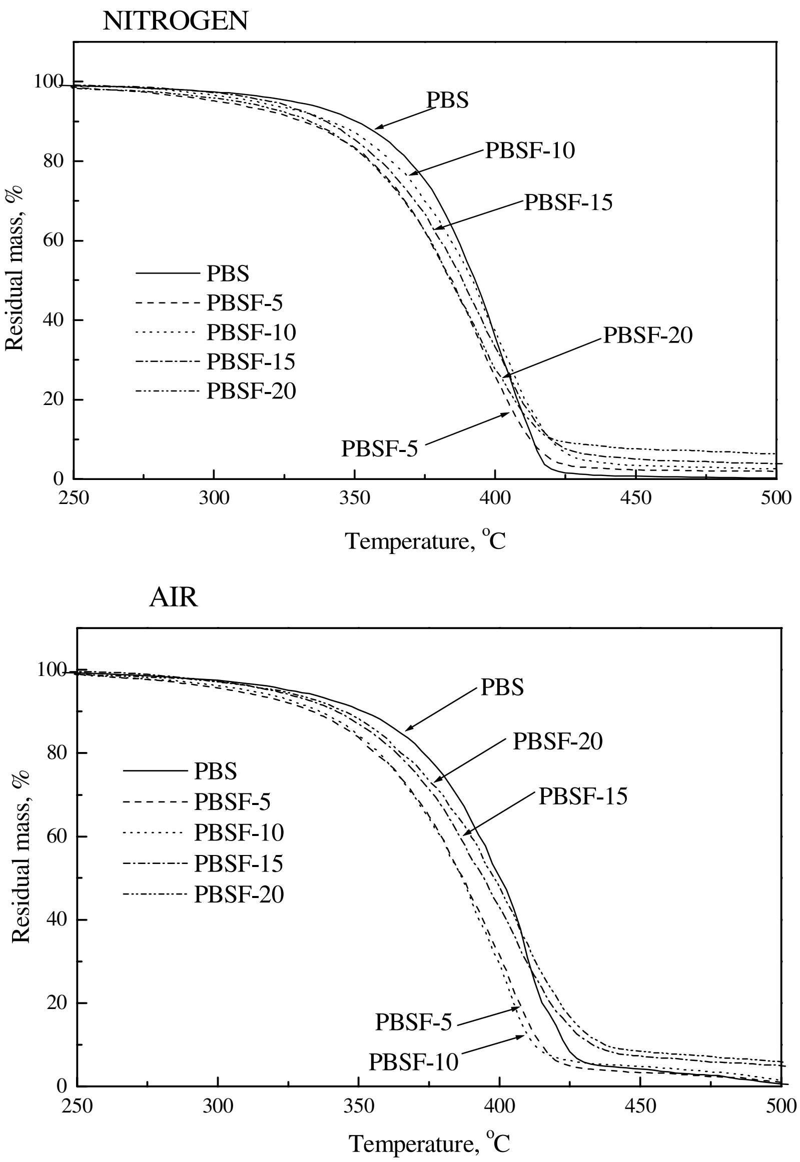


Fig.1.6 Thermal degradation of PBS and its copolymers under Nitrogen and under air, TGA curve (12).

1.8 Barrier properties

Polymers can have low permeability to gas, vapors and liquids, thus resulting in having good barrier properties, this is a key factor for packaging applications. The gases involved in food products life that must be taken into account are: O_2, CO_2, H_2O, N_2 and aroma compounds. Gas permeation process can be divided into 4 subsequent steps: surface condensation, solubilization, bulk diffusion and evaporation from the other side of the film.

PBS shows an intermediate behavior between breathing polymers and barrier polymers such as PET and PEN. Compared to PP, PBS is a poor water barrier but a much better oxygen barrier, mainly due its chemical structure and the polarity of ester bonds. Compared to PLA, has better oxygen and water barrier properties, mainly because of its higher crystallinity (5).

One promising alternative to the widely used, but poorly biodegradable, polyethylene (LDPE) and polypropylene (PP) is polybutylene succinate (PBS), which has similar mechanical and thermal properties, as we have seen in the previous paragraphs. Including all the different factors involved in this process is difficult, but in general the scalping properties of different polymers can be compared according to their sorption (S), diffusion (D) and permeation coefficients (P).

The permeation coefficient is a measure of barrier properties and can be calculated from the other two coefficients using the solution-diffusion model, where the sorption coefficient (S) can be obtained from the partial pressure of the aroma compound above the polymer and its equilibrium concentration in the polymer in the following form:

$$P = DS, \qquad (1) \qquad\qquad S = \frac{c}{p}. \qquad (2)$$

This general formulas (1) and (2) widely used for barrier properties can be applied also for aroma compounds. The concentration of the compound in the polymer generally depends on both its partial pressure and the physical state of the polymer.

Permeance is another important factor used in this field to represent the total amount of protection provided by a barrier material per unit area and is defined as the ratio between the permeance P and the thickness of the film, X. Siracusa et al (13) results indicate that during food contact a change in the crystallinity occurs, the small molecules absorbed act as a plasticizer often enhancing permeability. There is not a linear correlation between permeability and crystallinity because the sorption and diffusion process is influenced by many other factors. PBS showed an increase in permeability when polar molecules were involved such as water or ethanol, meanwhile a decrease occurred when an apolar one was studied such as isooctane.

1.8.1 Aroma Scalping

Aroma scalping can be defined as the elimination of aroma compounds from packaged food items, this can be firstly controlled by the choice of packaging materials. This is a key factor for costumers acceptance of the food product. Although the utilization of biodegradable polymers as packaging materials can greatly contribute to the sustainability of the packaging industry, their aroma scalping properties must be further investigated.

The undesired changes of flavor result from a number of factors:

- from aroma scalping; the sorption and transport of aroma compounds through the package, this is considered to be the key process controlling flavor changes.

- from the release of off-odours from the packaging material,
- from the chemical reactions (oxidation, hydrolysis etc.) that occur in the food item itself.

The extent of the flavor changes caused by aroma scalping depends on a number of factors: the basic properties of the aroma molecules in the food (concentration, polarity); the structure and parameters of the polymer such as polarity, glass transition temperature, crystallinity (14).
The list of characterized aroma compounds, in the article from Cìhal et al. (15), included common aroma compounds in foods: ethyl acetate, ethyl butyrate, ethyl hexanoate, hexan-1-ol, heptanal and (R)- (þ)-limonene.

The sorption isotherms of these aroma compounds were tested in PBS, LDPE, PBSA and PBS-PBSA blends films. The isotherms of the LDPE film displayed a pronounced “convex” trend (i.e. the type III sorption isotherm, there is poor compatibility between the compound and the polymer’s surface). This indicates Flory-Huggins mechanism of sorption. The isotherms of PBS films displayed slightly concave trends (i.e. type I sorption isotherm, the compound was more compatible with the polymer’s chemical structure). Overall, these observations appear to confirm that the aroma compounds of low polarity sorbs less in polymers of higher polarities (PBS and PBSA) than LDPE, this is mainly due to compatibility and solubility reasons.

The diffusion coefficients of all characterized aroma compounds in all tested films (except 1-hexanol in LDPE) increased as the equilibrium vapor activity of the aroma compound increased, thus indicating the occurrence of polymer plasticization. The diffusion coefficients was lower for the film containing PBS and higher for LDPE. This indicates that the diffusional contribution to the transport of aroma scalping compounds in PBS and PBSA based films is advantageously smaller than that in the LDPE film.

The coefficients of diffusion and sorption can be used for the assessment of the permeability coefficient, which is a meaningful aroma scalping property, using the solution-diffusion model.

PBS and LDPE had comparable permeabilities for the more polar compounds. Conversely, PBS had lower permeabilities than the LDPE film for the less polar compounds (ethyl hexanoate, heptanal and (R)-(þ)-limo- nene). At the same time, PBS showed smaller permeability coefficients than those of films PBSA and PBS-PBSA blends for all characterized aroma compounds. Overall, the PBS film showed slightly better barrier properties for all tested aroma compounds than those including PBSA. Furthermore, the PBS film revealed significantly better barrier properties for aroma compounds of low polarity than the LDPE film, which is presumably due to the higher polarity of PBS than that of LDPE.

1.9 Degradability

1.9.1 Susceptibility to hydrolisis

Polybutylene succinate, as avery aliphatic polyester, is sensible to hydrolysis of the esteric chemical bond. Hydrolytic chain scission can happen during harsh processing conditions, but also at room temperature, because of the presence of moisture in the atmosphere (10). Aging and degradation start right after production; storage conditions are then important for the final use of the polyester itself. With hydrolysis the average molecular weight decreases, thus decreasing the mechanical performance, but also the molecular weight distribution changes, as well as the concentration of end groups.

Changes in the average molecular weight and in its distribution bring modifications in thermal properties, crystallinity, polarity, in this case polarity increases (higher concentration of carboxyl and hydroxyl end groups), promoting water absorption and biodegradation. Degradation can be monitored using acidity measurements, thanks to the increase of the concentration of OH end groups.

One of the main parameters that influence hydrolytic degradation rate is pH (8). With higher pH the degradation rate is slower, also the weight loss is lower. As shown in Fig. 1.7 the Mw decreases steadily with time, thus meaning that hydrolytic degradation proceeds with random chain scission. Thanks to hydrolysis PBS films lose 15% of its weight after 15 weeks in a phosphate-buffered saline solution, at pH 7,2 (typical neutral soil).

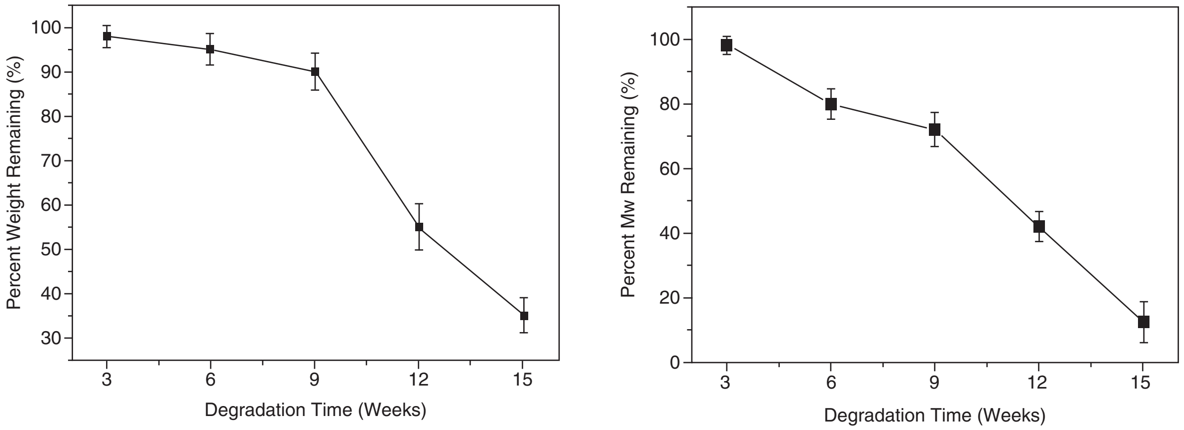


Fig. 1.7, Percent weight remaining and percentage Mw remaining after 15 weeks in PBS films immersed in phosphate-buffered saline solution at pH 7,2 (16).

Hydrolysis is promoted by the presence of water, thus water absorption rate is the main parameter involved, this depends upon the polarity of the polymer (end group

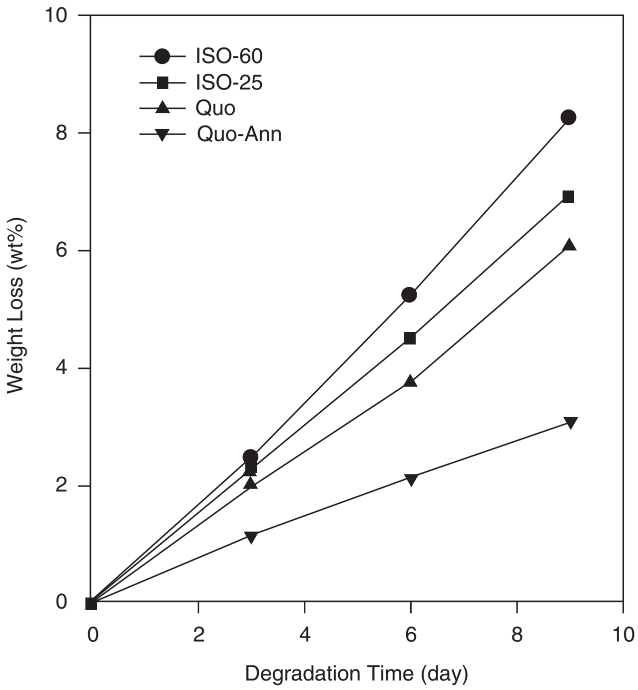
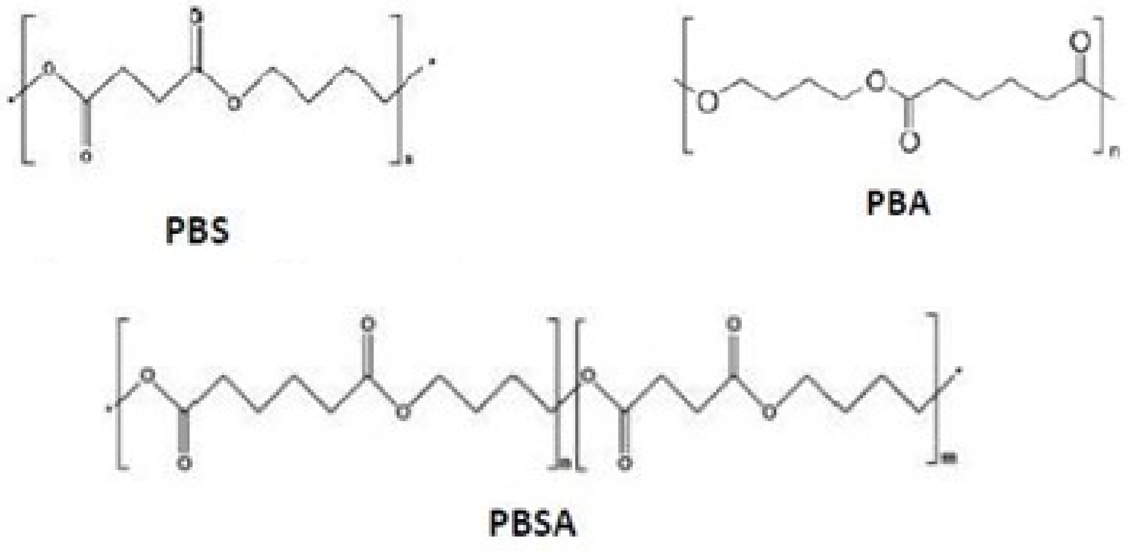


Fig. 1.8 Different weight loss percentages for PBS isothermally crystallized at 60°C (ISO-60), at 25°C (ISO-25), Quenched (Quo) or quenched and annealed at 70°C (Quo-Ann) (17).

concentration and molecular distribution) and crystallinity, which controls the diffusion process. Higher crystallinity percentage brings slower water diffusion, thus enhancing hydrolysis resistance, this parameter is primarily influenced by the thermal history.


PBS

PBA

PBSA

Fig 1.9. Comparison between chemical structure of PBS, PBA and PBSA (19).

Cho et al. (17), as shown in Fig. 1.8, analyzed the different degradation rate and weight loss percentages of PBS with different thermal history. For PBS quenched and annealed at 70°C the rate is slower and also the final weight loss percentage is lower than half the level reached with PBS isothermally crystallized at 60°C. In fact with quenching and annealing the crystallinity is higher, hence preventing water diffusion. It is also of interest that the structure of the spherulite itself played an important role, less packed spherulites such those resulting from isothermal crystallization at 60°C were degraded faster than more dense ones.

One of the investigated paths to enhance PBS hydrolysis is co-polymerization, in particular with butylene adipate (18). PBS itself has higher degradation rate than PBSA copolymers.
Has shown in Fig. 1.9 through a comparison between Polybutylene succinate and polybutylene adipate chemical structures, adipic acid aliphatic chain is longer than succinic acid chain, 6 carbon atoms versus 4. This brings to the final polymeric structure of PBA which has less sensitivity to hydrolysis thanks to the higher a-polarity and lower water absorption. PBSA is a tailored compromise between PBS higher polarity and PBS lower polarity, increasing the adipate comonomer content decreases the degradation rate.

PBS reaches 24% of weight loss in 25 days at 30°C in ammonium chloride buffer solution (pH 10), with just 20% of adipate comonomer this level decreases to 8%, with 80% of adipate the resulting polymer loses just 2% of weight in 25 days.

1.9.2 Enzymatic hydrolisis

Regarding enzymatic degradation of PBS it depends upon polarity, crystallinity and the specific solid state structure, in particular from the form in which the samples are produced. This is obviously linked to the surface/ volume ratio, the higher it is the easiest is for enzymes to attack polymeric chains causing bond scission. In fact enzymatic hydrolysis starts with surface etching that produces 4-hydroxybutyl succinate as main product, but also small quantities of 1,4 butanediol and succinic acid. This type of degradation proceeds from the surface of the substrate toward the bulk through erosion with subsequent weight loss of the samples. Firstly amorphous regions are degraded, here enzymes diffuse easier, then they penetrate further in the polymer. During this first step the molecular weight distribution doesn't change greatly, in fact the oligomers produced from the surface degradations are readily dissolved in the aqueous surroundings.

Lipases are water-soluble enzymes that catalyzes the hydrolysis of lipids, they are fundamental in digestion of dietary lipids such as fats and oils (20). Lipase has two main folded conformations; a closed one and an open one. Trough rearrangements of lipase lid the active site opens to access exposing a large hydrophobic surface. Another characteristic is the Oxyanion hole built of several hydrogen bond donors that help in the stabilization of the intermediate state that is created during the hydrolysis reaction (21).

However Area/volume ratio dependance is put in the background when crystallinity changes, in fact PBS fibers have lower degradation rate then PBS films (22). After two weeks incubation with lipase at 50°C and pH 6 the fiber’s loss was just of the 6%, on the other hand for films weight loss reached 76%. This discrepancy is mainly due to the higher degree of crystallinity and molecular orientation present in the fibers.

Lipase enzymes split bonds randomly in the polymeric chain, this is proved by Song et al. (23): PBS matrices with different molecular weight had similar degradation trend and rate.

1.9.3 Biodegradability

Biodegradation can be defined as the degradation of materials by naturally occurring microorganisms such as bacteria and fungi. This chemical process is carried out by enzymes and reactive moieties (basis, acids and peroxides) (24), their activity greatly depends upon some factors such us pH, temperature, nutritive molecules available, presence of water. Oxidase and hydrolase are the two most common enzymes involved in polymer degradation

Polybutyilene succinate can be degraded by microorganisms into water and CO_2 with naturally occurring enzymes after disposal in different conditions such as compost, burial, environmental conditions and activated sludge (8). PBS is biodegradable in compost trough aerobic reactions in a pH range of 7-8, 50% humidity and 60°C; it reaches the 90% of biodegradability after 160 days. In soil there is a great difference between the use of powder or films, both degraded at 25°C, 60% for 28 days: films reach just 1% of biodegradation meanwhile powder reaches the 17% (25)

The biodegradation rate depends upon crystallinity, degradation conditions (pH, humidity, temperature, type of microorganisms), polymer chemical structure (molecular weight, copolymer ratio). With harsher conditions, such as in compost and moist soil, the biodegradation rate is higher than in less aggressive environments as

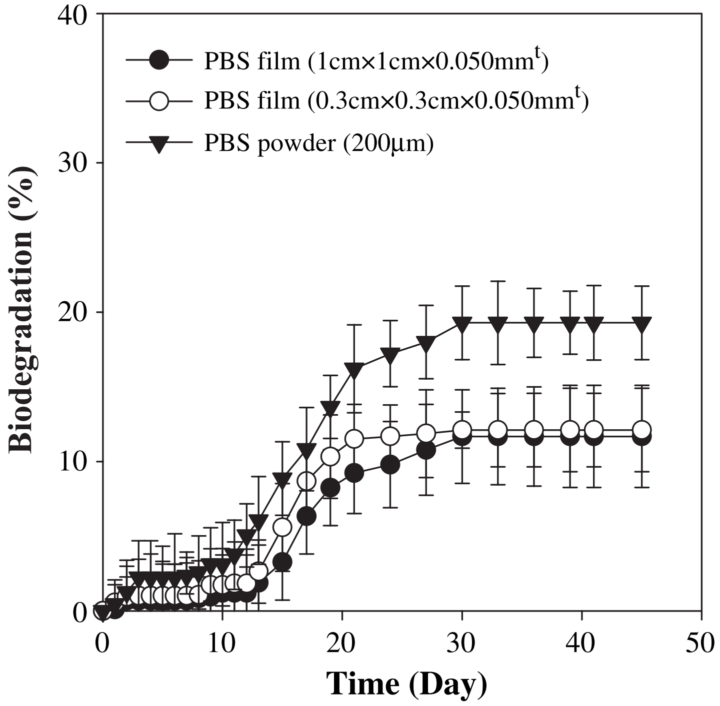


Fig 1.10 Biodegradation of PBS specimens with different shapes in an animal fodder compost. (26)

sea or water; biodegradability depends mainly upon the microorganisms existing in the environment.

The standard protocol for biodegradation involves compost, in order to determine if the plastic is biodegradable and compostable, here the biodegradation goes under controlled conditions: 50-60% of RH and 60-70°C. In this test, where the norm UNI EN 13432 is applied, sanitized, fertile and stabilized soil is produced. The final quality of the compost is to be tested, byproducts and conversion rate are controlled.
For PBS the biodegradation rate in compost is susceptible to the specimen shape and size, it is considered a slow degrading polymer (26). As shown in Fig. 1.10 PBS, after the initial lag phase of 10 days, reaches a plateau level of biodegradation of 20% for 200 um powder, and 12% for films. The surface/volume ratio in this case is fundamental for the reaction rate, with higher fragmentation the microorganisms present in the medium degrade the polymer matrix easier.

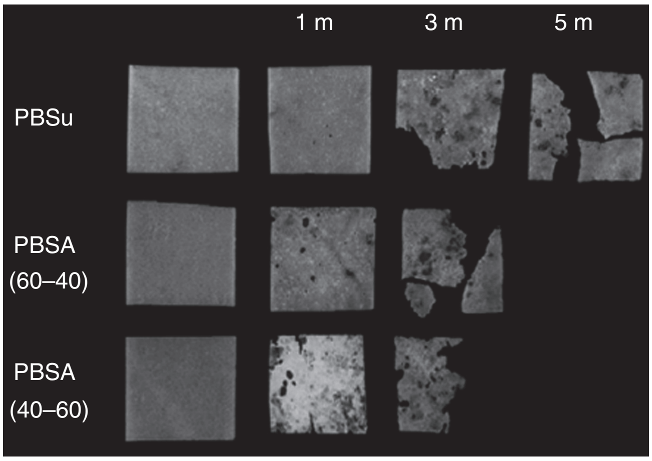


Fig 1.11. Photographs of polyesters and copolyesters after soil burial degradation for 1, 3, and 5 months (8)

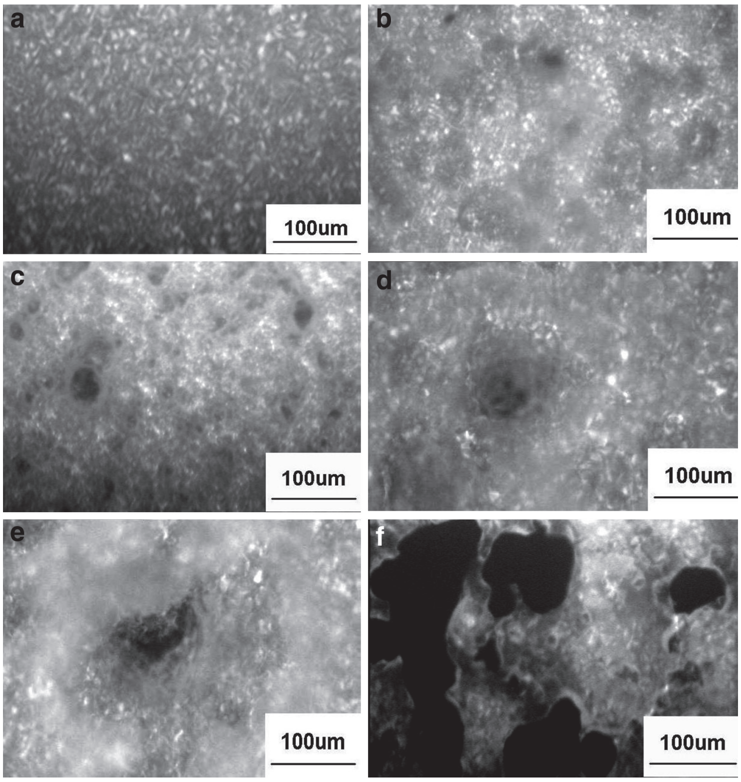


Fig. 1.12 Polarized optical micrographs of PBS degraded in activated sludge for different periods of time: before biodegradation (**a**); degraded for 1 week (**b**), 2 weeks (**c**), 4 weeks (**d**), 6 weeks (**e**), and 10 weeks (**f**) (8)

Regarding co-monomers, the presence of adipic acid in this case enhances weight loss and biodegradability, PBSA in fact reaches higher levels of weight loss, up to 80% in the same conditions. Several microorganisms able to degrade PBS have been spotted, such as: Bacillus stearothermophilus, Microbispora rosea, Excellospora japonica and Excellospora viridilutea, and Aspergillus versicolor (27).

In soil has been estimated that 0,2-6% of the total bacteria present are suitable for PBS degradation (28). The biodegradability of copolymers depends greatly upon the composition, this in fact influences polarity and crystallite of the product.

Another interesting environment where biodegradation of PBS should be studied is activated sludge, this is a process employed for wastewater treatment that uses aeration and a biological substrate of bacteria and protozoa (29). This is a biological process used for removing carbonaceous or nitrogenous residues with basically an oxidation process with biological reactions involved. The microorganisms introduced in the wastewater, thanks to the oxygen introduced in the mixture, reduce the organic content. In this type of environment PBS and its copolymer degradation is fasten than soil burial. When in soil PBS film degrade trough surface erosion, so that the sample maintain the original form and then break down into pieces. when in activated sludge big holes are formed and the films modifies its original shape as shown in Fig 1.12 and Fig.1.11.
In activated sludge the molecular weight is a significant parameter, with higher molecular weight loss and degradation rate are lower, also the presence and quantity of comonomer is an important factor.

1.10 Processing

PBS is a thermoplastic and can be processed in different ways such as extrusion, injection moulding, film blowing and thermoforming. It also can be used to produce fibers to obtain filaments and non woven textiles. This biodegradable polyester has the classic shear-thinning behavior when melted; viscosity decreases with the increase of shear rate.

The processability of the different grades depends upon their thermal stability, viscosity, and crystallization rate mainly, nevertheless is to take into account that all of these properties are sensitive to the water content and also to the moisture exposure in terms of time. Therefore particular attention is to be given to the storage of PBS granules and to the drying process before processing, in order to decrease the water content. Prior to processing water content should be lowered below 0,1% (10), even small traces of water can bring hydrolysis at high temperature.

200°C can be chosen as threshold value for the processing temperature (5), after that the melt undergoes a critical decrease of viscosity. After 30 minutes at 210°C the viscosity decreases of the 50%; a possible path to enhance thermal stability is trough copolymerization with other monomers such as terephtalic acid. For PBS and its copolymers this decrease is due to the weak intermolecular interaction between the chains that starts when temperatures 20°C higher than the melting point are reached.

Fig 1.13. PBS Granules (10).

Usually grades with Mw under 100 000 are used for extrusion and injection moulding, whereas higher Mw are used for techniques where high melt strength is necessary, this also ensures smooth processing. To fasten the crystallization rate and allow fast processing nucleating agents are used, for example talc and ciclodextrin were successfully employed (5).

Another option is to adopt the differentiation made during the early stages of Bionolle's production between macromolecules with different morphologies. Linear chains are preferably employed for injection moulding and filament winding, highly branched ones are used for foam production, sheet extrusion and film casting.

PBS grades adapted to various processes are available on the market, with viscosities adapted to standard plastic processing methods, but film production and extrusion blow moulding are still missing (10). Succipack highlighted some of the main changes needed for further usage of this matrix, for example:

- for injection moulding a faster crystallization is needed to decrease cooling time and allow processing with competitive timing in comparison to that of the most widely used polymers.
- for thermoforming a higher modulus and better cohesion are needed
- for film blowing a stronger melt is recommended to ensure bubble stability and ensure smooth processing.

To improve PBS processability it is usually blended with PLA, TPS, PBSA, PBAT or Talcum powder, more often used as nucleating agent. Thanks to this blends thermo-mechanical properties change but it also has to be considered a shift in processing conditions.

1.11 Recyclability of PBS

For packaging recycling two main routes are available: thermal desorption, which is a physical process that eliminates volatile contaminants and depolymerization, which is a chemical process that leads to monomer or oligomer valorization. The main challenge in this field regards food-contact norms; is not effortless guaranteeing norm compliance after recycling. In the case of PBS, since it is biodegradable and its main application is in food packaging industry the most investigated end of life scenarios are the ones which involve biodegradation and composting.

Trough thermal desorption the main contaminants of the solid plastic matrix are removed, increasing their volatility, these gases are then collected. The desorber heats the substrate with and heated screw, or using rotatory fired systems, infrared waves or microwaves. For offgas treatment there are three option available, depending on the gas toxicity; discharge in the atmosphere, collection in the condensed state or elimination, usually trough thermal destruction (30). After this first step food packaging can follow the usual recycling path with milling, separation, washing, drying and conditioning (24).

On the other hand monomer recovery is a chemical process that for the european norms is not classified with the other recycling routes but is considered as an alternative source for monomers. Polyesters can be easily hydrolyzed in low molecular weight compounds with the help of hydrolytic enzymes produced by microorganisms. Therefore hydrolysis can be achieved with chemicals or with enzymes, using lipase and esterases, the great majority of enzymatic hydrolyses is achieved using lipase in water, carbon dioxide or organic solvents (31). Obviously the use of solvents, often halogenated chemicals, should be avoided for environmental and safety reasons, hence "green" routes have been investigated in the recent years.

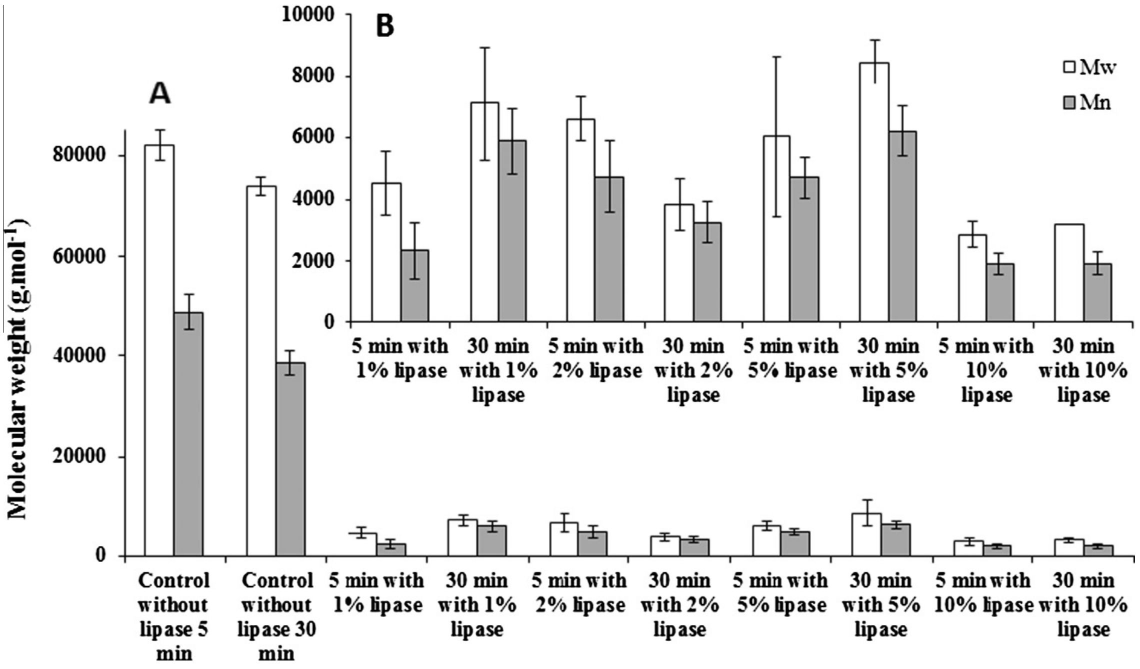


Fig. 1.14. Average molecular weight decrease (Mw & Mn) with different percentages of lipase and different extrusion times. (31)

Jbilou et al (31) chose lipase B from C. Anthartica because of its thermal stability to perform hydrolysis during a continuos reactive extrusion process. The main advantages of this prospected processing are the lack of solvents, the use of a continuos process with an enzyme. In fact enzymes are delicate molecules that often lose their scission ability at temperature above 80°C.

The weight average molecular weight of the polyester decreased from 82 000 to 45 000 g/mol after 5 minutes in presence of 1%wt of lipase B as shown in Fig 1.14. The highest quantity of succinic acid released was obtained after 30 minutes extrusion with 10% of Lipase B present. During the extrusion process the enzyme efficiency decreased, thus the residual activity was monitored in the extrusion conditions, resulting in 40% residual activity after 5 minutes at 120°C with PBS and 25% residual activity after 30 minutes in the same conditions. To implement the process on an industrial scale lower percentages of lipase should be used, this can be achieved with water addition during the process because it can be a limiting factor and better homogenization of the melt.

1.12 Impact and LCA approach

Life cycle assessment is a technique used to determine the environmental impact of a material, an object or a product, associated with some stages of its life (32). It can be conducted from cradle to grave, including all the steps of the product's life cycle, from raw material production to recycling and disposal, or from gate to gate, including just the steps carried out inside the factory's gates. Several indicators are available, in order to assess different aspect of environmental impact, for example: water consumption, carbon dioxide footprint, energy consumption etc. This tool is often used to have an idea about the real impact of new or old processing techniques and products, in order to make better decisions.

The evaluation of Polybutylene succinate environmental impact is particularly challenging with LCA approach because it is still a developing technology and to fully address the problem a clear overall life cycle is needed. Therefore a fully developed LCA study can reproduced just when the material has been fully developed and introduced in the market.
To overcome these difficulties an ex-ante approach can be used to forecast the potential impact of this new material.

At the very early stage of development of a new material, such is in this case, the available informations are few and production at pilot scale cannot be directly compared with industrial production. To include all the advantages brought by a biodegradable and bio-based matrix a cradle to grave approach has to be used, meanwhile for the usual petrochemical polymers a gate-to-gate view is used.

Cheroennet et al. (33) Compared PS, PLAS, PLAS/starch and PBS, with a cradle to gate methodology. When addressing biodegradable polymers usually the step in which their environmental impact lowers significantly is trough degradation and composting, whereas the production stage as higher impact than oil-based plastics. This can be mainly imputed to the fact that biopolymers in general are a new technology so production and processing methods are not optimized such is in the case of usual commodities. Thus not including the end of life when studying this kind of plastic prevents the reader to have a complete overlook to the environmental impact, this choice can be understood and motivated with the general lack of information about the new matrices. Then we will consider just the comparison between the production stage of PBS and PLA, excluding PS for the reasons above.

Bio-based Polybutylene succinate has the lowest water impact and Carbon footprint, as shown in Fig. 1.15 The unit considered was a box of 8x10x2,5 cm with carrying

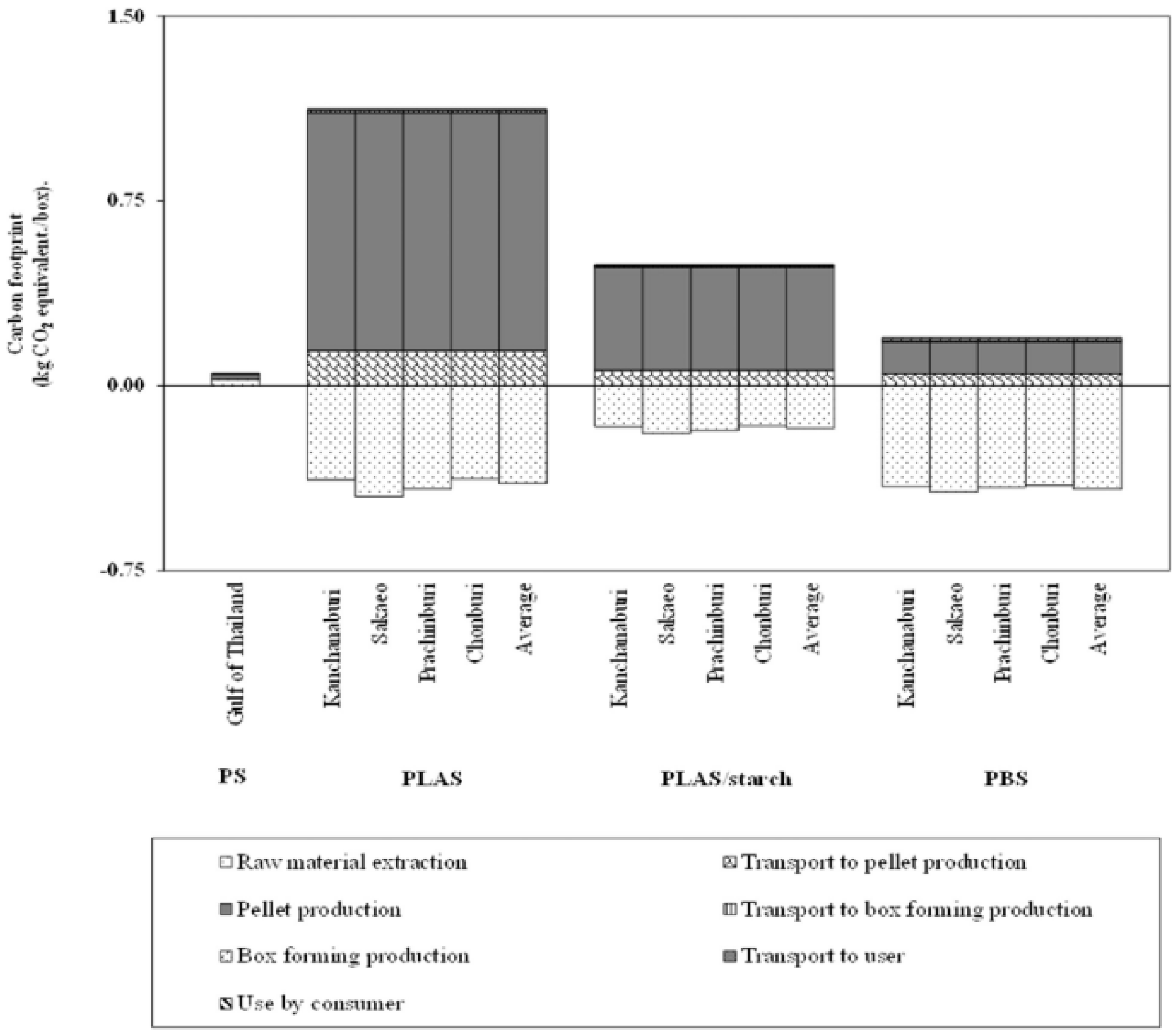


Fig. 1.15 Comparison between PS, PLAS, PLAS blended with starch and PBS on their carbon footprint, divided with the different stage of life and raw materials and production from different areas. (33)

capacity of 100 grams, a comparison between different production regions for the bio-source was also carried out. As expected PS impact is considerably lower during raw material production and processing (pellet production), but during raw material extraction there is a quantity of carbon dioxide absorbed by plants that lower the overall carbon footprint, that is not present for oil-based plastics.

Tecchio et al (31) conducted a study on bio-based PBS and how its impact changed from pilot scale to industrial. The industrial production brought a significant decrease in greenhouse gases production. A comparison between different production techniques for the succinic acid extraction was also conducted highligting that sugar cane with electrodialysis extraction process is the most favorable.

Fig. 1.16, Proposed applications for PBS from Showa-Denko (34).

1.13 Applications

Thanks to its biodegradability and its possible bio-derivation PBS is a promising candidate in the field of biopolymers for packaging, in particular food packaging, cosmetics and agricultural applications. Polybutylene succinate can be processed into films, bags, boxes or cutlery, in agriculture can be used to produce mulching films (10) as shown in Fig (16).
Another interesting market share for PBS is in fishery, for fishing nets, or also civili engineering and forestry, where material recycling is problematic. It can be produced as a drug-delivery system or for implants in medical applications.

Food packaging is one of the key fields for biopolymers; it has to maintain the quality, appearance and safety of products preventing spoilage. Packaging has also to extend shelf-life and protect the article during transportation and storage, it has to perform as a barrier to prevent microbial contamination, water vapor, carbon dioxide, aroma and oxygen permeation. To guarantee these requirements biopolymer mechanical, thermal and barrier properties are essential, it is also of great importance the aging behavior in different conditions, especially toward moisture content, in fact vegetable, fruits and animal product produce and contain high quantities of water.

Three key aspects have to be addressed: processing, performance and cost. As Showa-Denko case[1] teaches us, as also many other similar situations in the production or transformation of biodegradable or bio-based polymers, cost is the fundamental factor. The use of package permeates our everyday life, the consumer is overwhelmed with plastic wrapping and waste management is becoming more and more challenging: 60% of the waste produce by the average citizen in the so called developed countries is made of plastic packaging. In this scenario, where the quantities are insanely huge the value associated to the single products is low, thanks also to the competitive price that oil-based plastic still has. The role of

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[1] Showa-Denko pioneered PBS production, but in December 2016 they announced the closing of this production line because the market is not ready to fully accept bio-based polymers and the sequent increase of packaging cost.

Fig. 1.17, Proposed applications for PBS from Mitsubishi chemicals (35).

packaging itself is fundamental to avoid food losses and provide safe products to the consumer, new technologies work toward developing products with antimicrobial or anti fungal surfaces, or also signaling microbiological changes. In this scenario nano composite technology is a promising solution.

Different type of food products need diverse aroma and gas scalping properties, for example crunchy products needs are the opposite than those of fruit and vegetables. As Succipack project highlighted there is need for many grades of PBS, with tailored oxygen and carbon dioxide permeabilities. It as also tested the capability of PBS packaging in preserving food quality and safety with several different foods such as: raw chicken, turkey meat, vegetarian burgher, lettuce, ricotta cheese. In every case PBS was compared with the usual commodity polymer used for the specific application (PET, PP etc.) with good results, showing a great potential. Moreover, with modifications to PBS barrier properties, enhanced shelf life was achieved (10).

Fig. 1.18. Labels “Ok compost” and “Ok compost home” from Vincotte (36).

Mitsubishi chemical corporation has developed a line of PBS biodegradable (EN 13432) products including: coated paper for food, used for cups and oily food wraps, it is resistant to elution to oil and vinegar and is also resistant to percolation of sauces and oils. The PBS grades produced are claimed to be processable in LDPE machinery, have excellent printability, low heat seal temperature and excellent heat seal strength (35). BioPBS can also be used for injection moulding, in environmental friendly applications, thanks to his good impact property, dimensional stability and flowability, shorter cycle time compared to other bioplastics is achieved.

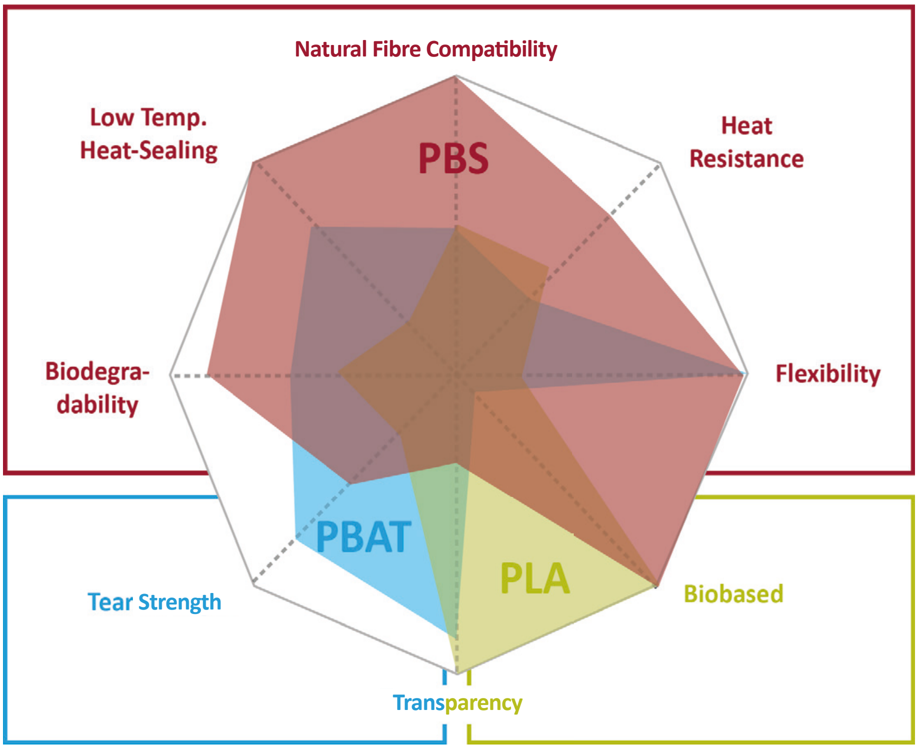

Fig. 1.19, Comparison between PBAT, PLA and PBS. (37)

The polyester resin produced can also be employed for soft and flexible films, designed for dry lamination and higher gas barrier properties than LDPE, it is suitable for contact with weak acidic greasy food. Moreover sport equipment is another possible field of application, with grips, straps, flexible sea-side games, scratch resistant screens, shoes and balls.
BioPBS is compostable both in industrial situations and home, gaining Vincotte labels “OK compost and “OK compost at home” shown in Fig 1.18.

In comparison with PLA (polylactic acid) and PBAT (Polybutyrate) it has several strengths such as flexibility; PLA is brittle and PBS can be added in blends PBS/PLA to soften the second polymer. Polybutylene succinate has also higher compatibility with natural fibers, lower heat-sealing temperature, higher level of biodegradability with reference to the european norm EN 13432. (37)

1.14 Blends

Another interesting alternative to overcome PBS weaknesses is to blend this matrix with other polymers, that can be biodegradable or no, for example with starch, PLA, PHB etc (5). Blends morphology and properties change greatly with the chosen polymer and percentage, the main parameter in this case is miscibility.

Some authors (5, 38) report blends of PLA and PBS they are immiscible in melt in every composition, as shown in Fig. 20 with optical microscopy. The better results in terms of dispersion were obtained when 20% of PLA or 20% of PBS were respectively present (80/20 and 20/80). In this case the finest structure was achieved

$$E_b = \frac{E_1 E_2}{(\varphi_1 E_2 + \varphi_2 E_1)} \quad (3) \qquad E_b = \varphi_1 E_1 + \varphi_2 E_2 \quad (4)$$

with the dispersed phase regions not bigger than some microns. On the other hand Part and Im investigated the behavior of these blends and calculated the Flory-Huggins parameter to be -0,15; the negative value indicates full miscibility (39). Meanwhile Jumping et al. analyzed blend morphology with SEM microscopy and concluded that PBS was miscible with PLA up to 10% (40). The Young's modulus decrease in a quite linear trend, falling between the parallel model and the series model for blends displayed below.

These two models represent the upper and lower limits for phase separated blends, for the parallel model, the upper limit, the higher modulus component is the continuos phase, on the other hand for the series model the component with the higher modulus is the dispersed phase. The fact that the plot for PBS/PLA lays between them indicates that there is a partial compatibility, as shown in Fig. 1.20 (41).

The behavior of elongation at break is also extremely interesting, as shown in Fig. 1.20 with the addition of just the 10% of PBS the blend became ductile until 40% of PBS was reached. Even with higher values of elongation at break than pubs itself. In this range PBS formed a co-continuous phase, finely dispersed. Above 40% the elongation at break dramatically drops down to 12-19%, this indicates a change in morphology in the blends. Deng et al. supposed that when PLA becomes the minor component it doesn't form a continuos phase anymore and becomes dispersed in PBS, in which the adhesion is not good, this brings low ductility to the resulting material.

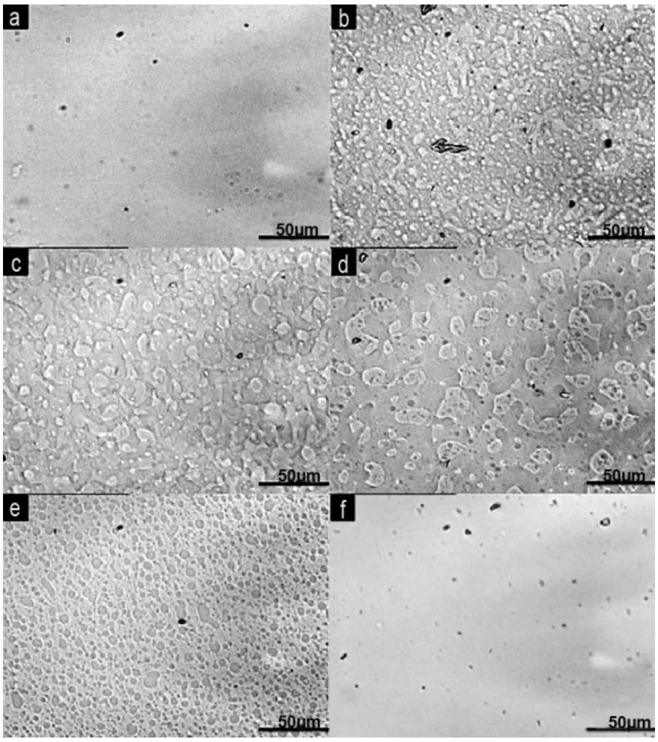

Fig. 1.20 Optical micrography of PLA and PBS blends in the melt state at 180 °C. PLA/PBS blend ratio: (a)100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 and (f) 0/100

This blends improve mechanical properties such as elastic modulus and tensile strength, without great loss in ductility. With a small amount of PBS, PLA can become ductile, with an increase of elongation at break from 24% to 200% with just 10% of PBS added (41).

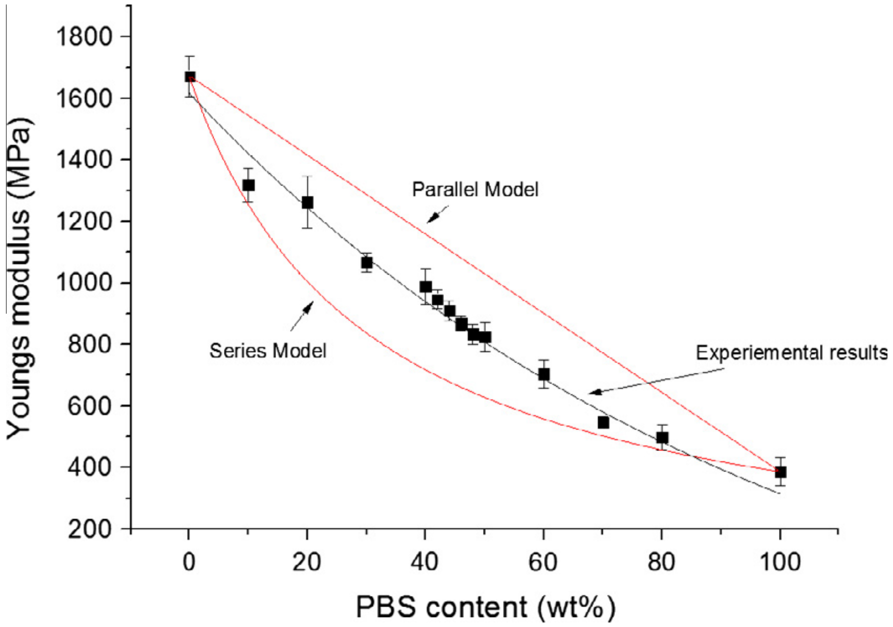

Fig. 1.21 Young's modulus variation for the blend PBS/PLA (41).

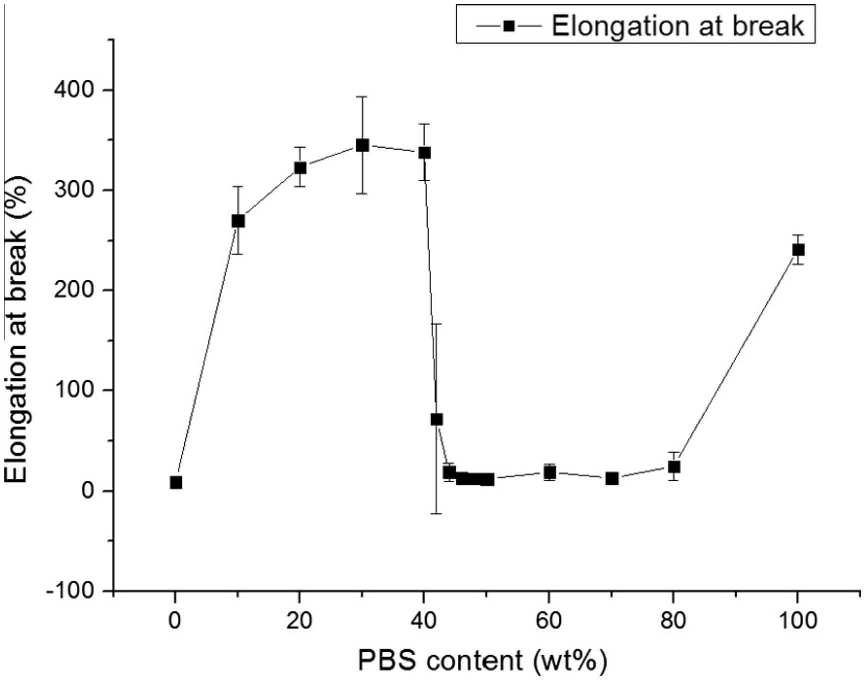

Fig. 1.22 Elongation at break variation for the blend PBS/PLA (41).

To improve crystallization rate in PLA/PBS blends the use of nucleating agents has been studied, to improve mechanical properties, process ability and productivity, obtaining faster crystallization. Nano-sized calcium carbonate and sodium benzoate were studied by Homklin et al. (42), this changed the blend morphology in most cases. The nucleating effect was present in both cases, but Sodium benzoate can absorb humidity and turn into benzoic acid, that can act as a catalyst for PLA hydrolysis.

Khalil et al (43) reported the production of Plasticized starch/PBSA films with controlled morphology in order to achieve selected water/oxygen permeation. These two biodegradable polymers are immiscible, so depending upon the processing technology and the ratio between them the morphology changed. Continuous phase of TPS and PBSA were highlighted just with 50-55% PBS or 55-60% of PBSA, the tortuosity and the swelling of the polar phase controlled the diffusion factor. This type of behavior is promising for the controlled release of polar migrants such as food preservatives.

1.15 Nanocomposites

Nanocomposites are a promising solution to enhance food shelf-life, for example with meat, cheese, paperboard for fruit juice. They act mainly on barrier properties, with lower permeabilities and diffusion coefficients of the material thus produced the packages used can have lower weights. This can lead to reduced packaging hence decreasing costs and waste production (44).
One of the most promising path is the mixture between polymers and clay, these ensure in fact low costs, high processability and low toxicity, revealing suitable for food contact.

In the recent years more and more interest has been showed in nano-composites using bio-polymers in order to follow the main trends in the packaging industry. Active packaging has become an interesting option when nano composite are involved; antimicrobial packages for example is a developing technology where the growth of undesirable microorganisms is controlled trough the use of silver nanoparticles. The presence if oxygen can cause degradative reaction in the product, to limit this problem passive barrier packaging is used such as aluminum foil or multilayers containing EVOH. With nanocomposites Oxygen scavenger systems can be used to eliminate the residual oxygen reducing the risk of bacterial growth.

To fully use this technology potential nanoscale dispersion has to be achieved, this is not easy; in fact the high surface area or high aspect ratio in the case of non-spherical structures brings high packing ability. The resulting agglomerates of nano structures are difficult to break in order to allow the permeation of the polymer matrix, the properties thus obtained are not at desired level.
Other usual fillers used are: Graphene, carbon nanotubes, silica and polysaccharide crystals. The first two cannot be used in the food packaging industry because of their intrinsic toxicity.

In polymer technology the use of layered silicate is the most promising way of tailoring their properties, the reinforcement obtained with the inorganic phase involves thermal and mechanical behavior. Phyllosilicates from the smectite group are used such as Montmorillonite, hectorite, saponite or laponite.

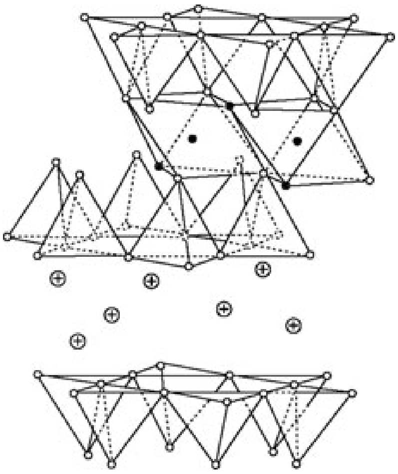

Fig. 1.23 Phyllosilicate lattice (44).

The lattice, as shown in Fig. 23, is made of layers thick 1 nm made of two tetrahedral sheets of silica, the share the edges with an octahedral sheet with alumina or magnesia. In this structure several isomorphic substitution are possible with the cation leading to an excess of negative charges. Between the layers a regular gap is created, cations of calcium or sodium that counterbalance the negative charge are usually located here. The interlayer space is also penetrated by organic cations or polar liquids, his structure has in fact high polarity. The basal spacing is a key parameter, the layer thickness ranges from 0,96 nm to 2nm, depending on the nature of the interlayer cation and the presence of absorbed water.

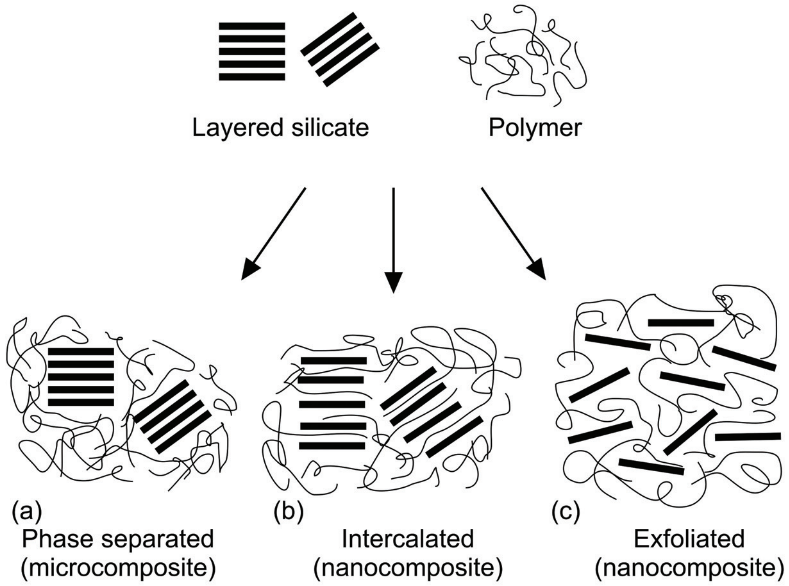

Fig. 1.24, Different possible morphologies for nanocomposites containing clay platelets (45).

The lamellae have high aspect ratio, the main problem when mixing clay and polymer is compatibility: the clay has usually an hydrophilic surface meanwhile the polymer is organophilic so the macromolecules don't enter easily the inter-layer space. To enhance compatibility the clay surface has often been modified with surfactants or organic cationic molecules that act as substituents for the smaller atomic cations. These are called organoclays; organically modified to ensure polymer-clay dispersion, their surface energy is lower to allow wetting from the polymer melt.

Three main categories of nano composite can be produced when mixing polymer and layered silicate, as displayed in Fig. 1.24. When there is low wettability the composite produced is a microcomposite, in fact the clay forms agglomerates at the micro scale; in this second phase very few or none macromolecules are present. If the dispersion is higher and the macromolecules enter the gap between the lamellae an intercalated nano composite is obtained. This maintains a peak in the XRD pattern because the ordered structure is still present, even if with broader space between the lamellae. The optimum state is the exfoliated nano composite where the macromolecules and the clay are well dispersed and distributed, thus resulting in the absence of lamellae ordered distribution.

Several methods are employed to prepare polymer-clay nanocomposites: in situ polymerization, polymer intercalation in solution, melt intercalation and emulsion polymerization.

In situ polymerization involves the use of the liquid monomer or a monomer solution, here the layered silicate undergoes swelling. When polymerization occurs the growing macromolecules include the silicate sheets.

Solution intercalation is based on the use of a solvent system where both the polymer and the silicate layers undergo swelling; chloroform, water or organic solvents may be used. Firstly the silicate is dispersed in the solution system and undergoes swelling, then the polymer solution is mixed and the macromolecules substitute the solvent molecules between the layers. When the solvent evaporates the intercalated structure remains.

When the polymer and the clay are not soluble in the same solvent emulsion polymerization is a smart solution: the solution with the monomer and the solution with the swollen silicate are mixed in order to create an emulsion. Then polymerization is carried out, including between the layers the macromolecules and when the solvents evaporate the resulting composite maintains the intercalated structure.

Melt intercalation is the most used technique because of the lack of solvents employed and the ease of the procedure; basically the clay and the polymer are mixed with processing equipment above the softening point of the polymer. This is the method also used during this work, dispersion and distribution of the clay are achieved trough the shear forces applied during processing that break the nanostructure agglomerates.

1.15.1 Effects on the polymer properties

Considering mechanical properties in 2002 Lee et al. produced a pioneering work on the biodegradable composite PBS/Cloisite 30B (46). The tensile strength increased of 15% with 5% of Clo30B, reaching a peak of 65% increase with 30% of Clo30B, elongation at break didn't change significantly and tensile modulus was increased of the 70% with 30% Clo30B and 10% with 5% Clo30B. Meanwhile with Cloisite 10A a peak was reached with 10% of clay after which the mechanical properties started to drop down, this can be ascribed to the lower compatibility between clay and polymer and the creation of agglomerates in the matrix that became start points for crack propagation. The increase of the mechanical properties can be attributed to the good rigidity of the clay.

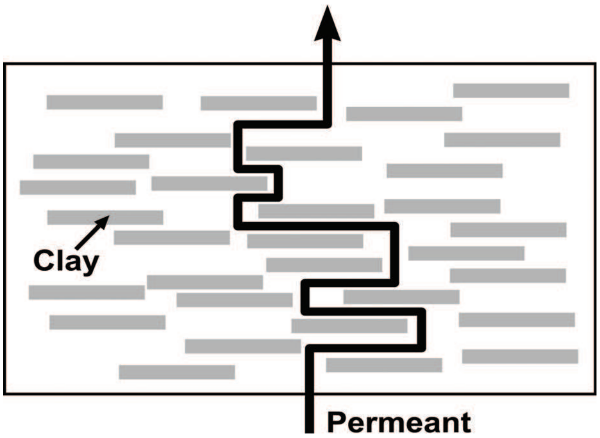

Fig. 1.25 Diffusion path of a permeating gas trough a nano composite containing clay platelets (48).

Thermal stability is also improved, the rigid network created by the lamellae operates as a rigid structure that keeps the polymer in place also when the softening starts, it also enhances crystallinity acting as a nucleating agent (47).

Barrier properties are also improved, against all gases because the mechanism that participate in this change is physical so it doesn't discriminate gases on their chemical nature. As shown in Fig. 1.25 the gas, in order to diffuse in the polymer has to go trough a more tortuous and long path thanks to the platelets disposition in the matrix itself. The extent of this enhancement depends mainly upon the clay aspect ratio and morphology. Chemical mechanisms can be included also; using an

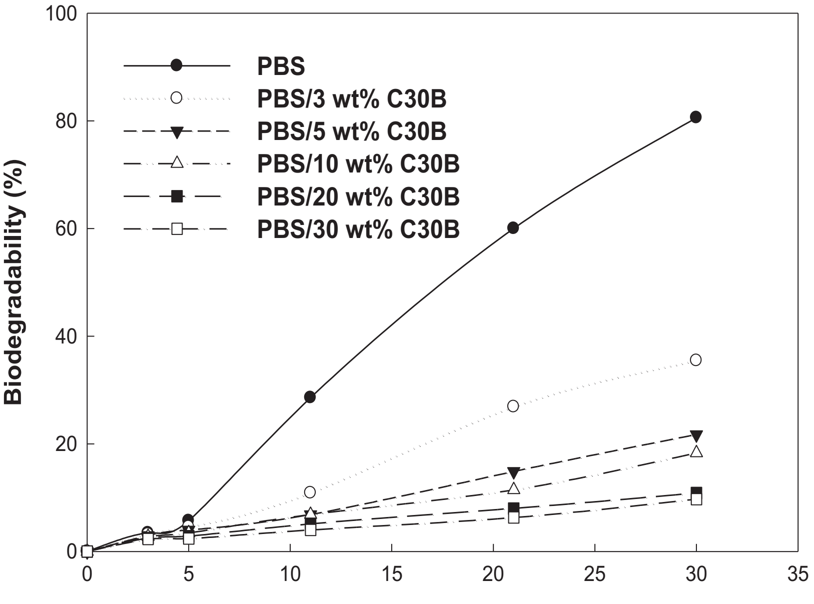

Fig. 1.26 Biodegradation of PBS with different percentages of Cloisite 30B (47).

hydrophobic filler will lower water absorption and diffusion, on the other hand an hydrophilic filler will lower oxygen and carbon dioxide permeation.

One of the main reasons for studying biodegradable polymers nano composite is to preserve their biodegradability, hence the presence of the filler shouldn't prevent microorganism to attack and degrade the polymer. For some biopolymers the presence of fillers enhances biodegradability, but for PBS biodegradability is significantly lowered by the clay presence as shown in Fig 1.26. The higher the presence of the filler, the lower is the biodegradation rate and level reached. This can be explained with the structure of Cloisite 30B, the ammonium groups contained have in fact antimicrobial activity against Gram-positive bacteria and bacteriostatic activity toward Gram-negative bacteria.

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Chapter 2 - Polyester reactor synthesis

2.1 Introduction

During the 30s Carothers and his group worked on the polycondensation of polyesters (1) but the number average molar mass (M_n) of the products was lower than 5000, keeping them from reaching an acceptable level for industrial applications. The resulting products were too weak and brittle resulting in high difficulties for processing and usage. 60 years later the group of Takiyama (2) finally succeeded to increase the molecular weight of the polyester produced up to 200 000 thanks to the use of new catalysts. From this moment on a few structures to produce PBS were built, marking the beginning of the development of the industrial production and application of PBS.

In 1993 Showa High Polymer built the first plant for PBS semi-commercial production where the polyester was produced under the name Bionolle. This was synthesized via melt condensation using also chain extenders to increase its molecular weight. Bionolle is the trademark of the polyesters synthesized and described by Takashi Fujimaki in 1997 (3), here we can find account of the first grades of PBSu and some of its co-polymers such as poly-butylene succinate adipate copolymer. The different grades produced were suitable for making films, sheets, filaments, laminates, injection-moulded products and many others applications.

The main problem related with this first semi-commercial production of Polybutylene succinate was related to the presence of chain-extenders that kept PBS from applications in medicine, cosmetics and food packaging because of the lack of bio-safety of these products (4). Therefore the main goal in this field became the production via direct melt polycondensation, achieved during the early years of 2000. PBS produced in this way has the same mechanical properties but better biosafety, in 2003 Mitsubishi chemicals built the first factory with a production line for PBS via direct melt condensation.

Many technical developments followed these early studies, in line with the increasing interest of the market and the public consumer toward a polymer that can be both biodegradable and bio-based. Succipack project is also noteworthy, started in January 2012 (5) with the aim of bringing innovation in the food packaging industry through the study of PBS and its properties. PBS was produced using 100% bio-based succinic acid, also 1,4-butanediol was produced via bacterial fermentation. One of the main goals of the project was to evaluate how the environmental impact could be increased by using monomer produced with biotechnologies, using solid state polymerization which lowers significantly the energy consumption.
Solid state polymerization is an industrial process where the starting materials are heated in the range between the melting temperature and the glass transition

temperature with constant removal of by-products. The amorphous state guarantees sufficient mobility to the chains to promote the reactions.

The main recommendations for further investigations were about the stabilization to oxidation at high temperature and the stabilization to hydrolysis, with the promising route of nanocomposites. These are important suggestions that were taken into consideration during the development of this work, to investigate PBS application in food packaging.

2.2 Reaction

The direct melt polymerization of Polybutylene succinate is a step-like reaction with a condensation reaction between one or more organic acids with one or mole alcohols with the elimination of small molecules like water. Functionality must be at least two. despite the direct polymerization with stoichiometric ration between succinic acid and 1,4-butanediol could be possible only low molecular weight is achievable due to lack of reactivity when the reactive groups fall below a certain concentration. In order to achieve higher molecular weight is possible to work with an excess of diol and splitting the reaction in two stages. In the first stage the reaction between acid and hydroxyl groups take place with elimination of water that is distilled off. In the second stage, conducted in high vacuum , the transesterification proceeds with elimination of the excess of diol. To achieve high conversion of the reactants the equilibrium must be moved toward the products, the easiest way to do that consists into the elimination of the by-products from the lateral reactions, for example oligomers.

The synthesis can be divided in two different phases; during the first stage there is the condensation reaction between succinnic acid and 1,4butanediol, during the second stage the real polymerization occurs. The reactor used has a total capacity of 150g of PBS, considering the condensation reaction as follows:

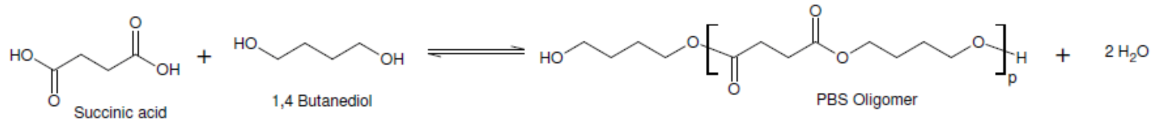


Fig 2.1. Condensation reaction with production of oligomers

We can calculate the weight of the two reagents needed, the esterification successfully takes place working with an excess of 1,4Butanediol, with a ratio between the reactants of 1,4. Therefore the quantities used are:

Tab 2.1 Relative quantities of reactants.

Reactant	g	mol
Succinnic Acid	102,66	0,87
1,4 Butanediol	109,62	1,218
Cat. TE (10%)	0,1125	0,112
Cat. TnBT (10%)	1,5	1,5

Adding more butanediol is not risky regarding the reactor capacity in this case because the stoichiometry used didn't consider the weight loss because of stripped oligomers. The two catalyzers, TE and TnBT are used in a solution with M=10% to allow an easier weighting procedure. Both of them are diluted with butanol, that is an alcohol with medium boiling point, in fact they will be added when the reactants are at high temperature. The chosen alcohol shouldn't evaporate immediately when it comes in contact with the melt, to avoid the evaporation and degradation of the catalysts.

During the first phase, as shown by the previous reaction, water is produced, thanks to that the progress of the reaction can be monitored. Then, when 31,4g of water (the expected weight of water from stoichiometric calculation) are distilled the first condensation reaction should be finished. Actually what is produced by the reaction in this first stage is a mixture of water and tetrahydrofuran, a byproduct produced by the dehydration of 1,4-butanediol. Water and THF coming from degradation of 1,4-butanediol are collected with water coming from esterification thus the total amount of distillate exceeds the expected value.Thus allows us to estimate the esterification yield with the quantity of water collected. The amount of water distilled should be more than 80-90% based on the stoichiometric amount before the beginning of trans-esterification to ensure a sufficient conversion of carboxylic and hydroxyl groups, otherwise the condensation reactions may continue during the second phase without allowing the polymer to reach high molecular weights.

The synthesis is carried in a silicon oil bath at initial temperature of 195°C, at this temperature all the reactants are liquids. The first part of the reaction starts when succinnic acid is completely melted and the reactants are well mixed by the rotating shovel. The melt has not a high viscosity since the molecular weight doesn't grow significantly during this step, the shovel rotates at medium speed of 400 rpm. Here the reactions proceeds with butanediol excess, in order to achieve a good conversion rate thus obtaining oligomers with hydroxyl end groups. These will promote the trans-esterification process during the second phase. The first catalyst is added when the reaction has reached the 80% of water distilled, then starting the first gradual vacuum with an highest point of 0,7 mbar. In line with the vacuum pump is applied also a cold trap; this technique is also recommended from the Technical Institute of Physics and Chemistry, Chinese Academy of science, (7). Therefore small molecules produced in the last part of the first stage and during the second stage condense and keep stable high vacuum conditions, the removal of these small molecular compounds boosts the reaction rate.

To start the second trans-esterification phase 34 gr of water can be considered as the threshold level, so that the first oligomers are produced. There is added TnBT and the second gradual vacuum is carried out with a final value of high vacuum reached at 0,1 mbar.

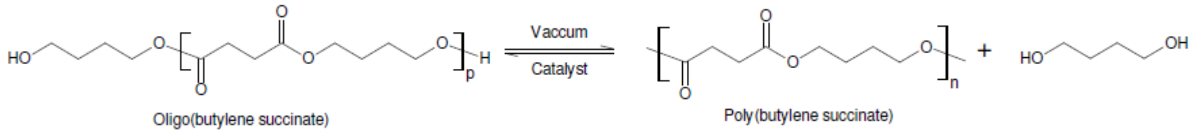


Fig 2.2. trans-esterfication reaction with production of PBS(6).

The reactor is shaped to optimize the polymerization phase, the rotating shovel has the perfect match with the glass walls that allows to mechanically break the polymeric chains to boost the reaction toward higher polymerization grades. This ensures a good and efficient renovation of the melt surface maximizing the evaporation of 1,4-butandiol and low molecular weight cyclic oligomers.

During the second phase, polymerization occurs as shown in Fig. 2 under vacuum conditions, the lower gas pressure and the higher temperature (250°C) of the bath promotes the elimination of terminal butanediol moiety with trans-esterification. Considering that the working conditions imply an excess of 1,4 Butanediol the chains at this stage will mostly end with the hydroxyl group, whose bonds are easier to break in order to allow further polymerization. Oligomers are produced and stripped away thanks to the vacuum system, they are condensed and collected in a glass flask. The rotating speed here is lower because the melt starts to increase its viscosity, the starting point is 260 rpm. As the molecular weight increases so does the viscosity and the torque needed to maintain the same speed. 130 Ncm is considered the threshold value for torque, once reached the rotating speed is decreased of 60 rpm until the torque limit value is reached again. The value of torque, the rotational speed as well as the melt appearance are the main parameters that give the operator an idea of the reaction progress. When the melt is not easily spread on the glass walls and the rotating speed as reached low values as 20-60 rpm with a high torque the polymer is ready and the reactor can be unloaded.

2.2.1 Catalysts

Organometallic titanates are used as catalyzers, completed with also other metals such as Sn or Sb where chlorine is substituted with chelating agents that shield the active metal ions. The metallic cation must have sufficient mobility to coordinate with the oligomers, and catalyze the reaction.

Tyzor TE is used at the end of the first phase, it is added when the threshold level of 80% of distilled water is reached, beginning with mild vacuum conditions. It is a triethanolamine titanium complex (8) that reacts with water forming a reactive hydroxy titanium chelate.

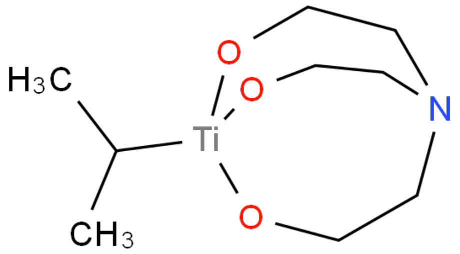


Fig 2.3. Tyzor TE (9)

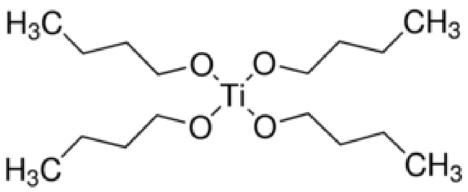


Fig 2.4. Tyzor TnBT (10)

The chelate then forms complexes with hydroxyl or carboxyl groups and acts as a Lewis acid catalyst for esterification and trans-esterification. The chemical structure with the usual cage structure is shown in Fig. 2.3 TE is specially recommended for the esterification phase for its excellent compatibility with water, which is the main byproduct during this stage, it is also an effective cross-linking agent for several applications. This catalyst is used in the form of a clear light yellow liquid which contains 80% active titanium complex dissolved in alcohol.

Tyzor TnBT (Tetra-n-butyl titanate) is used for the second phase, it is a reactive organic alcoxy titanate that comes in the form of a clear yellow liquid. It is very sensitive to moisture, hence it needs particular attention when added into the reactor, also because of that the number of possible additives used in the reaction is limited. It can be used as a Lewis acid for esterification and transesterification, in this work TnBT is added during the transesterification, when most of the water has already been distilled. It works as a Ziegler-Natta catalyst for polymerization.

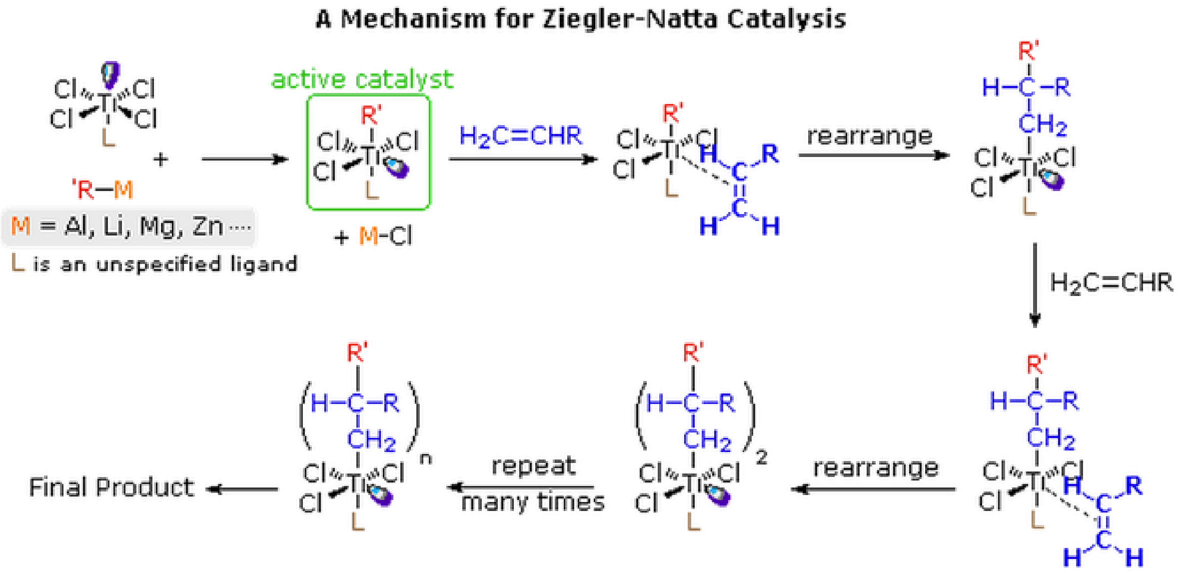


Fig 2.5. Mechanism for Ziegler-Natta catalysis in polymer production with titanate compound (11).

Karl Ziegler and Giulio Natta discovered in the 50's an efficient and stereospecific catalytic polimerization process, hence permitting the synthesis of unbranched, high molecular weight HDPE. This type of catalyst has been widely used over the years with success, also in the synthesis of polyesters.
Has shown in Fig 2.5 the metallic ion coordinates and orientates the monomer then allows the anionic growing macromolecule to bond with the monomer, then creating a new ion. Titanium is in the case the counter-ion which brings a certain orientation to the polymer.

In the past years different organometal catalysts have been examined for the transesterification process for the PBS two-stage melt polycondensation process. (12) For PET polyester condensation the most efficient is the titanium based catalyst, but because of the yellowing that it produces nowadays mixtures with antimony and germanium are preferred. The amount of catalyst used during the reaction must also be as low as possible, to avoid processing and aging problems due to the residual metallic presence. From the results shown in this study several helpful deductions can be extracted.

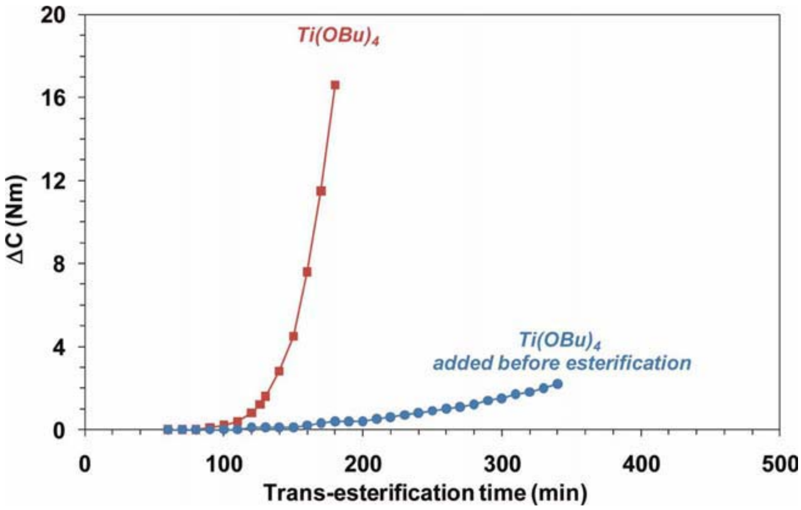


Fig 2.6. Effect on transesterification time and developed torque of 400ppm of TnBt added before esterification (blue) or after trans esterification (red) under vacuum conditions. (12).

Metal alkoxides loose their efficiency in the presence of water, producing condensed species and agglomerate, this was confirmed by their own experiment (12), as shown in Fig. 2.6 In both synthesis 400 ppm of catalyst were added, before the esterification part (blue line) and after the first phase (red line). The toque was monitored as a significative indicator of the polymerization level of the melt, the higher the torque, the higher the viscosity thus indicates a higher molecular weight reached. Adding the titanate before esterification subdues the catalyst to the presence of water, distilled during the first stage, inhibiting its capacities to catalyze trans-esterification. This can be deducted by the lack of torque increase after many hours of trans-esterification.

A threshold level for TnBT concentration was also identified between 100 ppm and 200 ppm, with 100 ppm of titanate there was not increase of torque after 6 hours of trans-esterification. Increasing the level of TnBT anticipates the growing of the torque, though changing little in the slope of the growing torque, thus meaning that the rate of polymerization is not affected significantly by this parameter.

2.2.2 Raw material production

To synthesize Polybutylene succinate the two main reactants are succinic acid and 1,4 butanediol. Succinic acid can be derived from petrochemical or bio-based feedstock, in the first case is produced with the hydrogenation of maleic acid (13) in the second case it derives from microorganisms assisted fermentation. From succinic acid 1,4-butanediol can be produced, with other various diamines and diols.

The LCA study from cradle to grave carried within the Succipack project (5) highlights that the production of succinic acid is the most influent step of PBS production in terms of emitted carbon dioxide and energy consumption. The trend nowadays is toward those routes that can guarantee an higher independence from fossil resources, several microorganisms were reported to produce succinic acid during their normal metabolic course. Some of them were indicated as the more productive ones, among them there is the recombinant Escherichia coli AFP184, which assures higher rates than the natural ones.

After fermentation succinic acid needs to be purified, this step is the most expensive in terms of money and energy consumption. The fermentation process offers more gentle conditions and independence from fossil resources, but it brings several disadvantages such as longer production times, high volumes of water needed and larger occupied space. To make it competitive the two main research routes investigated are (5): lower the costs of purification and increase the microbial productivity. The first step in order to obtain purified succinic acid is the separation of cell residues with ultrafiltration. Then the carboxylic acid is separated from the fermentation stew via precipitation with calcium hydroxide or calcium oxide. Finally the salt is treated with sulfuric acid then producing succinic acid and calcium sulfate as byproduct.

Thakker et al. in 2011 focused on the production of succinic acid from the recombinant Escherichia coli (14) with the aim of maximizing the conversion rate and efficiency. One other fundamental feature of the studied microorganisms is the ability to grow and prosper on various organic feedstock, in particular lignocellulosic derived biomass. To optimize Escherichia coli production genetic engineering techniques were used, introducing new metabolic pathways to improve succinic acid production from different carbon sources such as glucose, sucrose, xylose, fructose and glycerol. This last one is particularly promising because of its abundance, low cost and low levels of acetate during Succinic acid production which makes the recovery process less expensive.

On the other hand 1,4-butanediol can be produced with different technologies and from diverse raw materials, the usual process is the Reppe process and starts with acetylene, but it can also be produced from propylene oxide, 1,3-butadiene or n-butane. In the recent years bio-based paths were investigated, they mainly rely on bio-based succinic acid via hydrogenation (15).

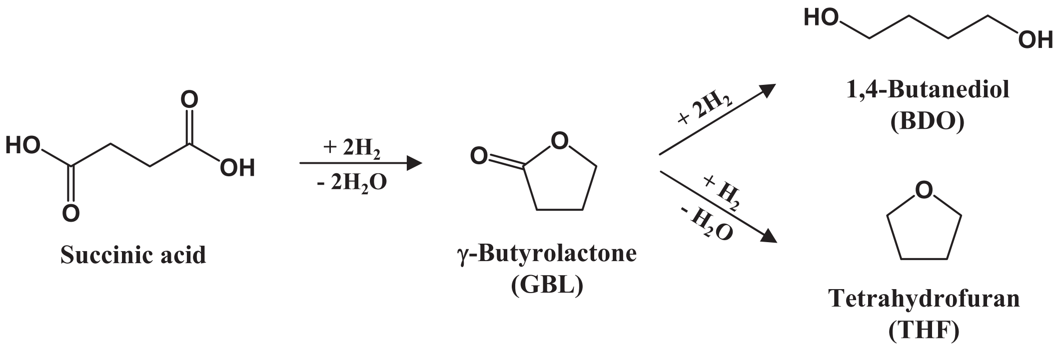


Fig 2.7. 1,4-Butanediol and THF production from succinic acid via hydrogenation (15).

In Fig. 2.7 one of the possible reaction pathways for succinic acid hydrogenation to 1,4-butanediol is presented. The reaction proceeds in two steps, with the production of THF as by-product, it is catalyzed by noble mono-metallic catalysts or bimetallic catalysts, such as the ones based on Re and Pd or Ru supported by mesoporous carbon, studied by Kang et al in 2015.

2.3 Parameters

Polybutylene succinate properties can be tailored varying some synthesis parameters during the process, in particular the present study focuses on acidity values. The main parameters addressed were:

- vacuum value
- bath temperature

These two were sufficient to obtain three matrices with different acidity values; with higher temperature the melt was subject to a higher thermal stress, thus resulting in worse degradative reactions, as those displayed in the previous chapter. Higher temperature hence brings to shorter chains, darker colors and also higher values of acidity.

On the other hand worse vacuum conditions carry oxidative and termo-oxidative reactions in the melt, due to the presence of higher levels of atmospheric oxygen and humidity. Better vacuum conditions, then lower pressure in the reactor, result in longer chains, lighter colors, better mechanical properties, lower acidity and melt flow index.

2.4 Prepared Batches

Several options were investigated regarding PBS synthesis, first of all different acidity values were obtained. As shown in Fig. 2.2 PBS ends with hydroxyl groups, then measuring their concentration with titration is useful to obtain informations about the molecular weight of the polymer, its sensitivity to the presence of water in the atmosphere and also its mechanical properties. A higher concentration of hydroxyl groups indicates shorter chains and also higher sensitivity to water because the matrix become more polar, thus enhancing its hydrophilicity.

To achieve different values of acidity the reaction conditions changed, worse vacuum conditions and higher temperatures produced lower viscosities and shorter chains. To obtain PBS2, with medium value of acidity, the silicone oil temperature was the same as for PBS1, low acidity, 250°C, but during the trans-esterification phase the last interval with 20rpm was conducted at atmospheric pressure. To achieve higher acidity with PBS3 the temperature of the oil bath was increased at 270°C, the vacuum conditions during trans-esterification were worsened from 0,1 mbar to 0,7 mbar and the last interval at 20rpm was conducted in atmospheric pressure.

The melt appearance was clear in the first stage of the reaction, turning then to yellow or light brown depending on the degree of thermo-oxidative stress on the reaction. Highest level of degradation brought to a darker melt, then to darker polymer batches, this is a direct consequence of the concentration of conjugated double bonds that absorb the visible light producing strong colors. This started to appear during the first moments of the polymerization phase usually, rising to darker colors during the second phase while viscosity increased.

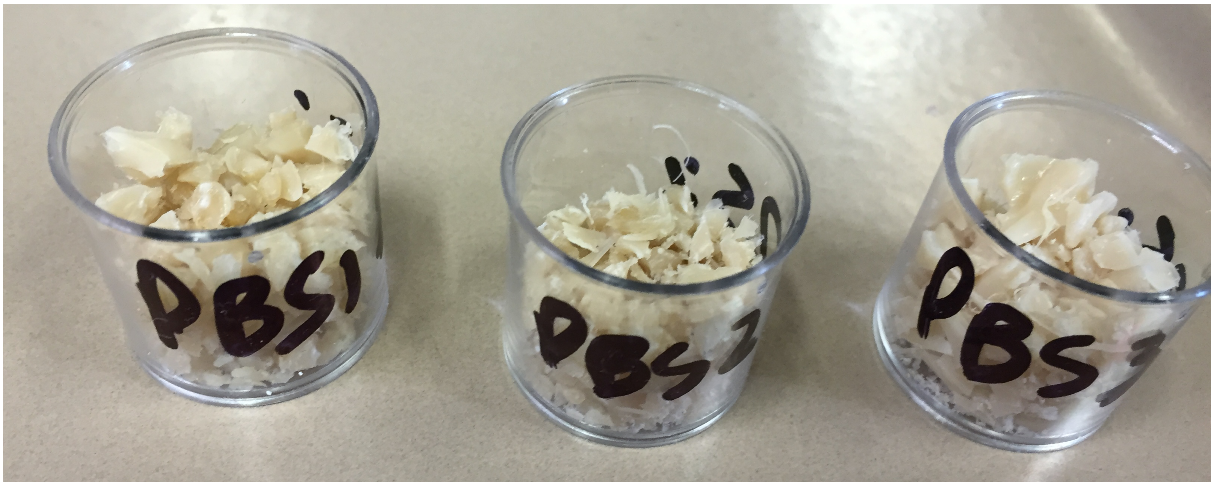


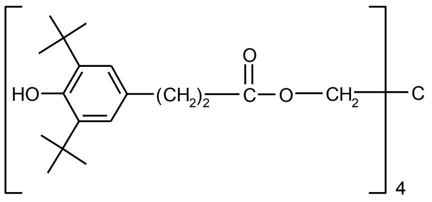
Fig 2.8. Comparison between granules of PBS1, PBS2 and PBS3.

2.4.1 Synthesis with additives

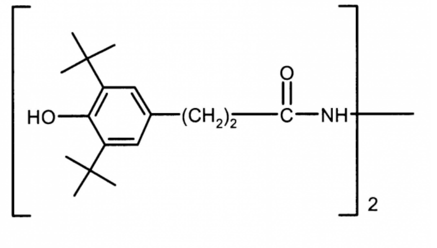
Then two batches with two different additives were prepared and characterized, one was synthesized with Irganox 1330, for thermal stabilization, and the other with Pripol 1009, for hydrolytic stabilization.

Between the different additives screened in this work (Irganox 1010, 1076, 1330, MD 1024 and 1425) the selected one was Irganox 1330. Mainly because it has to be taken into account how the additive can interact within the reaction environment, undergoing high temperatures up to 260°C and a harsh degradative ambient, it is then to be avoided the hydrolization of the additive itself or the creation of dangerous byproducts.

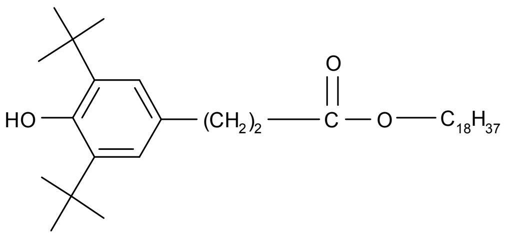
As shown in Fig. 2.9 the other four additives contain groups susceptive to hydrolysis, such has the carboxyl group -COO or carbonyl group -CO for Irganox 1010, MD 1024 and 1076.



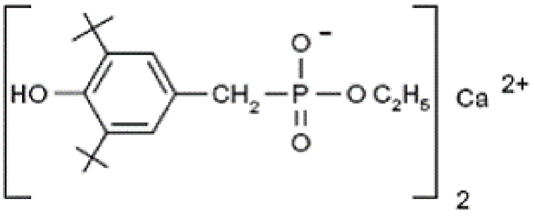
Irganox 1010



Irganox MD 1024



Irganox 1076



Irganox 1425

Irganox 1330

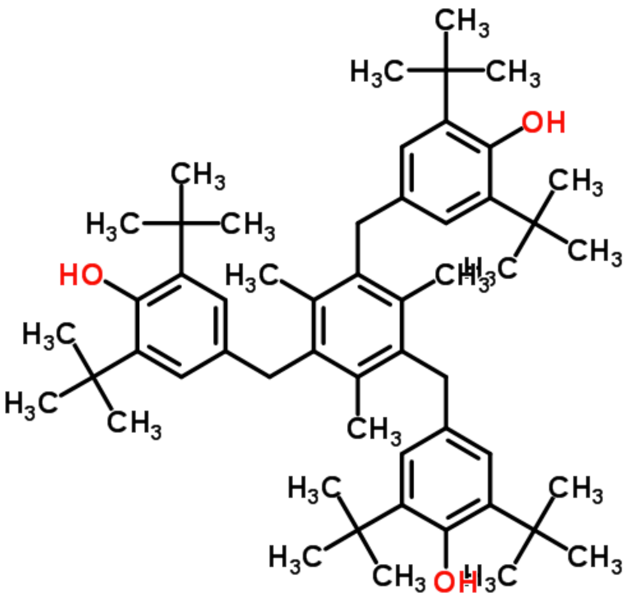


Fig 2.9.Chemical structures of Irganox 1010, 1076, 1425, MD 1024 and 1330 (16) (17).

Adding them with the reactants before the esterification stage would have submitted them to an environment with high hydrolysis risk: high temperature, up to 220°C, with the production of water as byproduct of the reaction. The same groups involved in hydrolysis are the ones that give high compatibility between the polyester and the additive, because of chemical bond similarity. An higher compatibility between the additive and the melt produces an high efficiency in thermal stabilization, achieved via extrusion (Chapter 3). Regarding Irganox 1425 also phosphate group is susceptive to hydrolysis because it is stabilized by the different resonance structures created with the hydrolytic scission. Therefore these additives would have been rapidly degraded by the reactor environment well before the moment when their protection was required.

Irganox 1330 is It is a sterically hindered phenolic primary antioxidant as shown in Fig. 9 for processing and long-term thermal stabilization (17). It is compatible with various substrates such as polyethylene, polypropylene, polyamides and polyester, it should protect the substrate also against termo-oxidative degradation, found in harsh aging conditions.

The recommended usage for polyolefin is between 0,05% and 0,3%, in this case 0,25% was added with the reactants, before the esterification phase. This quantity was chosen in order to allow comparison with the polymer produced by extrusion, with 0,25% of additive. The choice of adding it with the raw materials was made in order to begin the protection against oxidation and degradation from the very early stages of the polymerization.

This influenced also the final color of the batch with varied from the usual pale yellow to the light orange also seen during harsh aging of the blends of industrial PBS with Irganox 1330 (Chapter 3). In this case phenomena of termo-oxidation occurred, so it's likely that the same type of degradation occurred during this synthesis due to the high temperatures of the oil bath, from 190°C to 250°C, and the presence of small quantities of oxygen during the esterification phase, before reaching high vacuum conditions. The melt had also different appearance from the very first stages of the reaction, during the esterification it was not clear as for the previous synthesis, it also

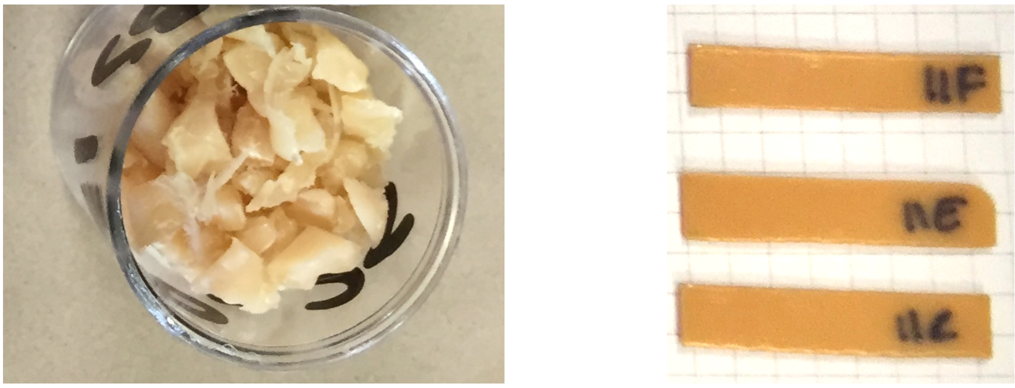


Fig 2.10.Color comparison between PBS with Irganox 1330 added during synthesis (left) and during extrusion (right). .

turned to the orange-brown color before than usual, immediately after the addition of the first catalyst.

Pripol 1009 is a dimer acid that can be copolymerized with polyesters such as PET and PBT to enhance water resistance and flexibility. It is made of 100% renewable content (18), with its long chains Pripol reduces water sensitivity shortening the drying process and reducing water absorption. This is particularly desirable for biodegradable polyesters such as Polybutylene succinate because of the sensitivity to hydrolysis of the polyester chemical bond as in the reaction displayed in Fig. 12.

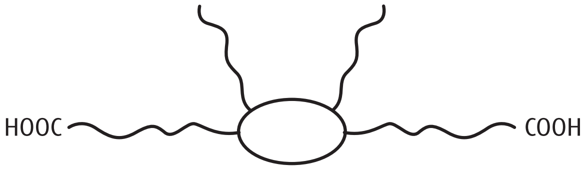


Fig 2.11.Chemical structure of Pripol 1009 (19).

This is one of the main problems related with the industrial use of PBS as a biodegradable polyester, as seen with the different aging procedures at room temperature and different RH, just atmospheric water can start these reactions degrading the polymer. Degradation results in shorter chains, broken by the hydrolysis reaction, with a subsequent lower viscosity and higher acidity, hence bringing worse mechanical properties.

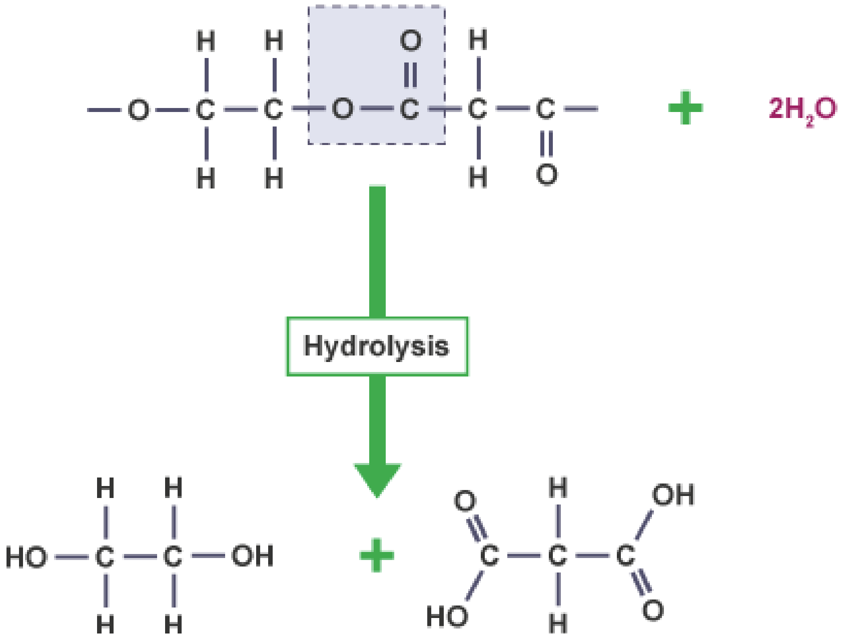


Fig 2.12. Polyester hydrolisis reaction (20).

PBS has high hydrophilicity thanks to its ester groups so it easily absorbs humidity from the atmosphere, the drying process is then fundamental before processing the matrix with the micro-extruder or the two platen press to avoid further degradation. Its hydrophilicity is although necessary to guarantee biodegradability, just with the presence of polar groups microorganisms and their enzymes can start digesting the matrix, but this cannot be an obstacle for industrial processing and packaging applications. the higher the concentration of hydroxyl end groups the more sensitive to water the matrix is, resulting into a faster degradation of the properties; a reliable index to investigate it is acidity.

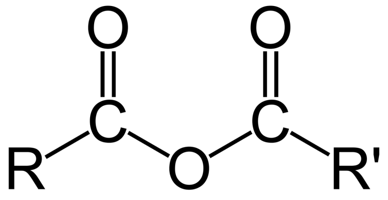


Fig 2.13. Anhydride group (21).

Adding Pripol 1009 directly during synthesis, just before the trans-esterification process, brought to a copolymerization of the fatty acid that entered the polymeric chains then creating anhydride groups in the polymeric chain as shown in Fig. 2.13.

The reaction that brings to this copolymerization is outlined here as follows in Fig.2.14, water is produced as a byproduct and two anhydride groups link the fatty diacid with the macromolecules of polybutylene succinate. The condensation was possible thanks to the high temperature and the presence of growing chains, as analyzed in the following chapter the addition of Pripol 1009 during the extrusion process had no positive result. The dimer acid has two carboxyl groups that can be linked with two other carboxyl groups from PBS macromolecules, hence eliminating the hydroxyl groups that have high hydrophilicity.

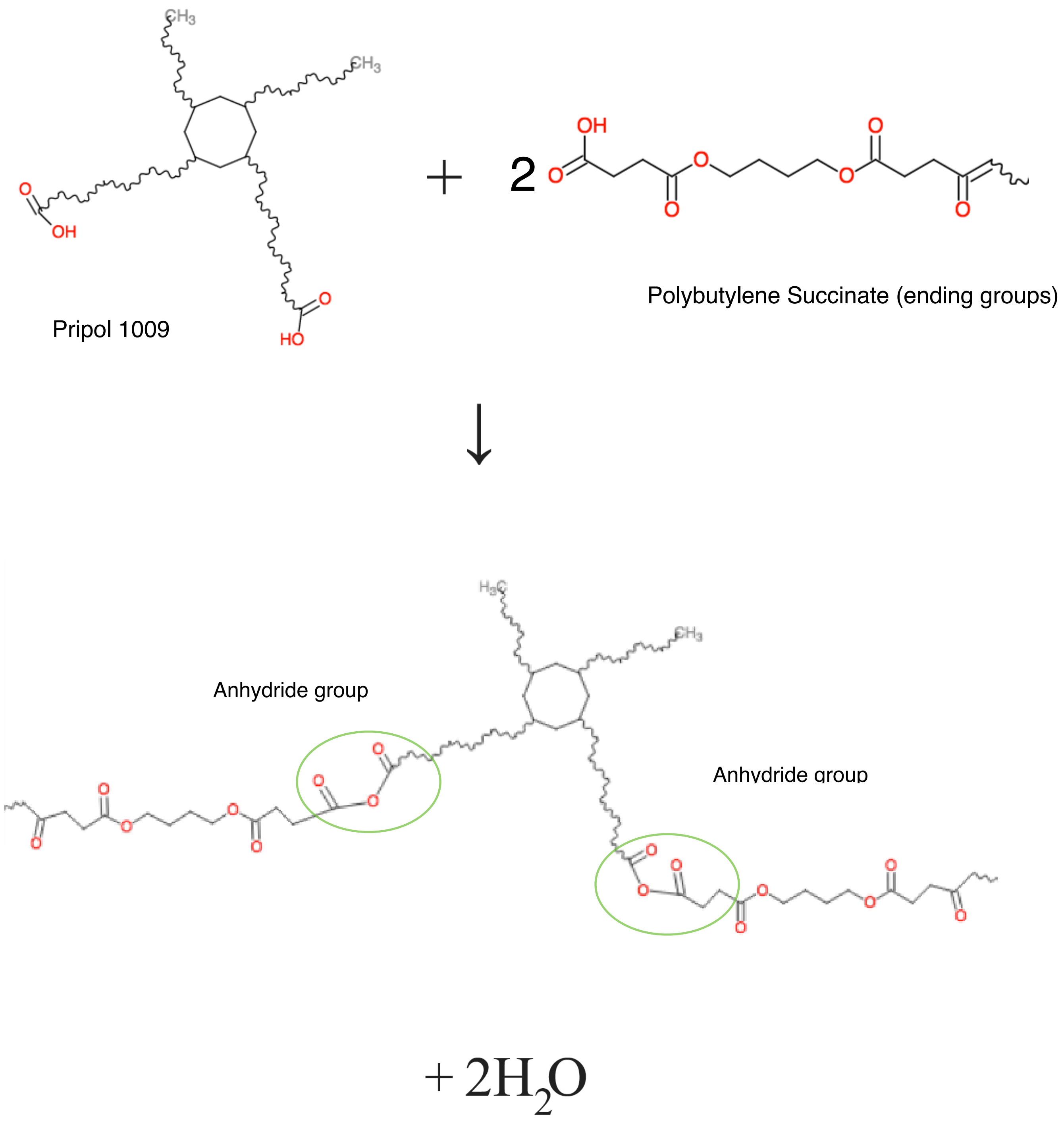


Fig 2.14. Reaction between PBS and Pripol 1009 with the creation of anhydride groups and water as byproduct.

The additive quantity was calculated considering PBS number of hydroxyl groups available for the condensation reaction compared to those of Pripol, an effective way of evaluating the concentration is thought a comparison between PBS acidity and Pripol acidity. For PBS an ideal value of acidity was considered, 20 meq/Kg, confirmed with the first Polybutilene succinate with Pripol produced. The calculation conducted is summarized in the table below:

Tab 2.2 Relative quantities of reactants for the synthesis with Pripol 1009.

	Acidity (mgKOH/g)	Ratio PBS/Pripol	Quantity (g)
Pripol 1009	196	$4*10^{-3}$	0,6
PBS	0,78	1	150

0,4% Pripol was added in the reactor, this quantity is well comparable with the other additives, whose range is between 0,25% and 5%.

Adding the fatty acid during the trans-esterification was a compelled choice, in fact including it with the reactants could bring problems during the first stage of the reaction, keeping the esterification from completing and then compromising the success of the overall reaction. Adding it at the beginning of the trans-esterification reaction when the macromolecules were not well grown is a compromise between

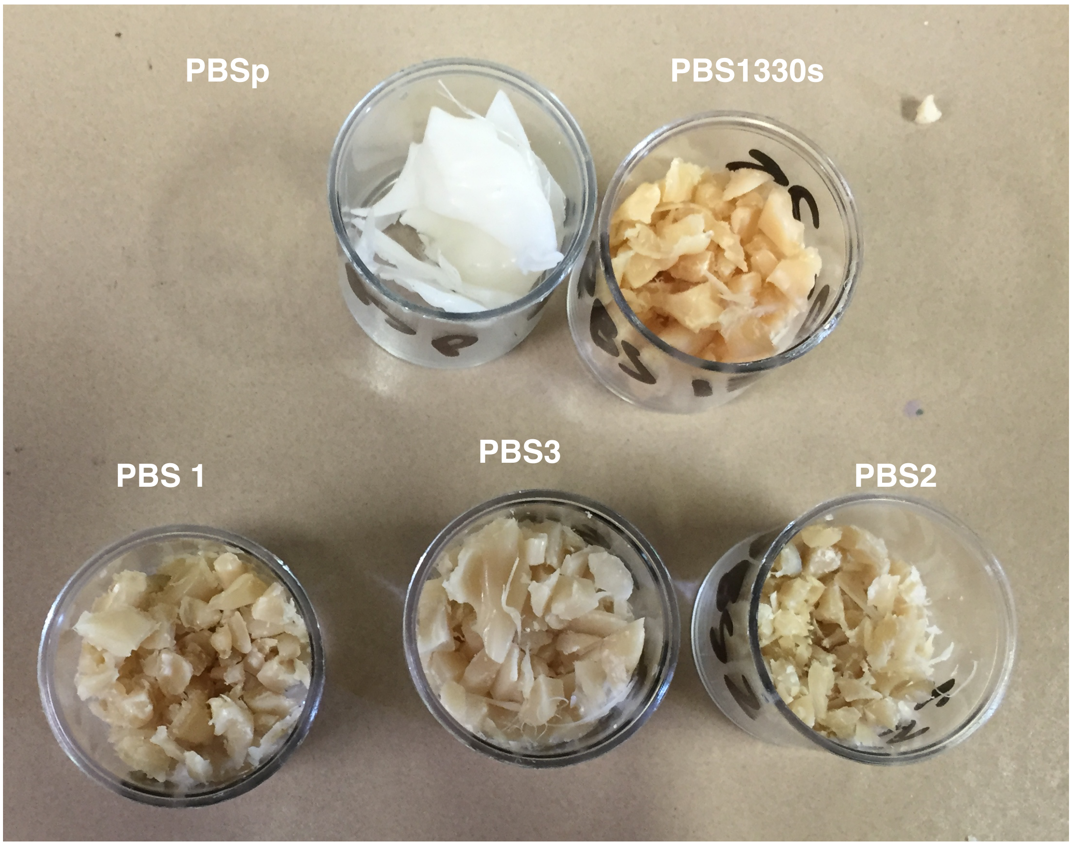


Fig 2.15 Comparison between PBS1, PBS2, PBS3, PBS with1330 and PBS with Pripol 1009 added during the synthesis.

the first option discussed and a possible integration in the end of the polymerization reaction. The second choice was not implemented because it would bring an high degradation of the reacting melt and the catalyst, forced to be exposed to the oxidizing atmosphere to allow Pripol 1009 addition.

The resulting polymer has enhanced water resistivity, but different rheology from the other batches. The melt didn’t succeed to reach the threshold value of 130 Ncm used during the previous synthesis before lowering the shovel rotating speed. To maintain comparability between the different batches we chose to limit the trans-esterification time to four hours, this can be also motivated with choices linked to the industrial process and its timing. Longer trans-esterification would make the new polymer difficult and expensive to produce for its final application for food packaging. The polymer rheology was nothing like the other PBS, with a torque of 110Ncm or even lower, 70Ncm, after the first stages of trans-esterification the reactor became unstable, thus forcing to lower the shovel speed.

The melt appearance was also particular, a bright white color was reached with also an opalescent look, with a viscosity higher than the others but a value of MI far higher than the other polyesters.

2.5 PBS Characterization

In Table 2.3 the results from the characterization of the five main batches and the industrial PBS used in this work are displayed:

Tab 2.2 Acidity value, intrinsic viscosity and MI of the prepared batches.

	Acidity (meq/kg)	[n] (cm^3/g)	MI (g/10min)
PBS1	12	0,992	8,6
PBS2	32	0,999	15
PBS3	53,5	0,960	19
PBS pripol	21	1,08	-
PBS 1330	12	1,17	11
Industrial PBS	51,5	0,5	6

2.5.2 DSC characterization

For PBS sample the DSC was run from -50°C to 200°C, at 10°C/min, with a cycle of “heat-cool-reheat”, the sample analyzed were PBS1, with low acidity, PBS2, with medium acidity, PBS3, with higher acidity, and PBSp, with Pripol added in synthesis. PBS with Irganox 13330 was not analyzed because no change in rheology was expected, in fact Pripol entered the polymeric chain creating anhydride groups meanwhile Irganox 1330 didn't react with the growing molecules.

The polymer in this case has no real processing thermal history, the granules were taken directly after reactor synthesis, but it can present variation between the two heating cycles due to the different cooling rates. From curve the second heating curve informations about the material itself can be deducted, the first heating on the other hand corresponds to the manufactured product. The melting temperature is approximately 119°C, this gives the idea of a high viscosity molten polymer because it needs to be processed 60°C higher than its melting point. This is confirmed by the MFI values that are around 5-8 g/10minutes.

The peak shown in the cooling is clearly a crystallization peak because: it is an exothermic transition, it has about the same area as the melting peak and is not far from the melting temperature. The difference of 55°C between the melting peak and the crystallization peak can be attributed to the degree of supercooling. The crystallization peak was found during the cooling cycle, at 65,3°C for PBS1, 68°C for PBS2 and 83°C for PBS3. This can be imputed to the different length of the polymeric chains, shorter chains such as those of the more acid polyester crystallize easier, at higher temperature.

The glass transition temperature can be found from the heating curves to be approximately at -25°C. The melting peak is not very sharp neither is the crystallization, this indicates the presence of different sizes of crystallites, but is present in both heating curves, so the polymer has a high crystallization rate. Considering PBSp its crystallization temperature is about 68°C and melting temperature 119°C like the other PBS samples.

In all the samples characterized, even if for PBS3 is not too clear, there is the usual cold crystallization peak for polyesters. In this moment a small percentage of the polymer crystallizes right before melting, PBS is able to crystallize above the glass transition when heated.

The analysis of the crystalline present in the four samples was also conducted measuring the area under the melting peak, in order to spot differences in the overall crystallization due to different chain lengths, with the following results:

Tab 2.4 Melting temperatures and Crystallinity peak area of the different batches.

	T peak (°C)	Peak area (J/g)
PBS1	114,5	65,4
PBS2	113,8	58,8
PBS3	118,3	82,7
PBSp	113,8	73,1

No significant change in the melting temperature was observed; the man difference was fund between samples at low acidities (PBS1 and PBS2) and PBS3 with high acidity. PBS3 presented higher values of peak area, thus indicating an higher overall crystallinity due to shorter chains that can pack easily. PBSp also presented higher values of crystallinity, this can be linked to the fact that Pripol 1009 added into the chains made the chains more flexible, thus allowing more lamellae formation.

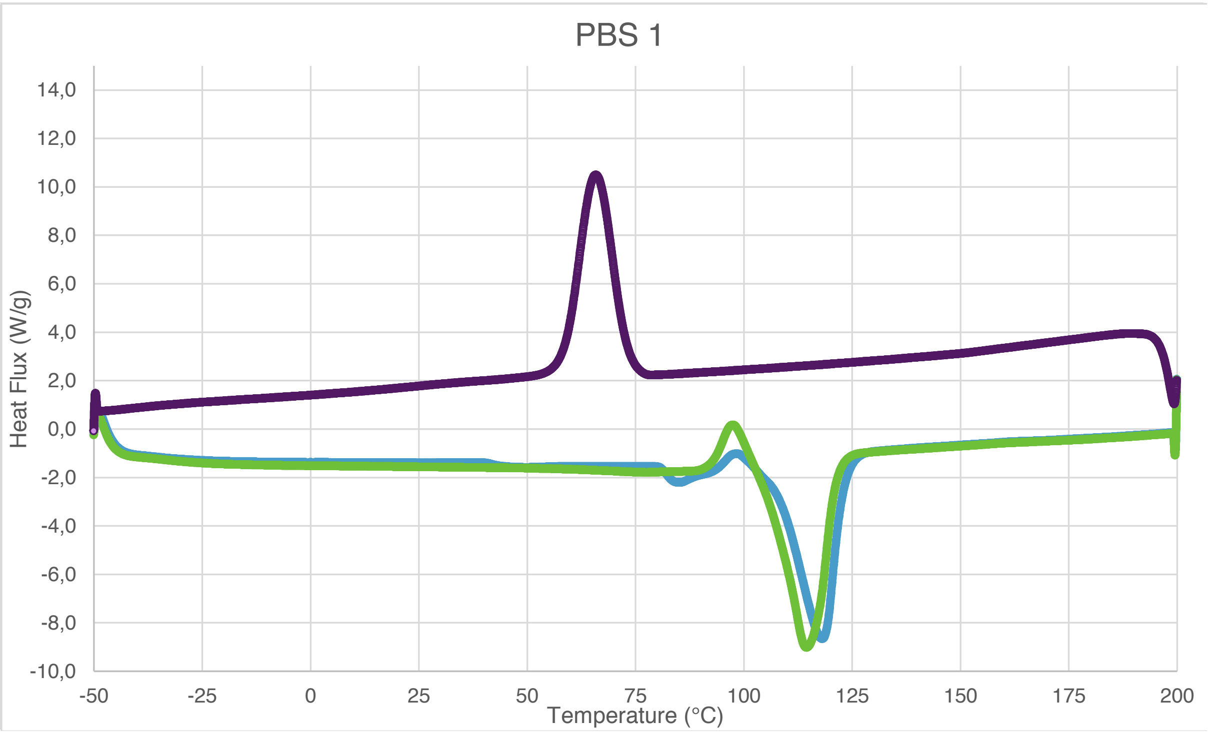


Fig 2.16. PBS1, with lower acidity, DSC graph, First heating (green), cooling (purple), second heating (blue).

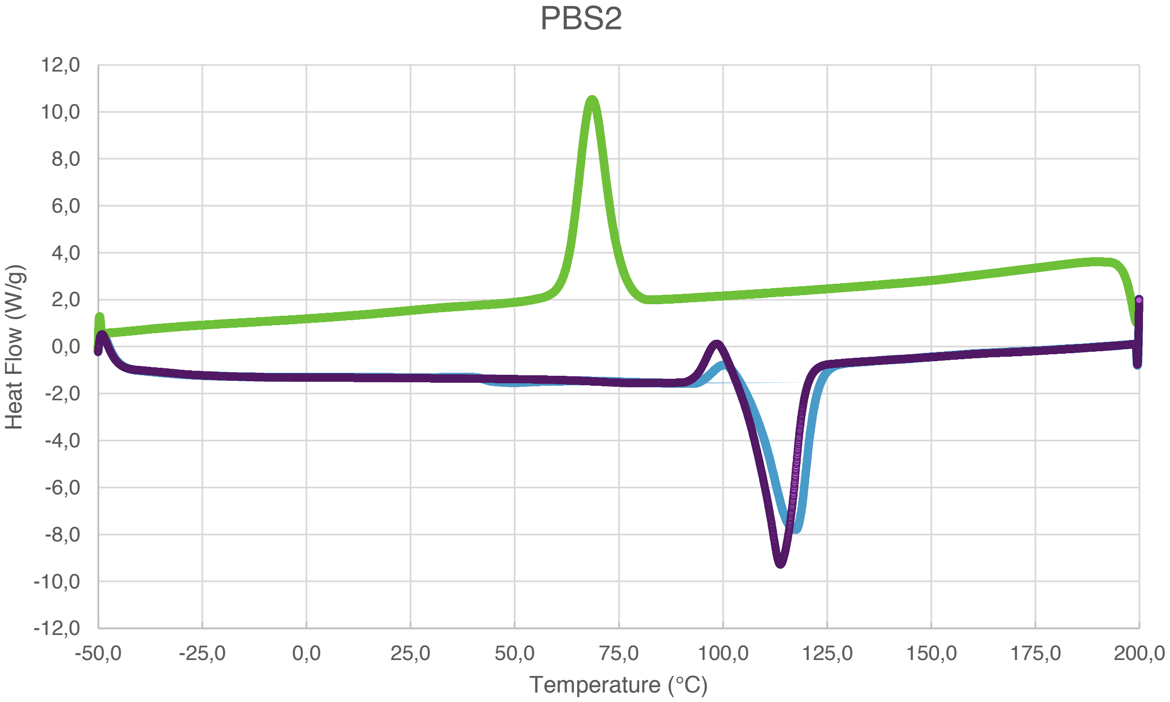


Fig 2.17. PBS2, with medium acidity, DSC graph, First heating (purple), cooling (green), second heating (blue).

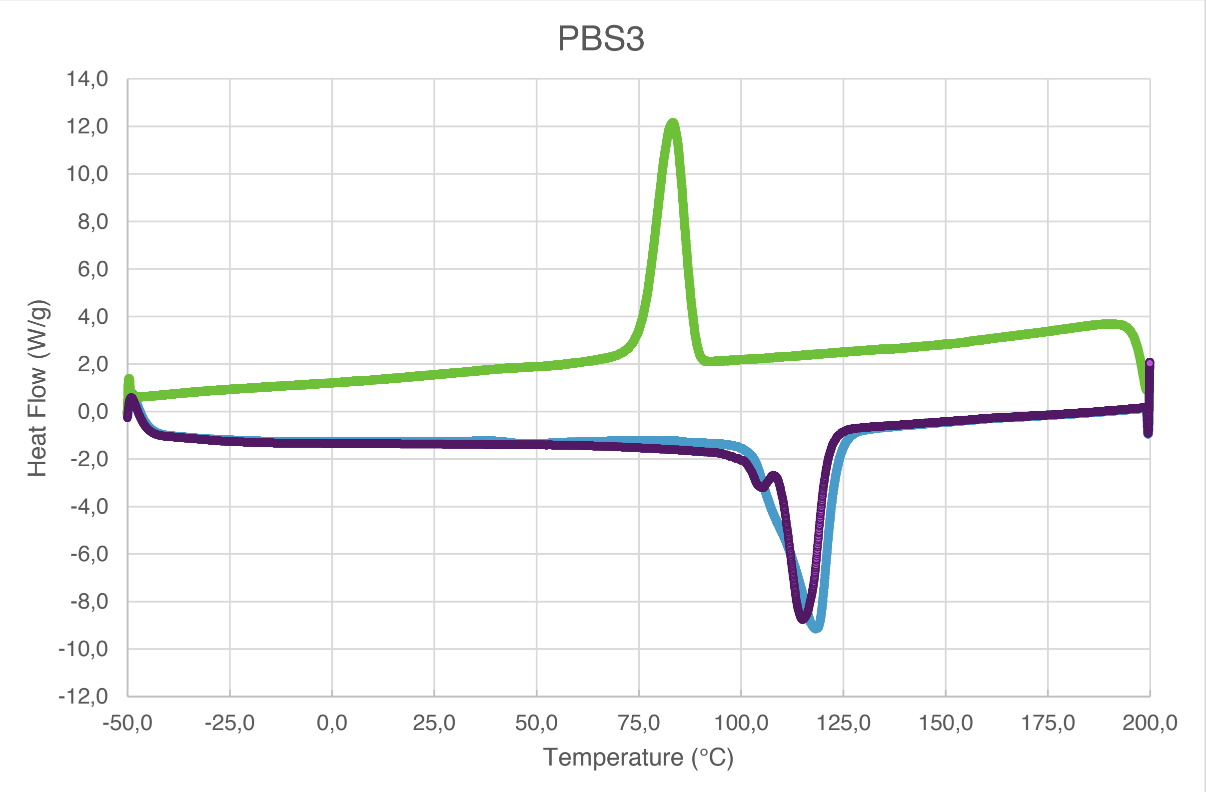


Fig 2.18. PBS3, with higher acidity, DSC graph, First heating (purple), cooling (green), second heating (blue).

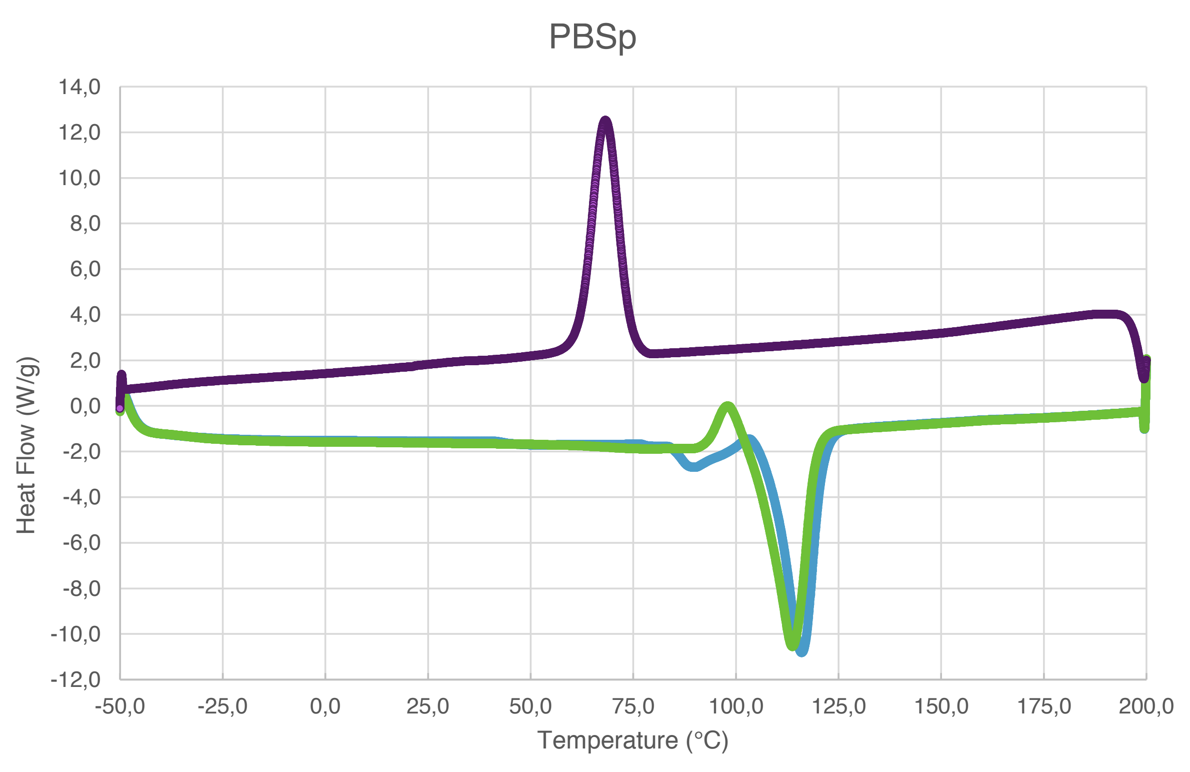


Fig 2.19 PBSp, with Pripol 1009 added in synthesis, DSC graph, First heating (green), cooling (purple), second heating (blue).

2.6 Other production methods

Several options are available regarding PBS synthesis such as: solution polymerization, condensation polymerization followed by chain extension, solid state polymerization, lipase catalyzed synthesis.

Solution polymerization involves the dissolved reactants in solvents such as xylene or decahydronaphtalene. In this case the removal of small molecular byproducts is promoted hence allowing lower reaction temperature involved, lower oxidation of the growing polymer then, but longer production time, also reaching peaks of 72h (22).

Chain extension is similar to direct melt condensation, yet it includes a further step where chain extension is performed. Chain extenders are bifunctional products that can react with the macromolecules forming a linear structure with higher molecular weight has schematized in Fig. 2.20.

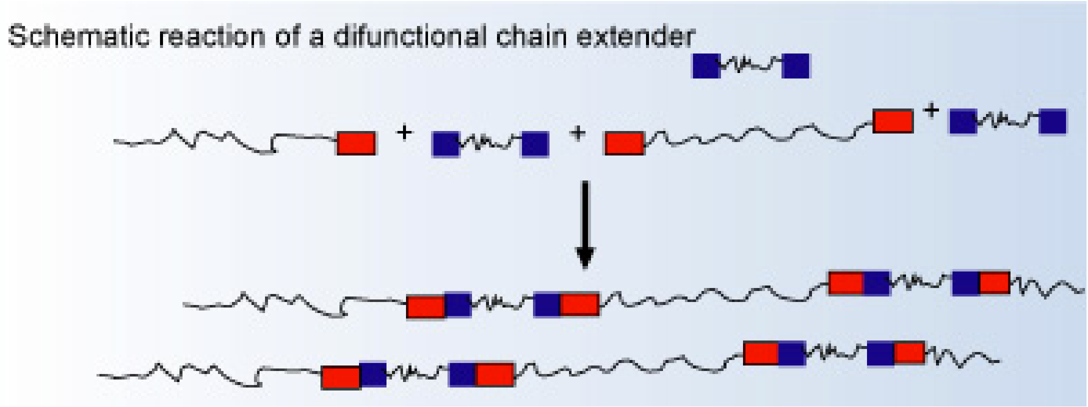


Fig. 2.20 Schematization of difunctional chain extender reactions. (22)

These molecules extend the linear macromolecular chains thus increasing the molecular weight, therefore the mechanical properties are enhanced, some widely spread examples are alcohols such as ethylene glycol, 2,3-butane diol, 1,4-tetramethylene glycol, but also bifunctional amines, both aromatic and aliphatic, acids and anhydride (22). These compounds are not suitable for food contact because of their bio toxicity, consequently the products obtained via chain extension are not used in medical, cosmetics and food applications. In the case of Polybutylene Succinate the chain extender reacts with carboxyl and hydroxyl end groups with a condensation reaction and the production of water as by-product. The choice of the molecule is influenced mainly by the most spread end-groups in the Polybutylene succinate, diisocyanate and anhydride will be used for hydroxyl-terminated PBS and oxazoline and expoxy are better employed for carboxyl-terminated PBS (23). In Bionolle production hexamethylene diisocyanate was involved (3).

Lipase catalyzed synthesis of PBS has been recently developed and it offers milder conditions than the previous ones presented. In 2006 Azim et al (25) reported the use of lipase B derived from Candida antarctica for the synthesis of PBS. The reaction temperature used was considerably lower than the usual reaction routes, during polymerization the chains were maintained between 80°C and 95°C. Although the reaction time increased up to 21 hours; on the other hand the polyester synthesized by lipase catalyzation has lower values of the polydispersity index thus meaning narrower mass distributions.

Solid state polymerization has been successfully used for polyesters and for polyamides (5) polymerization. The reactants are heated at a temperature above the glass transition temperature but lower than the melting point, in order to provide the macromolecules enough mobility for interaction. By-products are constantly removed to boost the reaction with the help of inert gas or low pressure environments. This technique was successfully used to increase the molecular weight of PBS oligomers with lower molecular weight. In fact, the effect of solid state polymerization is remarkable just when the presence of reactive groups is high, thus preventing the use of this technique when high molecular weight oligomers are produced.

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Chapter 3 - Aging and Thermal stabilization

3.1 Aging and degradation

Plastics undergo a change in their properties during their lifetime; degradation reactions occur and modify the initial morphology and chemical structure of the polymer itself often resulting in a loss of functionality. This decline affects the product durability and its applications. The degradation reactions can be initiated by several factor such as UV light, oxygen, water, temperature, enzymes, weathering agents, chemicals. Some of these processes are briefly explained in the following paragraphs, in particular the focus is on those involved during the process of aging actuated in this work.

3.1.1 Physical Aging

At room temperature, all amorphous materials try to reach thermodynamical equilibrium through a process called physical aging. The macromolecules slowly rearrange in order to achieve higher crystallization percentages if the material is at higher temperatures than the glass transition. The main consequences are a decrease in enthalpy and volume, increase in density and modulus; the material becomes more brittle. Physical aging doesn't involve chemical reaction, hence is a reversible process that can be erased by heating and cooling the polymer over again.

The main effect of physical aging is on failure, in fact it drives fracture from ductile to brittle, it results in a decrease in time to failure and elongation at break, that for films is fundamental. The effects of physical aging on craze growth fatigue and crack propagation are still not clear (1). In semicrystalline polymers the effects on mechanical properties is not as noticeable as in fully amorphous ones, also the relaxation time associated to physical aging is higher in fact crystalline regions constrain the amorphous macromolecules and their movements.

3.1.2 Thermal Degradation

Degradation, in polymer science, has a broad meaning, in fact due to the high molecular weights involved, also little chemical modifications can significantly vary the mechanical properties. Thus it can be defined as every chemical modification of the macromolecules that results in a variation on the polymer properties. Breaking 0,1% of the covalent bonds between the carbon atoms in the backbone chain is enough to drastically decrease the mechanical properties. Thermal degradation involves all the degradative reactions where temperature is the main initiating factor, that usually occurs during the early stages of the material's life: for example during extrusion or other industrial processes. The aim of heat stabilizers is to slow down the degradation processes and preserve its properties for its usage. The different degrading agents can contribute with synergetic power to the degradation of the formula, so it can be present thermal, mechanical, thermo-oxidation or photo-oxidation, that are some of the major causes of degradation in the case of packaging.

In the case of thermal stabilization there are two main properties that must be addressed: thermal resistance and heat resistance. Thermal resistance can be defined the higher temperature at which the material can be exposed without variation above a well defined limit. This kind of behavior is due mainly to chemical bonds such as C-C, C-H, C-O and C-N that dissociates between 150°C and 500°C. The initial thermolysis process is followed by multiple reactions that can amplify the degradation, breaking more covalent bonds and splitting the backbone chain. The shorter fragments tend to evaporate, because of their low molecular weight they are volatile compounds. Eteroatoms and other substituents can also produce different reactions, not only the fragmentation of the backbone but also crosslinking and cyclization (2).

Regarding thermal stabilization the mechanisms developed may vary with the temperature in which the component must operate. For low temperatures (100-300°C) the main goal is to remove the effects due to the presence of low energy bonds and have a higher decomposition temperature for covalents bonds between carbon atoms. Saturated chains undergo degradation at higher temperature than unsaturated backbones, in the second case the electronic stabilization and delocalization weakens the bond, lowering the decomposition temperature. For the applications of PBS pure thermal degradation won’t be the major cause of failure, but it can be involved in the overall process.

For polyester one of the typical reactions involved in thermal degradation is hydrogen β transfer that involves an unstable state that leads to chain scission with the production of macromolecules with carboxylic end groups and olefinic end groups (2).

3.1.3 Photo-Oxydation

Usually the reaction between organic polymers and oxygen is negligible, but has to be considered when radicals are generated thanks to the effect of heat or UV

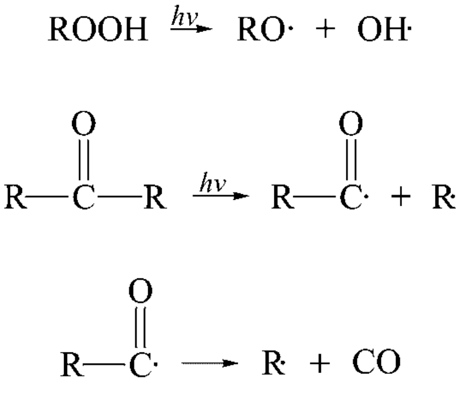


Fig 3.1 The creation of macro radicals initiated by UV light through the scission of carboxyl end groups and hydroxyl end groups (3).

radiation. The absorption of UV light can produce radicals by cleavage, in particular of carbonyl and hydroxyl compounds as shown in Fig. 3.1 (3).

This kind of process brings to the cleavage of polymeric chains, crosslinking reactions, development of volatile products and formations of oxygenated groups. Oxidation occurs with a radical mechanism that follows the pattern shown in Fig. 3.2.

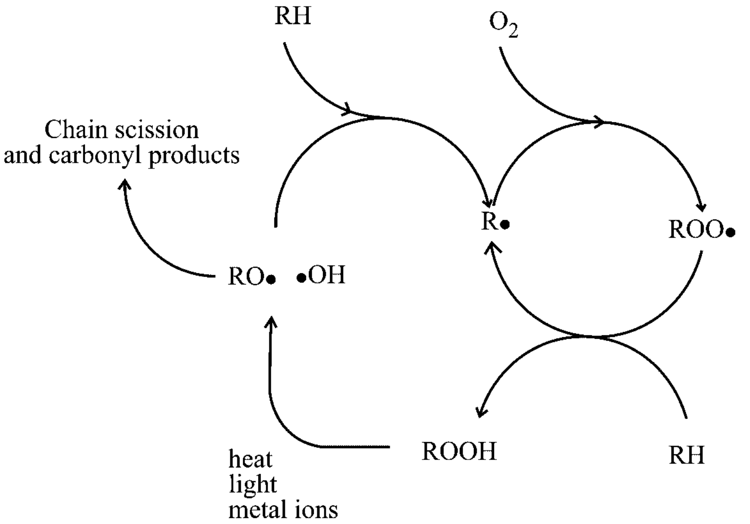


Fig 3.2 Oxidation cycle, that can be initiated by heat, light or metal ions (3).

The starting reaction that creates the macro radical doesn’t involve the presence of oxygen but can be enhanced with the presence of structural and chemical impurities in industrial polymers. For example polyolefin materials became photo reactive because of the the presence of oxidized groups developed during storage. Chain reaction is spread by macro radicals P- and POO-, the first ones have higher rate of the oxidizing reaction, the second are slower. In fact hydrogen extraction is slower and strongly depends on the polymer structure, such as the number of other hydrogens related to the carbon atom. Crystallinity also plays an important role, crystalline regions are far more resistant then amorphous ones because oxygen diffusion is slower. Termination occurs with the combination of P- and POO- radicals (2).

The effects generated by the oxidation of polymers are irreversible, for instance we must consider: the yellowing, loss of gloss, chalking and cracking on the surface. Mechanical properties undergo a general decay with dropping of tenacity and elongation at break. The oxidation stability depends on a number of factor that can be deduced from the mechanism briefly showed above: morphology, oxygen permeability, chemical structure can be firstly recognized as the most important (4). The product loses its esthetic appearance with yellowing, loss of gloss, chalking, discoloration or the appearance of surface cracks.

Oxidation usually conducts to failure, in fact the usual loss of toughness enhances the polymer brittleness and the products fails with cracking. In some cases this loss of mechanical properties is gradual, so it can be noticed, in others it can be very fast, in the end of a long period where the properties are stable. The embrittlement happens because chain scission changes the load equilibrium between crystalline and amorphous regions. When degradation starts in the amorphous regions it removes their ability to transfer load to the crystallites and to conduct the plastic flow, this leads to higher brittleness. The surface undergoes recrystallization to relieve stress, thanks to chains that are more free in this region where oxidative degradation starts, thus creating cracks. At a certain point the balance between plastic flow and crack propagation is irreversibly moved toward brittle fracture and fracture trough cleavage occurs (4).

All polymeric materials should be protected from oxidation with the help of low molecular compounds called antioxidants, these inhibit and delay the oxidation processes. As showed in Fig 3.2 this is a complex process, with different reactions involved whose importance change depending on the type of chains involver, so the additives duty varies with the polymer matrix. Nevertheless with the term antioxidant all the compounds that inhibit or delay all these processes are identified. These are divided into 5 classes: chain inhibitors that interact with radicals, UV absorbers, quenchers, pigments and antioxidants.

3.2 Additives

Additives are usually organic molecules that are added to polymers with different aims, from helping melt processing to protection from aging, usually they are added in small amounts, from 0,05% to 0,5%. That change into the polymer property can have as main goal the stabilization of the product against the main aging factors such as heat, light or water, or they can also provide functionalization (5).

Additives can be divided into three categories:

- Polymer modifiers, that usually alter physical or mechanical properties such as plasticizers or impact modifiers
- Performance enhancers that provide additional functionalities, such as flame retardants, antioxidants, light stabilizers, heat stabilizers.
- Processing aids to improve processing itself or modify the surface properties of the final products, such as slip agents or lubricants.

The food packaging industry extensively uses additives and their usage is regulated by the international agencies that investigate toxicity and their migration. They are usually added to the polymer matrices during the manufacturing process, under the form of master batches or blends of two or more additives.

Other important parameters to consider when considering the use of additives are volatility, physical form, taste and odor, performance, cost, safety issues, color stability. Additives are in the fluid or solid form, so they can be compounded with the polymer after the polymerization process, thus providing protection since the first stages of the thermal history. If possible they have higher molecular weight in order to avoid its volatilization during storage, they also have to be stable and don’t migrate toward the surface. Compatibility and solubility are other important parameters, if the solubility limit is exceeded exudation of the additive occurs; a very thin surface film is created with surface loss, stickiness and less printability.

3.2.1 Antioxydants

Antioxydants are used to reduce the degrading effects of oxidation, also during processing, thus acting as thermal stabilizers
Polyesters usually require little antioxidants during thermal processing, usually phosphorous compounds during polycondensation to form complexes with the catalyst residues and lowers the number of hydroxyl end groups, thus resulting in higher hydrolytic stability. With higher hydrocarbon content phenolic antioxidants are needed because the polymer, such as in this case PBS, is more susceptible to oxidation.

Antioxidants must not provide unwanted color while protecting the polymer matrix, otherwise pigments to disguise these changes should be used. When the end applications involve food contact, personal use or medical use taste and odor must be taken into account.

3.2.2 UV stabilizers

UV stabilizers are used in plastic technology to prolong the products life inhibiting the photo-degradation processes initiated by UV light emitted from the sun. This type of degradation needs chromophore groups to absorb the light, in particular one one of the ways in which UV stabilizers can work is trough the inhibition of the photo initiation process. The UV absorber enters in competition with the chromophores, absorbing the UV light and returning to the ground state with no harmful reactions (2). Other types of UV stabilizers are those which work by radical scavenging and hydroperoxide decomposition, in some cases they lose efficiency with time, because the process consumes their ability to protect the polymer, in other their protection mechanism is regenerated. These different mechanisms can be combined to act synergistically.

3.2.3 Hindered phenols

These molecules (InH) whose sample structure is shown in Fig 3.3 are hydrogen donors and react with peroxyl radicals, instead of polymer chains. In- radical is resonance stabilized as shown in Fig 3.4 (7) and can react further to extract other hydrogens with a maximum of two radicals terminated .

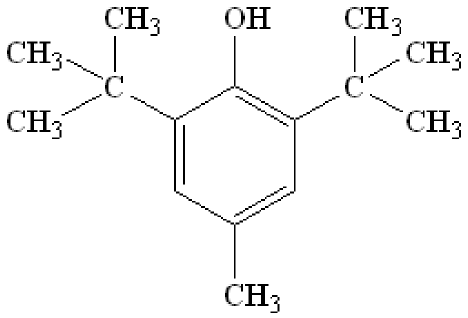


Fig 3.3 Hindered Phenols, sample structure (6).

This series of reactions result in the interruption of two kinetics chains with the formation of a peroxide and an hydroperoxide as shown in Fig 3.5.

Substituting the methyl chain on one side (para position with OH group) the additive can be adapted to different types of matrix, choosing chains with similar structure and chemical properties to the polymer that will be the solvent. The efficiency of the additive depends on his radical-trapping ability, its compatibility with the substrate and its resistance to extraction. Mainly the differences in their effectivity can be attributed to different solubilities in the polymer matrix, thus the additive should be selected choosing the most compatible one. Compared with the other types of additives hindered phenols are capable of guaranteeing thermal stability and

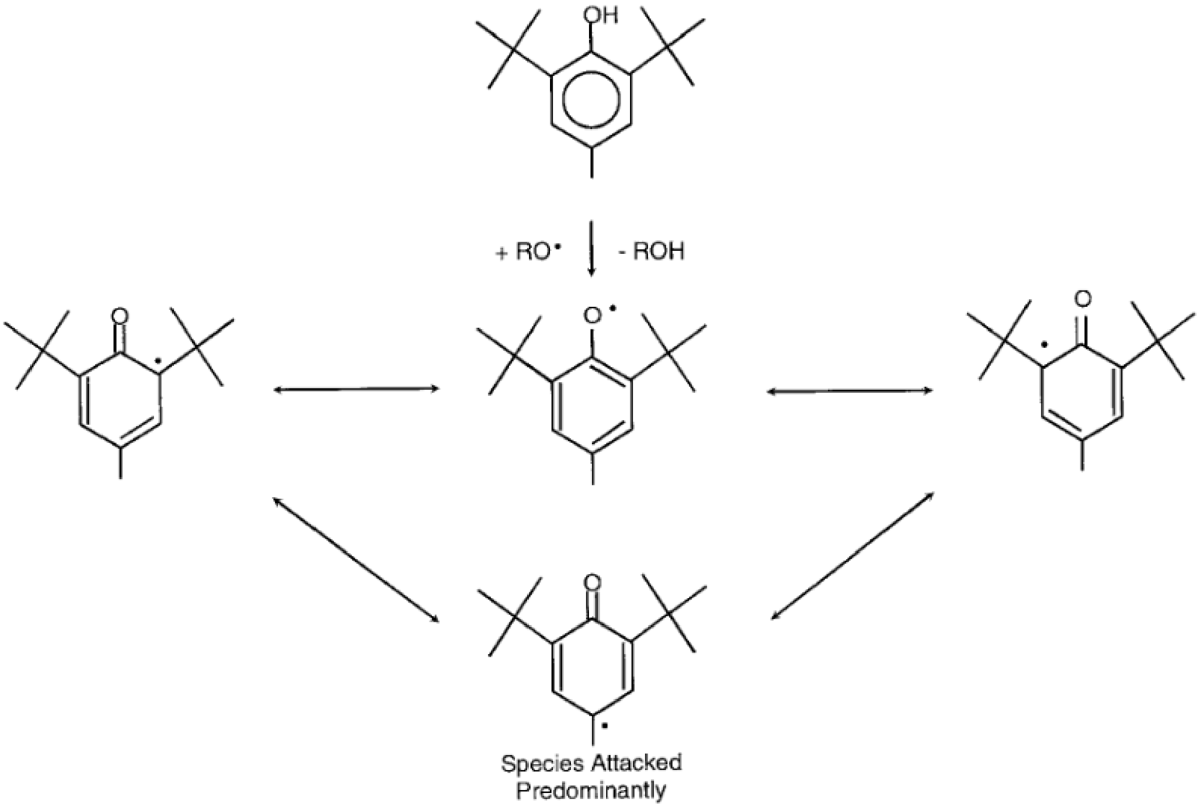


Fig 3.4 Hindered Phenols, radical termination and resonance stabilization (7).

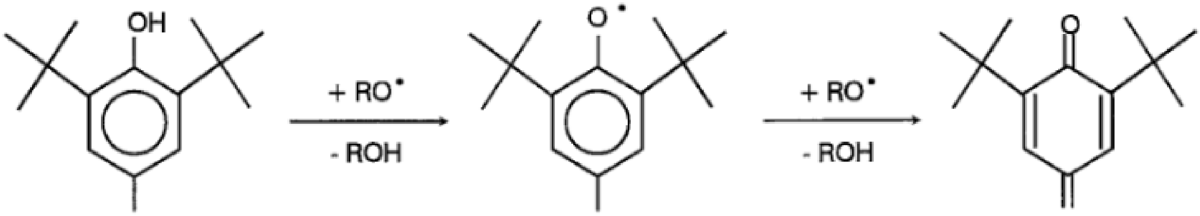


Fig 3.5 Termination of two macro radicals by hindered phenols (7).

protection below the melting point and also above it, during melt processing (8), hence were the chosen ones for the present study.

3.3 Polybutylene succinate state of the art

Regarding PBS thermo-mechanical degradation the main effects are developed during the processing step, especially during extrusion where temperature and shear stress are higher. When processed at temperature higher than 190°C it suffers from branching and degradation reactions (9), resulting in bimodal molar mass distributions. Georgousopoulou et al. (10) studied the effect of typical stabilizer Irganox 1010 and Irgafos 168 on the extruded polymer. Adding them in low percentages (0,1 %) had a positive effect, while higher quantities of additive had negative ones. The degradation results in higher polidispersity index, increased solution and melt viscosity, but similar value of carboxylic end groups. The thermal properties of the extruded polyesters were constant, this is important when reprocessing and recycling is taken into account.

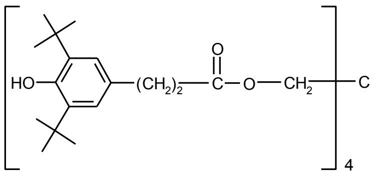
Processing temperature has an important effect on PBS degradation, with higher extrusion temperature branching was higher and faster in terms of reprocessing steps. The formation of branches didn’t influence the melting temperature, but decreased the crystalline percentages.

As antioxidant and stabilizer the addition of PEO has been investigated, thus increasing the biopolymer stability and enhancing biodegradability (11). PEO was added during synthesis in various amount in order to enter the polymeric chain in the form of soft segments, thermal stability was improved buy the presence of these segments even if the degradation mechanisms didn’t change. Also starch has been investigated for this particular use, both in blends and in additive form, in fact it is cost effective and readily available (12).

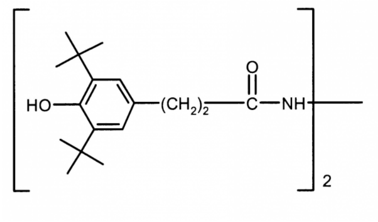
3.4 Additives used

Under Irganox tradename there are different antioxidants and antiaging products for processing and long-term thermal stabilization. Irganox 1010, MD 1024, 1330, 1425 and 1076 were included in the screening process conducted in this work to determine which additive was the most efficient with polybutylene succinate. They are efficient in inhibiting the discoloring process of organic substrates, their structures are shown in Fig 3.6; to the basic chain inhibitor are attached different chains adapted specifically on different polymers. Varying the length, the heteroatoms and the types of bonds in the additional chain the additive is fitted to different matrixes: in the case of PBS Irganox with oxygen as the main heteroatom, carbonyl groups, ester and ether groups for example, and a polar back chain should be the most compatible one.

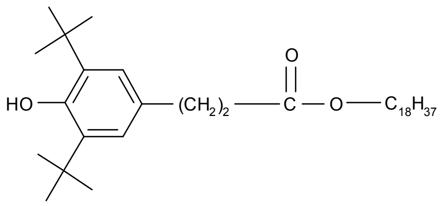
Irganox 1010 can be used in polyolefins, such as polyethylene, polypropylene, polybutene but also polyacetals, polyamides and polyurethanes, polyesters (15). It should be added in small quantities between 0,05% and 0,5%. Irganox 1010 is also



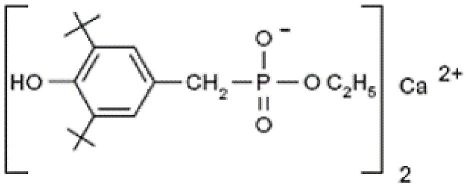
Irganox 1010



Irganox MD 1024



Irganox 1076



Irganox 1425

Irganox 1330

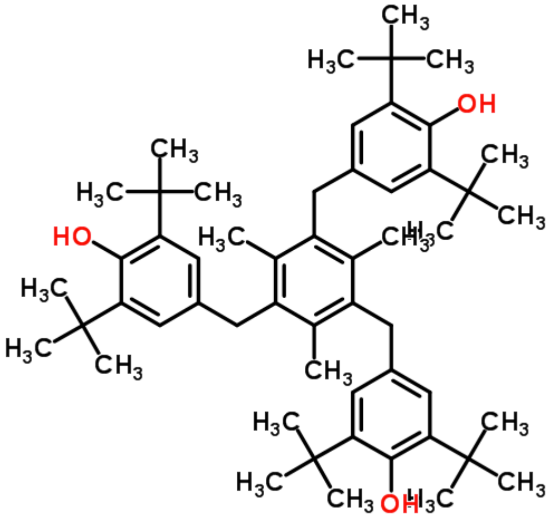


Fig 3.6.Chemical structures of Irganox 1010, 1076, 1425, MD 1024 and 1330 (13) (14).

found to be the chosen one for PBS in different other cases found in scientific literature, in particular during the studying regarding SUCCIPACK European Project, with Irganox 1010 (optimum level 0,1% with 5 twin extruder cycles) and/or Irgafos 168.

Irganox 1425 can be used as well for polyolefins, it has low volatility and good resistance to extraction (16). Especially, it is suitable for matter with large surface area, including polyester fiber and PP fiber, and offers good resistance to light, heat and oxidization. It contains phosphorus in its chemical structure and is claimed to offer protection against thermo-oxidative degradation, discoloring and has high resistance to extraction.

Irganox 1076 is a highly efficient sterically hindered phenolic antioxidant that is also mainly recommended for polyolefins. This compound, as also the others, is odorless, stable to light and is claimed to have excellent color retention. It protects the substrates against thermo-oxidative degradation (17).

Irganox MD1024 is a metal deactivator, thus meaning that avoid metal impurities to start catalyzing thermo-oxidative aging and a phenolic antioxidant. It provides processing stabilzation and it is usually used for wire and cable resins, styrene and its copolymers (18).

Irganox 1330 is also a sterically hindered phenolic antioxidant and offers excellent dielectric properties, it is claimed to be compatible with most used commodity polymers such as PP, PE, PA, PVC and linear polyesters. This additive is particularly recommended for those applications that need high resistance to water extraction because it reduces water carry-over (19).

3.5 Experimental Overview

In the previous chapters the main problem related to polymer aging and Polybutylene succinate state of the art was depicted, from here this work starts and proceeds further in this field of research. The main goal then is to understand which additives can stabilize PBS against thermal degradation, aging and oxidation, to achieve that different steps were followed.

An initial screening of the effect and compatibility of some industrial additives was carried out. The ones mentioned in section 3.4 were extruded with industrial grade PBS, that had high acidity value. In order to analyze the aging curve firstly polybutylene succinate curve was to be determined; the matrix change in Young's modulus was analyzed over a period of 15 days, 42% RH and 60°C. Then the different additives were tested under accelerated aging conditions, explained further under section 7, analyzing the change in Young's modulus over 15 days, two composition values for each additives under 42% RH and 60°C. After the first initial screening the best additive for PBS compliance was determined and the less efficient was also found.

This best additive was chosen for further experimentation including it in PBS matrices synthesized with different acidities, to investigate how this influences aging. The samples were aged and tested in harsher conditions with 38% RH and 80°C because the synthesis matrices used had lower acidity values.

Room temperature aging was also investigated, in order to study longer time periods of 30 and 45 days, testing the change in the polymer structure and properties trough solution viscosity and titration. Here were tested polybutylene succinate with different acidity values, with Irganox 1330 added during synthesis, with Pripol 1009 added in synthesis and with Irganox 1330 and MD 1024 added during the extrusion process. These 9 samples were preserved in 4 different environments; 15%, 20%, 50% and 80% Relative Humidity.

Sample preparation and observation - UV vis

The sample solution of the PBSs were prepared in order to have 50 ppm of additive, concentrations higher than 0,5% of polymer in diclorometHane were too viscous and not clear enough for an UV-Visible analysis. 0,2 grams of polymer for Irganox 1010, 1076, MD 1024,1330 in 0,25%; 0,1 grams for 0,5% blends were diluted in 10 ml of diclorometHane and stirred vigorously at room temperature. In the case of Irganox 1425 it was initially diluted with 4 ml of diclorometHane then brought to volume with methanol to dissolve the additive and stirred vigorously at room temperature.

Sample preparation - Micro twin extruder

The first blending was made on PBS industrial grade with high acidity, dried at 80°C for three hours, with different thermal, UV-stabilizers and fillers. Given the density of PBS as 1,26 g/cm^3, to fill 15 cm^3 the needed weight was approximately 17,5 g. For Irganox serie we chose to add 0,25% and 0,5%, for clay and talc the 5% was used, for Pripol 3% was chosen with the following results of weight needed:

Tab 3.1 Additive quantities for compounding with micro twin extruder.

Additives	Quantities	Weight (g)
Irganox / Irgafos	0,5%	0,088
Irganox / Irgafos	0,25%	0,044
Clay / Talc	5%	0,875

The polymer was loaded at 30rpm, them processed for 5 minutes at 100rpm and extruded at 50 rpm, all the operations were conducted at 180°C under nitrogen. PBS proved to be sticky on the filling system so the initial loading was conducted using a spatula and the closing piston. This procedure brought with it uncertainty and errors about the real quantity of additive effectively present in the matrix (investigated afterwards with the UV-Visible spectroscopy), also due to the volatility of the powders.

With Irganox MD1024 and 1330, to avoid the loss of additive, the polymer was heated with the premixed additive at 80°C for one hour. The alternative procedure seemed to be ineffective, in fact the powder was aspirated by the ventilation system and part of it remained in the glass container.

Due to the matrix stickiness, the loading was slow and PBS had time to retain water, almost 20 minutes passed from the start of loading to the moment in which extrusion started, causing the classic water popping sound during extrusion.

Sample preparation - Platen press

For this study's purpose the plates were heated at 180°C, the polymer granules were put into the mould and left to plasticize for 2 minutes, then the samples were kept for other two minutes at 100 bar, then cooled under pressure, to avoid shrinkage and deformation subsequent to a free cooling. When the temperature reached the value of 70°C with water cooling the moulded polymers were extracted. After water cooling, pressured air flew trough the cooling system in order to clear it from residual water and increase the speed of the subsequent heat cycle and moulding. When the samples could be handled without gloves they were cut into the desired shapes, eliminating scraps.

The samples for the aging process and water absorption were moulded with this procedure. For water absorption 18 samples 60x60x1mm and 60x60x1,5mm were moulded, three for each type of polymer-additive combination. For temperature aging, samples 50x50x1mm were moulded, from which DMA samples, 30x6x1mm were obtained.

3.6 Accelerated Aging

In order to investigate the effectiveness of the selected additives accelerating aging procedures were used with constant temperatures above room conditions and constant humidity. For the initial screening of five types of Irganox on the industrial polybutylene succinate 40% RH and 60°C were chosen as conditions, the temperature chosen is lower than the one reported in Succipack project (9) and other experiments about polybutylene succinate aging because the polymer matrix had high acidity level hence is very sensitive to hydrolysis and aging itself. During the second aging procedure an higher temperature was chosen, 80°C, in line with the ones used in other researches, because in this case the polymer from reactor synthesis had lower acidity value, therefore it is less sensitive to hydrolysis and degradation.

Change in modulus and aesthetic appearance was detected over a period of 15 days using DMA tests in tension mode, over a small number of samples for each combination of polymer and additive.

Sample preparation and procedure used

The experiments on Polybutylene Succinate were carried with an Isotherm at 32°C, on samples of 6x30x1mm each. These were all measured with high precision gauge, with special attention on the variability and errors carried within the measure itself. In fact, in order to calculate the Modulus values very precise measures of width and thickness of the specimen are needed, while the length is automatically measured by the instrument.

The procedure was conducted at a set frequency of 1 Hz, with a preload of 0,01N, the screws were tightened with a torque of 3Nm, to avoid sample's fracture or deformation. To assure the elastic behavior of the sample the chosen strain amplitude was 0,05%. Before the procedure the samples were put in a climatic chamber at 24°C and 50% RH for 24 hours, in fact from the first measurements high variability of the curve of storage modulus was detected. This is mainly connected with PBS sensitivity to moisture, in some minute the polymer absorbs humidity from the atmosphere and the modulus drops, as shown in Fig 3.7. Then in order to have reproducible and reliable results all the samples were kept in the climatic chamber until the measurement was conducted, to avoid different exposure times in the open atmosphere that could affect the obtained results. In Fig 3.7 a sample curve for PBS modulus drop in time is showed, because of that also the DMA procedure chosen was very quick and the Young's modulus value considered in the calculations was taken into the first minutes.

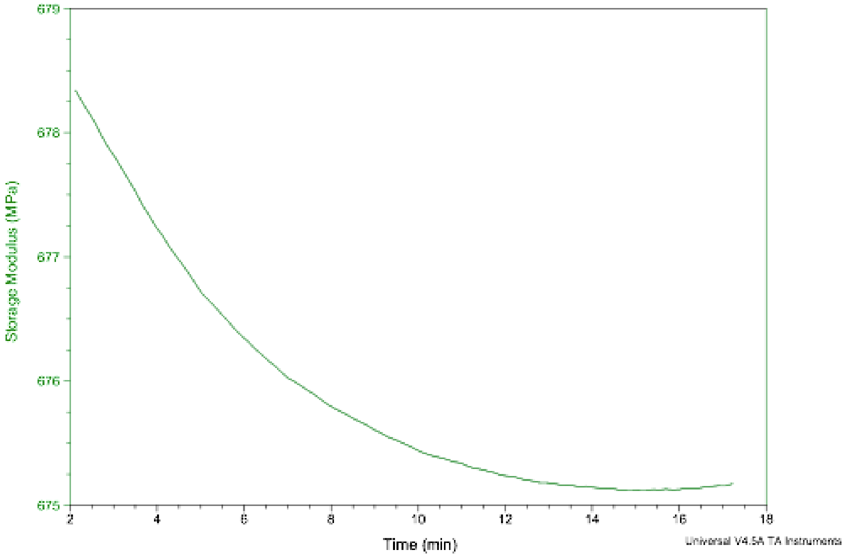


Fig. 3.7 DMA curve of industrial PBS drop in storage modulus versus time.

3.6.1 Controlled Relative Humidity in Temperature

To assure constant humidity a closed system was made, with saturated salted water, in order to guarantee 40% RH at 80°C and 60°C, the chosen temperatures for the heat aging. Magnesium Nitrate was chosen and the RH at 80°C can be calculated using the following data; in fact the variation of Relative Humidity is linear with temperature. Thus using the equation resulting from the interpolation of Magnesium Nitrate RH values at different temperature shown in Fig 3.8, RH at the chosen one can be calculated. At 80°C the RH will be of 38% and at 60°C RH is 42%.

3.6.2 Polybutylene Succinate Accelerated aging curve

Firstly the curve of Polybutylene succinate itself was to be determined, in order to assess the right aging conditions for this polymer. A temperature of 60°C was successfully used for aging studies. For the industrial PBS used firstly to determine the aging procedure itself a temperature of 60°C was chosen, due to its high acidity

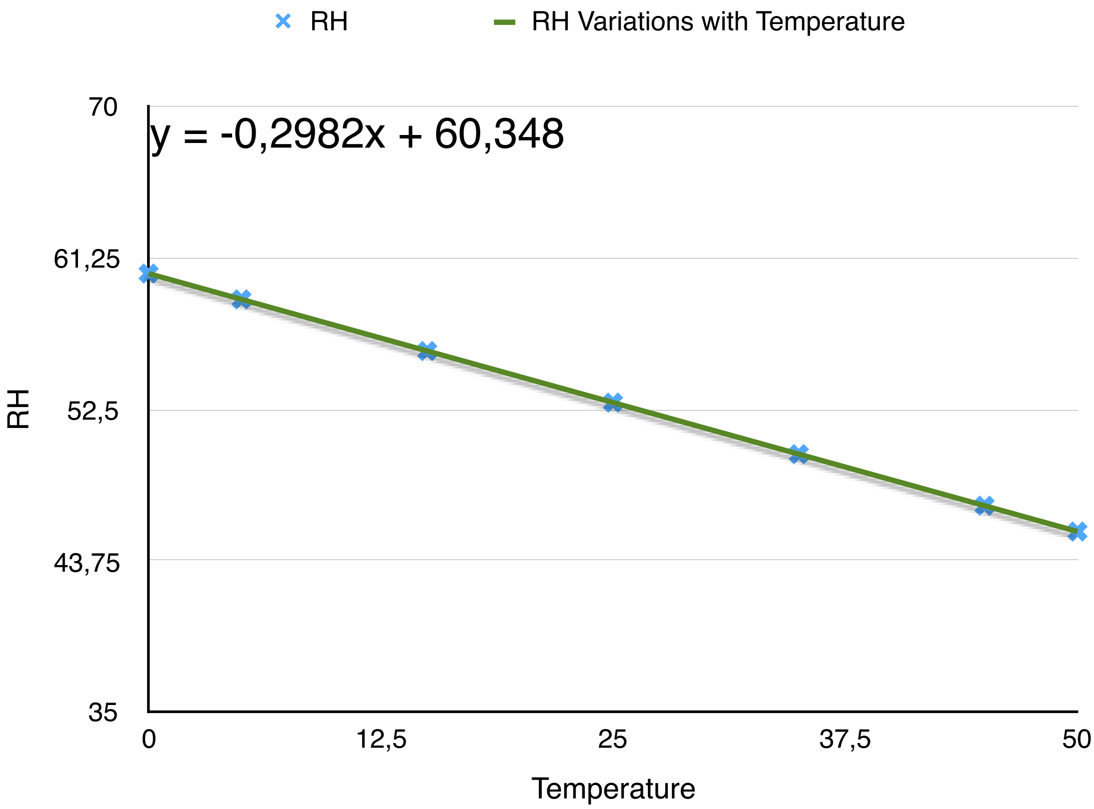


Fig. 3.8 RH curve versus temperature of Magnesium Nitrate solution.

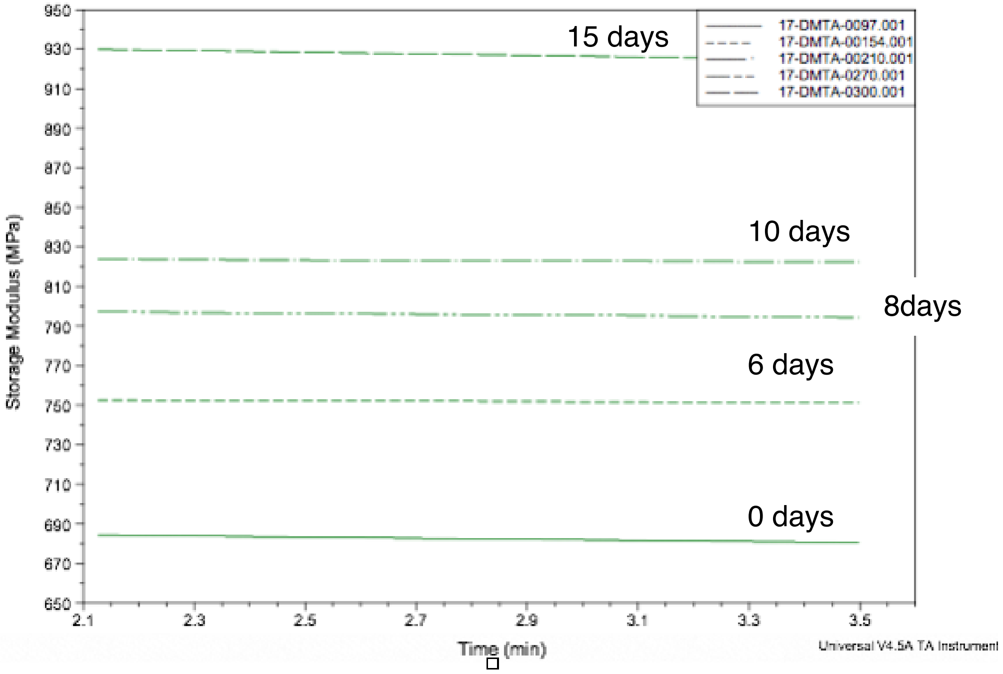


Fig. 3.9 Storage modulus values for industrial PBS at 0, 6, 8, 10 and 15 days.

faster degradation was expected. 15 days was the chosen period of time for the aging procedure to be conducted and firstly the PBS was tested at 4, 6, 8, 11 days. From these first results the procedure was adjusted, no significant modification was observed between day 0 and day 4, then the further investigation was taken on day 6, 8, 11, 15 and also PBS aging curve was repeated with the new procedure.

The results are the one showed in Fig. 3.9 and Fig 3.10 most of the samples examined fractured in a fragile way when tested the 15th day. In the Fig 3.10 the growing in the modulus can be appreciated, for one of the samples, increments lower than 10% shouldn't be taken into account because they are into the usual instrumental error related with DMA procedure. The final increment from day 0 to day 12 was of the 32% on average, the final curves are displayed in Fig 3.15, as shown just one sample survived till the last day.

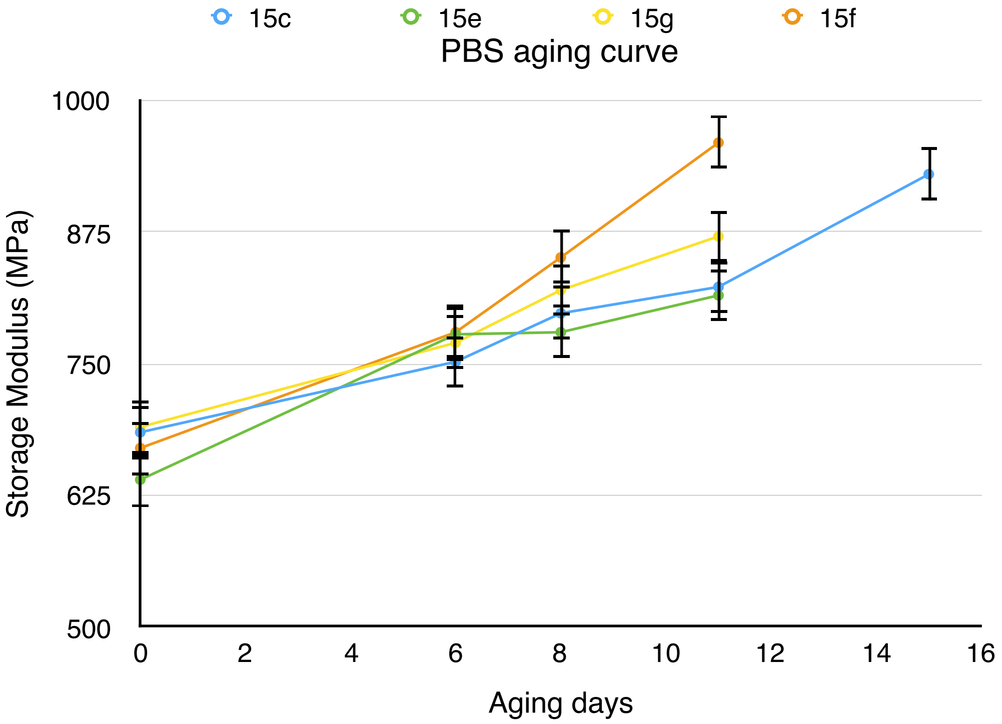


Fig. 3.10 Increase in PBS sample storage modulus versus time.

The increase in modulus made the sample more brittle than the original one, this indicates shorter chains and higher crystallinity percentages. After acknowledging that this procedure fitted the polymer and the chosen time of investigation we proceeded to additive screening with the same matrix.

3.6.3 Additive screening with industrial PBS

5 additives (Irganox 1330, MD 1024, 1076, 1010, 1425) were extruded in two different quantities (0,5% and 0,25%) on the industrial PBS matrix order to investigate which ones were the most efficient ones against harsh thermal aging. Here following the results in Fig 3.11, 3.12, 3.13, 3.14, 3.15, 3.16.

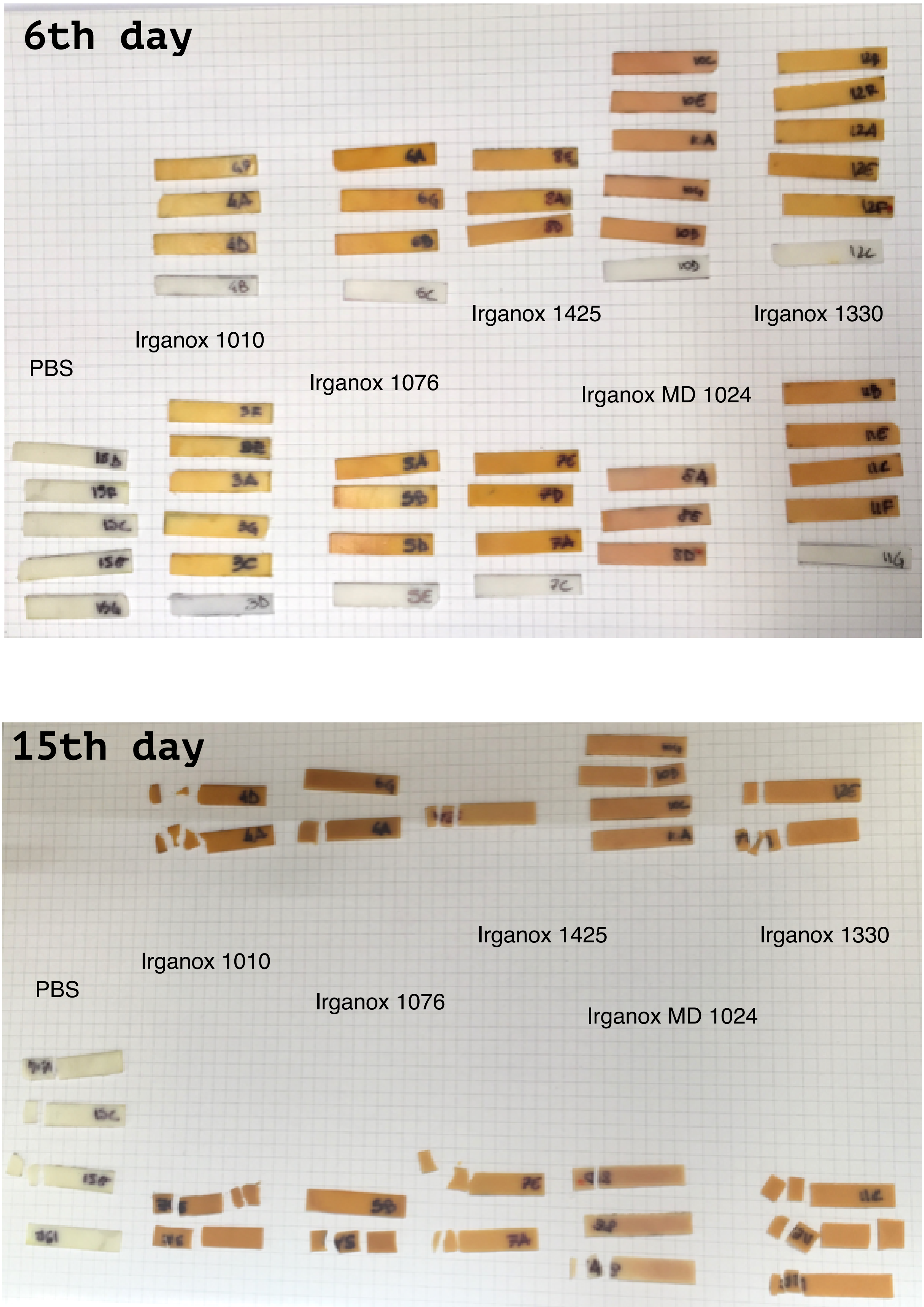


Fig. 3.11 PBS sample with Organic 1010, 1076, 1425, MD 1024 and 1330 at the 6th and 15th day of aging and their change in aesthetic appearance.

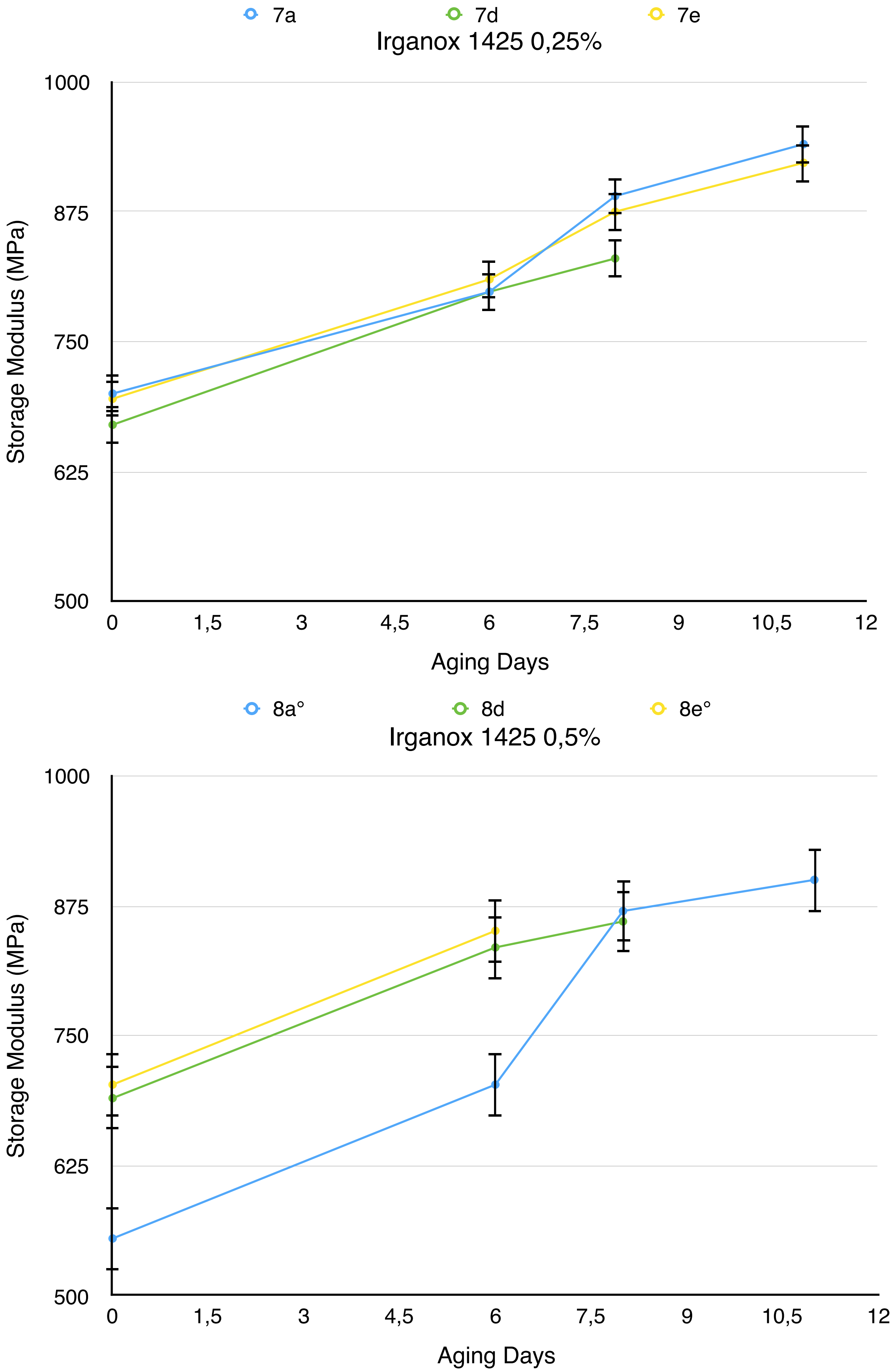
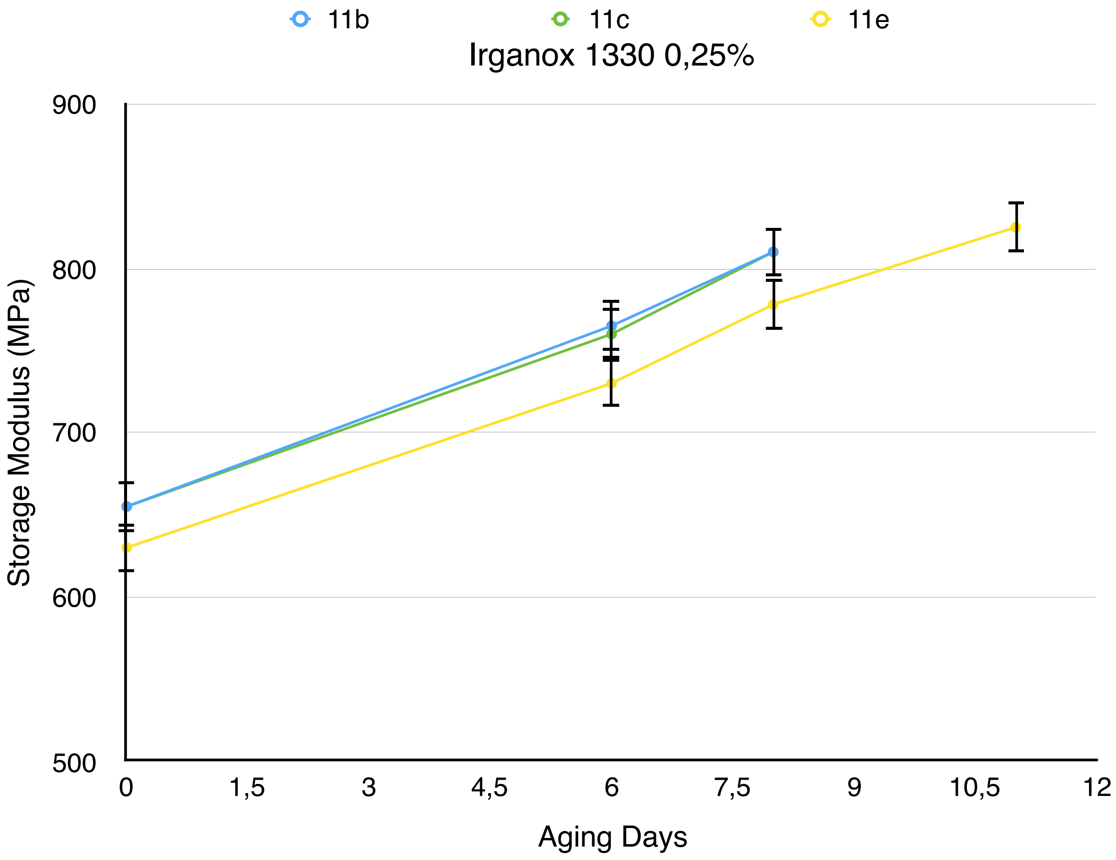


Fig. 3.12 Increase in PBS and Irganox 1425 sample storage modulus versus time.



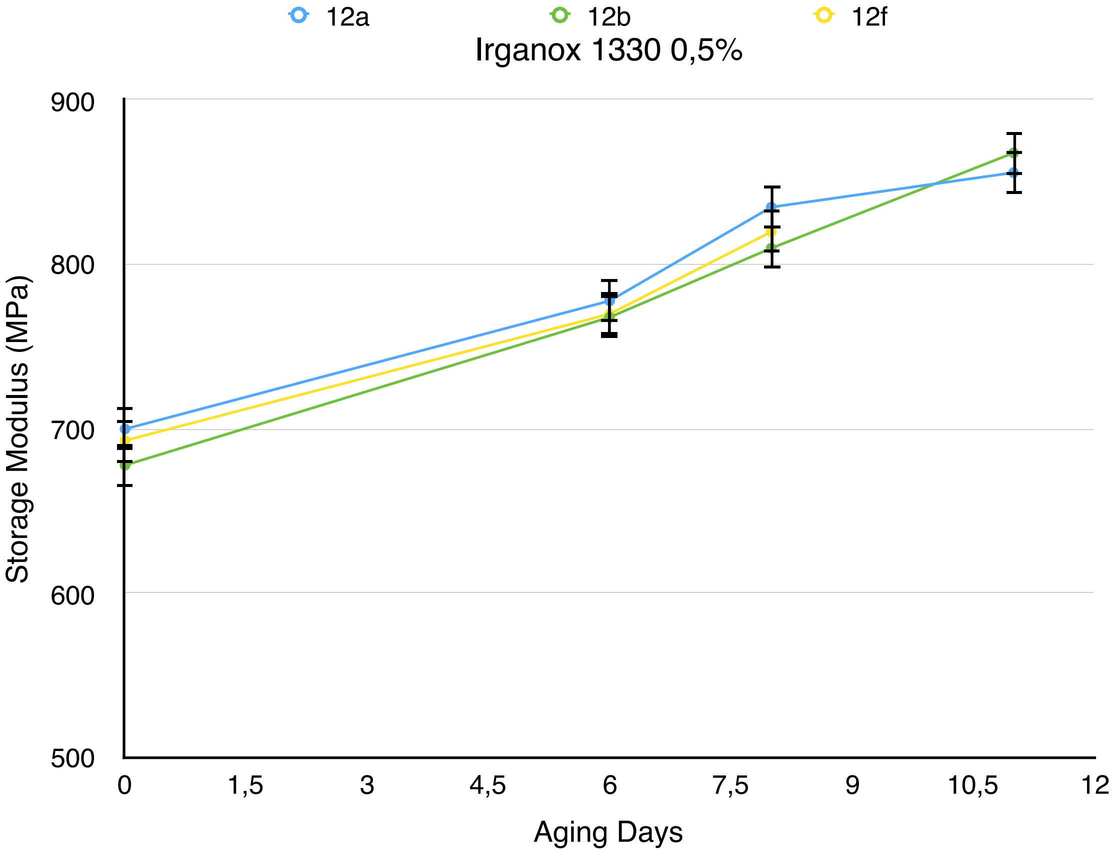
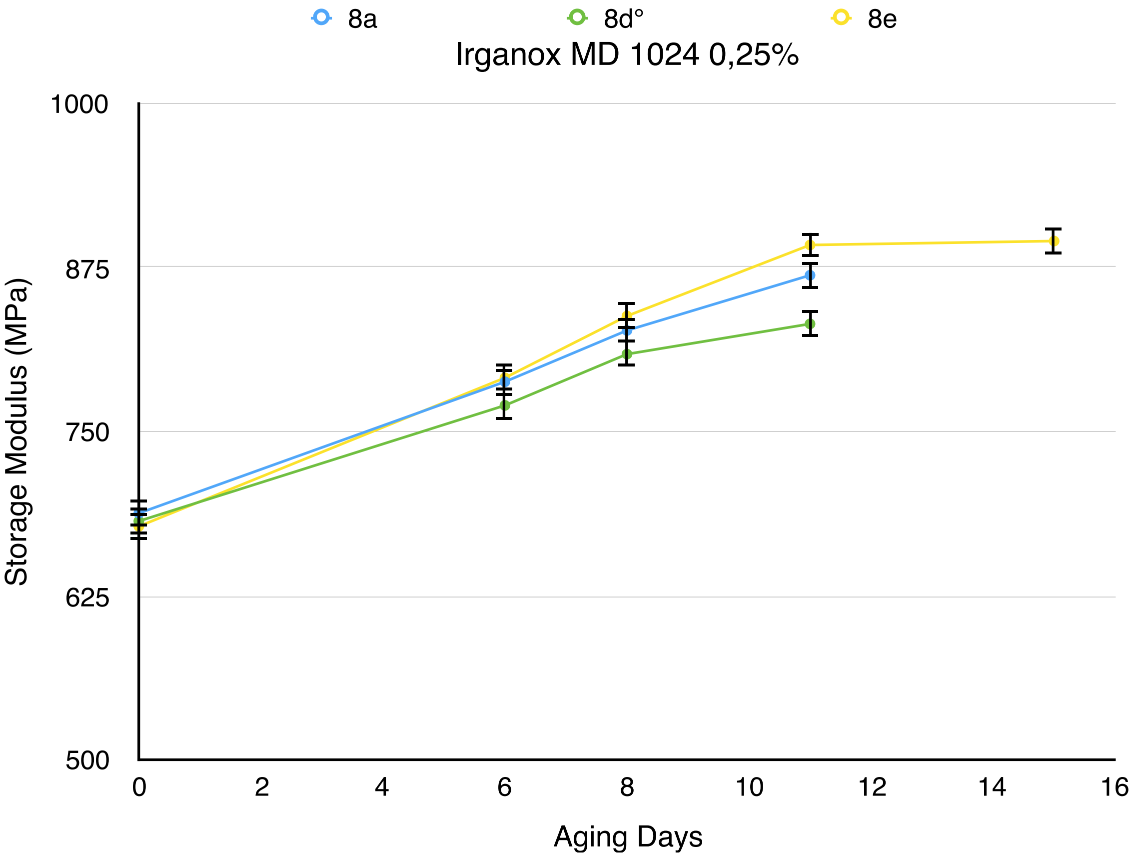


Fig. 3.13 Increase in PBS and Irganox 1330 sample storage modulus versus time.



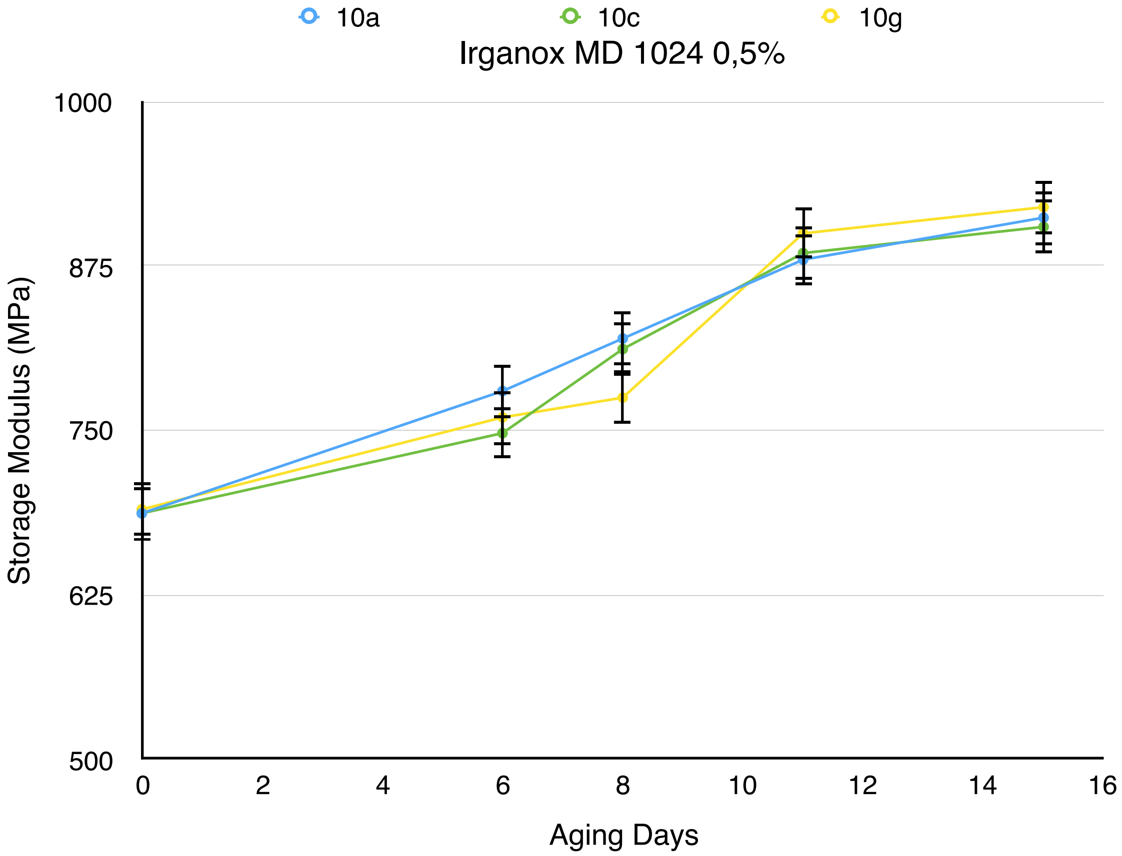
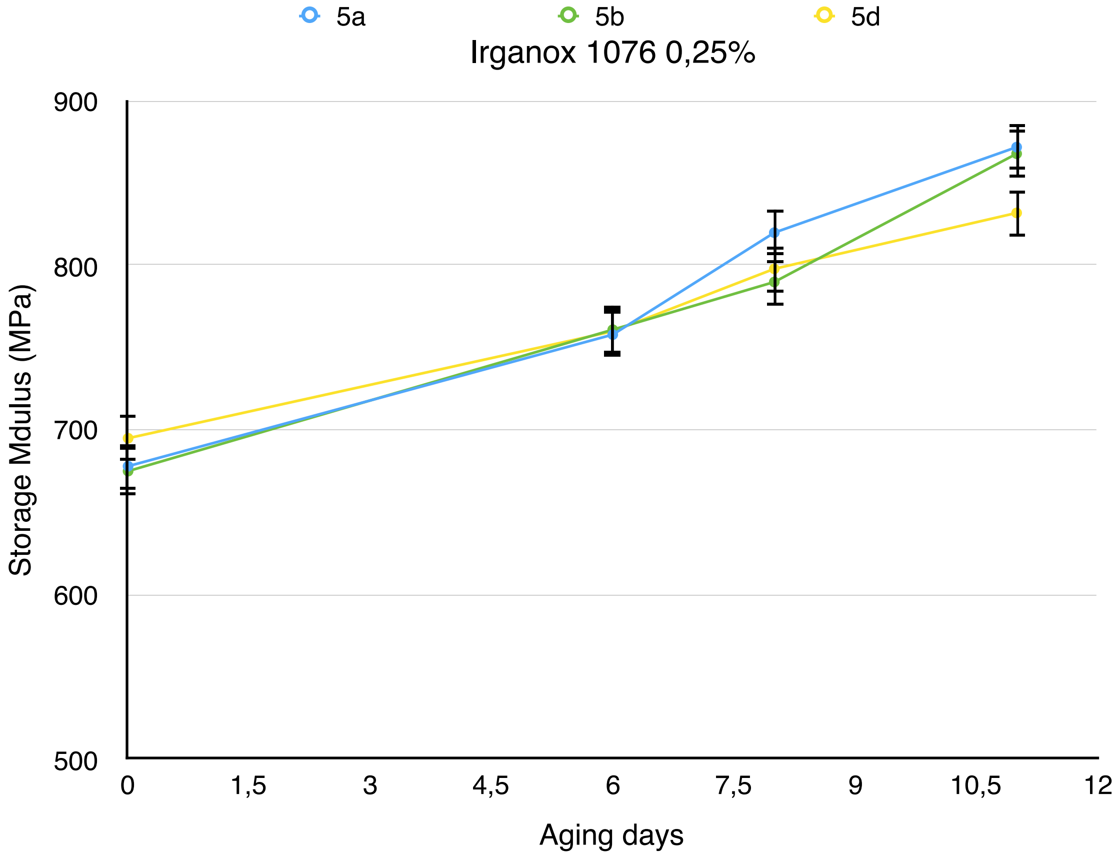


Fig. 3.14 Increase in PBS and Irganox MD 1024 sample storage modulus versus time.



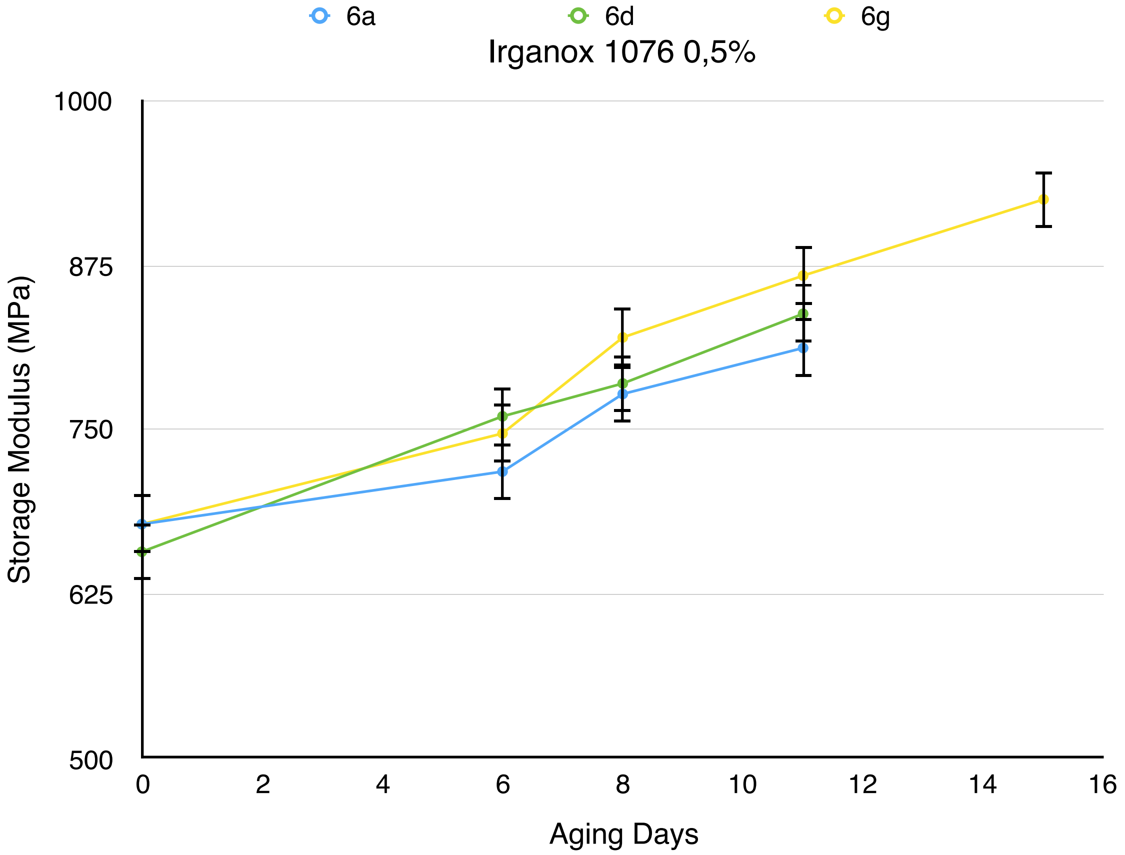
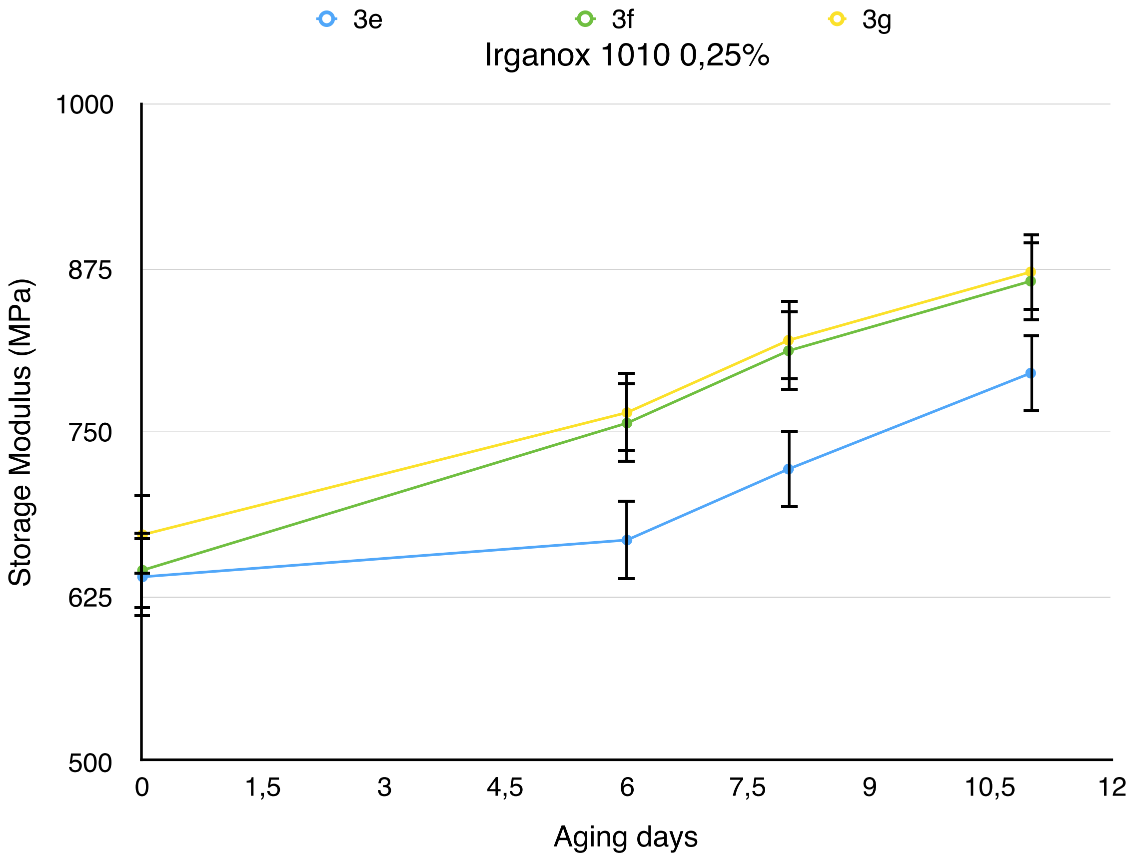


Fig. 3.15 Increase in PBS and Irganox 1076 sample storage modulus versus time.



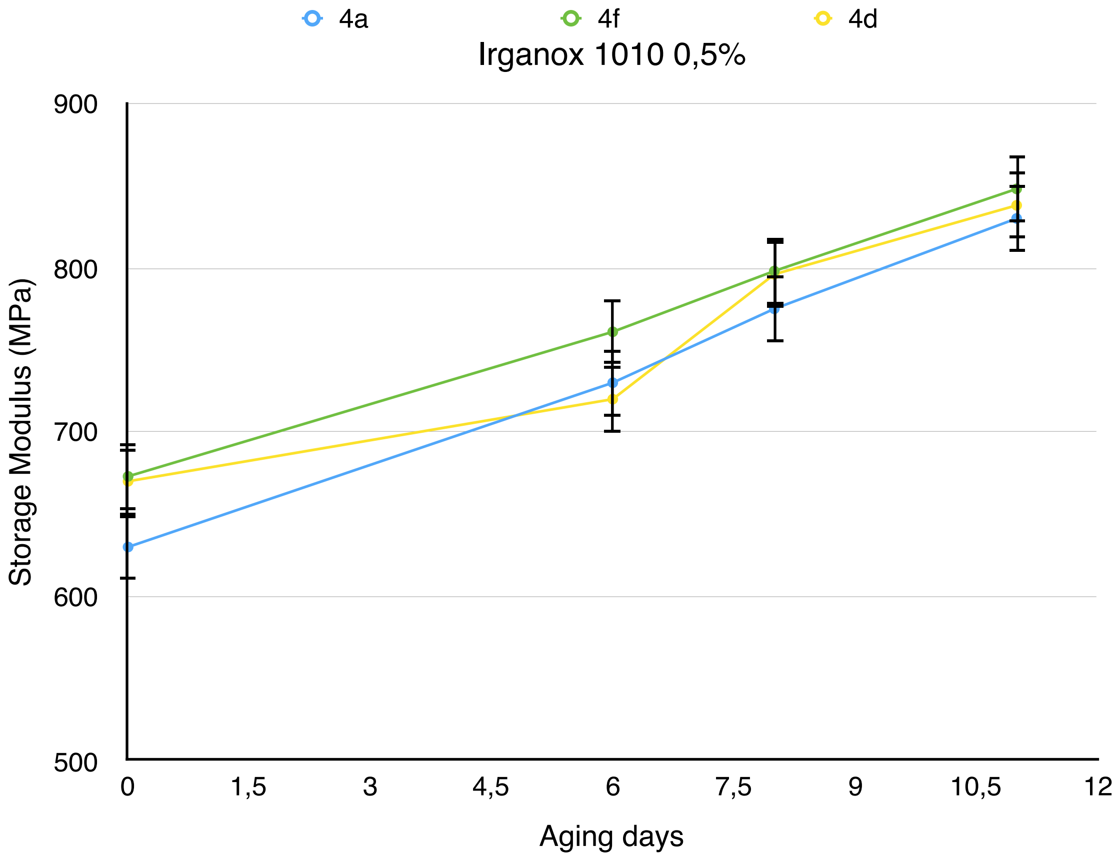


Fig. 3.16 Increase in PBS and Irganox 1010 sample storage modulus versus time.

For every combination of polymer and additive percentage 3 samples were aged. As shown from the graphs every sample showed more or less increase in its Young's Modulus, but very few of them survived until the 15th day. From this first screening the additive that was more efficient and the one that was less efficient can be spotted. Here following a sum up of the average increment of the modulus and the survived samples at the 11th day and 15th day:

Tab 3.2 Average increase in modulus by the 15th day.

	average increase (%)		average increase (%)
Irganox 1010 - 0,25%	27,3	Irganox 1010 - 0,5%	25,55
Irganox 1076 - 0,25%	23,79	Irganox 1076 - 0,5%	23,33
Irganox 1330 - 0,25%	30,69	Irganox 1330 - 0,5%	23,11
Irganox 1425 - 0,25%	29,9	Irganox 1425 - 0,5%	38,55
Irganox MD1024 - 0,25%	24,81	Irganox MD1024 - 0,5%	26,88

Tab 3.3 Number of samples survived by 11th and 15th day.

	11th	15th		11th	15th
Irganox 1010 - 0,25%	3	0	Irganox 1010 - 0,5%	3	0
Irganox 1076 - 0,25%	3	0	Irganox 1076 - 0,5%	3	1
Irganox 1330 - 0,25%	1	0	Irganox 1330 - 0,5%	2	0
Irganox 1425 - 0,25%	2	0	Irganox 1425 - 0,5%	1	0
Irganox MD1024 - 0,25%	3	1	Irganox MD1024 - 0,5%	3	3

The more efficient additive is Irganox MD 1024 (0,5%), not because of the lower increase of Young's modulus, in fact it is in line with the others; but it was the only one that guaranteed the survival of all the PBS samples until the 15th day. All the other additives weren't able to prevent fracture after the 11th day and no data were collected because the samples broke during the securing procedure in the DMA clamps or during the pre-measurement. The worse one was Irganox 1425, as shown from the tables and the graphs this samples were the first ones to break at very early stages of the aging procedure (from the 6th day on), it was also the additive that brought the highest increase in the Young's modulus. All the other samples had an average increase between 23% and 30% and they weren't able to guarantee survival up to the end of the aging procedure.

3.6.4 PBS from reactor synthesis with different acidities and additives

The influence of different acidity values and different relative humidity was also investigated with room temperature aging for 30 and 45 days, with RH values of: 15%, 19%, 55% and 78%. The sample tested were of PBS with three acidity values, low, medium and high, PBS with Pripol 1009 and Irganox 1330 added in syntehsis, PBS with three acidity values with Irganox MD 1024 (the best additive as shown in the previous paragraph), and PBS with medium acidity with Irganox added during extrusion. At 30 days the results in terms of change of acidity value and intrinsic viscosity value are shown in the following table:

Tab 3.4 Change in acidity values at different RH values by 30th day.

Acidity value	Day 0	RH=15%	RH=19%	RH=55%	RH=78%
PBS1	12	15	16	18	16
PBS2	32	29	25	32	26
PBS3	54	56	55	47	56
PBSp	21	15	14	12	15
PBS1330s	12	27	26	21	23
PBS2+1330	27	32	31	24	27
PBS1+MD 1024	18	23	16	11	14
PBS2+MD 1024	23	28	29	21	22
PBS3+MD 1024	41	49	47	37	45

Changes above 3 points in the acidity value should be taken into account, in order to include instrumental errors. Not a clear trend can be determined with these value, nor descending nor ascending with different RH values;

- for PBS 1 an overall increase of acidity value was spotted, with a medium 55% of increase and no significant difference between different humidities,
- for PBS2 an overall decrease of acidity was found, with an average 20% of decrease and no significant trend between different humidities
- For PBS3 no trend was found and no significant increase in acidity was found.

From these first results it can be seen that with lower acidity value the difference is higher, meanwhile when acidity is higher the polymer is less influenced by the aging itself and the presence of humidity.

Regarding the batches with additives added during synthesis of extrusion:

- With Pripol 1009 and overall decrease of acidity value was spotted, with an average decrease of 30%, but no significant difference between different humidities,

- With Irganox added in synthesis (PBS1330s), an overall increase was found, with a medium increase of 105% and a descending trend toward higher humidities.
- Regarding PBS with different acidities and Irganox MD 1024 added during extrusion no real trend was found, with higher acidity an average increase of 8% was found, while for medium acidity, PBS2 at lower RH values an increase was observed and at higher RH the samples presented no difference. PBS1 presented a mean decrease of 10% for the acidity value.

Tab 3.5 Change in Intrinsic viscosity at different RH by the 30th day.

[n] Value	Day 0	RH=15%	RH=19%	RH=55%	RH=78%
PBS1	0,992	1,1289	1,0972	1,1032	0,9745
PBS2	0,9999	1,0812	1,0031	1,0017	0,9097
PBS3	0,9657	0,9357	0,9428	0,8999	0,9605
PBSp	1,0812	0,9825	1,0065	0,9357	0,9249
PBS1330s	1,1722	0,9911	1,1073	1,0615	1,1146
PBS2+1330	0,9432	0,9633	1,0179	0,9588	1,0022
PBS1+MD 1024	1,0511	1,0882	1,0774	0,9567	1,0322
PBS2+MD 1024	1,0691	0,9801	0,946	1,0256	0,8987
PBS3+MD 1024	0,94837	0,9605	0,95	0,9176	0,9185

Changes above 5% should be taken into account, in order to include instrumental errors. Regarding intrinsic viscosity these should be linked with the value of acidity, with higher values of acidity the number of end hydroxyl groups is higher, the indicated shorter chains and lower viscosities. This is applicable to the all the batches of PBS but the one with Pripol 1009, in fact, introduction the fatty acid in the main changed the rheological behavior, as also discussed in Chapter 2. The following comments shall be made in the case of PBS with different acidity values:

- For PBS1 an overall increase in viscosity was observed, with higher values for the environments at low humidity percentages, with an average value of 8,5%.
- For PBS2, with medium acidity values, an overall increase of viscosity was observed for the environments at lower RH%, for 78% RH a decrease of 10% in intrinsic value was reported.
- For PBS3 an overall decrease in intrinsic viscosity was found, with an average value of 4%.
- In every case, at the higher acidity value a decrease in intrinsic viscosity was observed.

Regarding PBS batches with additives the following observations can be made:

- PBS that presented medium and high acidity values such as PBS2+MD1024, PBS3+MD 1024, PBS2+1330 were degraded more at higher RH. This effect is seen just in these batches because their higher acidity is responsible to the higher sensitivity to humidity.

- PBSp and PBS1330s also underwent significant decrease in intrinsic viscosity at higher humidity percentages.

The results after 45 days in terms of acidity value and intrinsic viscosity as shown in the Tables below:

Tab 3.6 Change in acidity values at different RH values by 45th day.

Acidity value	Day 0	RH=15%	RH=19%	RH=55%	RH=78%
PBS1	12	13	13	15	16
PBS2	32	26	23	28	26
PBS3	54	43	49	46	52
PBSp	21	23	20	24	23
PBS1330s	12	12	12	12	14
PBS2+1330	27	26	28	27	27
PBS1+MD 1024	18	14	13	13	14
PBS2+MD 1024	23	22	24	23	24
PBS3+MD 1024	41	38	39	40	42

Tab 3.7 Change in Intrinsic viscosity at different RH by the 45th day.

[n] Value	Day 0	RH=15%	RH=19%	RH=55%	RH=78%
PBS1	0,992	1,1006	1,0741	1,0436	0,9927
PBS2	0,9999	1,0315	1,0679	1,0168	0,9595
PBS3	0,9657	0,9525	0,9764	0,8745	0,8069
PBSp	1,0812	0,9477	0,9675	0,9663	0,9244
PBS1330s	1,1722	1,0551	1,0148	1,0021	1,0572
PBS2+1330	0,9432	1,11711	0,9843	0,9383	0,9659
PBS1+MD 1024	1,0511	1,1180	0,9526	1,0079	0,9971
PBS2+MD 1024	1,0691	0,9519	0,9963	0,9520	0,9414
PBS3+MD 1024	0,94837	0,9435	1,0170	0,9051	0,8696

Some difference can be spotted, compare with the results from the 30th day, yet no significant change has been found. This is mainly attributed to the timing, at room temperature the degradation processes are much slower, thus implying that the change in PBS properties occur in longer period of times.

The following observations can be made regarding the change in Intrinsic viscosity:

- PBS3, with higher acidity shows clearly the influence of higher humidity percentages, with an average decrease of the 13% when under high RH values, meanwhile no significant variation was found at 15% and 19% RH.
- PBSp and PBS1330 also showed the same trend of PBS3, with a significant decrease in intrinsic viscosity at higher RH values with 16% decrease for PBSp and 10% for PBS 1330. No real comparison between the effect of the two additives can be made though because the quantities used are very different.
- A significant descending trend can be spotted also with the extruded matrix with MD 1024, where a decrease of 6%, 11% and 9% is found with increasing levels of acidity. This shows that higher acidity gives also more susceptivity to hydrolysis, leading to higher levels of degradations.
- In general, more aggressive environments, such as 55% RH and 78% RH are the ones in which the most important difference can be spotted, here the degradation can be seen also at the 45th day.

Considering the acidity value it can be observed that:

- For PBS1, PBS3, PBSp and PBS 1330s no significant change was spotted, while PBS3 decreased its acidity on an average of 12%.
- No significant difference was also found for the extruded samples: PBS2+1330, PBS1+ MD1024, PBS2+ MD1024, PBS3+MD1024.

The environments where the aging procedure took place were not controlled in temperature, just the samples at 55% RH were steadily maintained at 27°C, the others ranged from 25°C to 35°C during the aging period. The unexpected changes in these parameters can be imputed to the uncontrolled temperature, but mainly to inhomogeneous samples. The characterization was conducted on small quantities of the samples, not allowing an average value to be found.

3.6.5 Additive aging analysis with UV-Visible spectroscopy

Since the very first measurements for samples aging a significant change in color was detected, as displayed in Fig 3.11, since day 6 the samples assumed bright yellow-orange shades each different for every additive used. In Fig 3.11 the difference between the sample original color and the final shades can be appreciated, also at the 15th day the majority of the samples underwent failure. Here the difference between the most efficient additive, MD 1024, and the worse one is well highlighted.

To investigate how the additive itself aged an UV analysis was carried out on solutions of 50 ppm concentration of additives, before and after 15 days aging in the same conditions, the spectra are showed below:

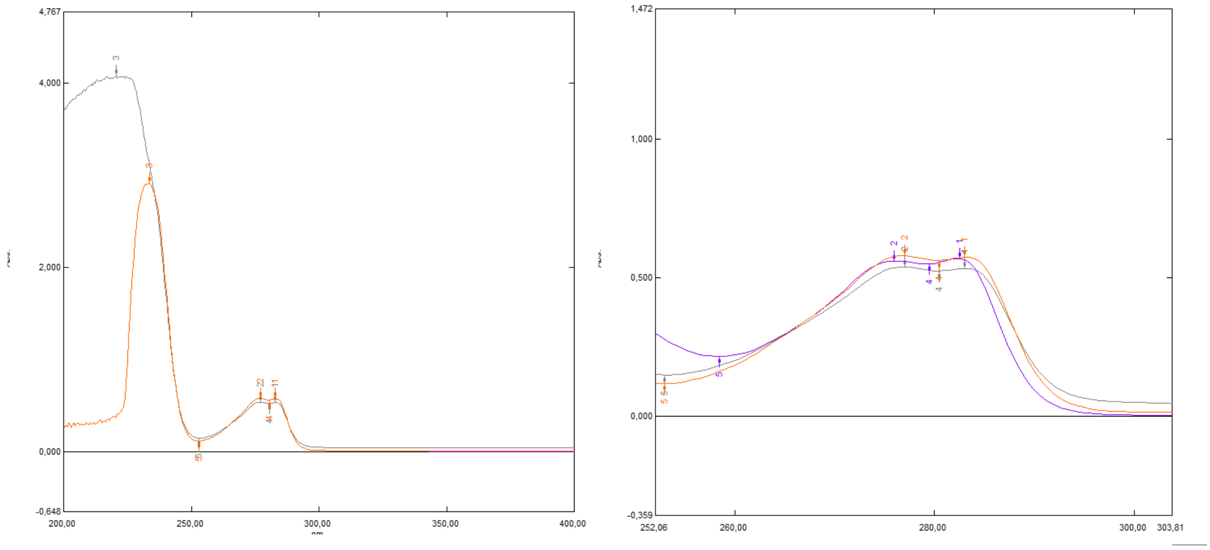


Fig 3.17 Irganox 1330, orange curve is at 0 days grey curve is after aging 15 days at 60°C, 50% RH. On the right a focus on the characteristic peak zone at 280 nm.

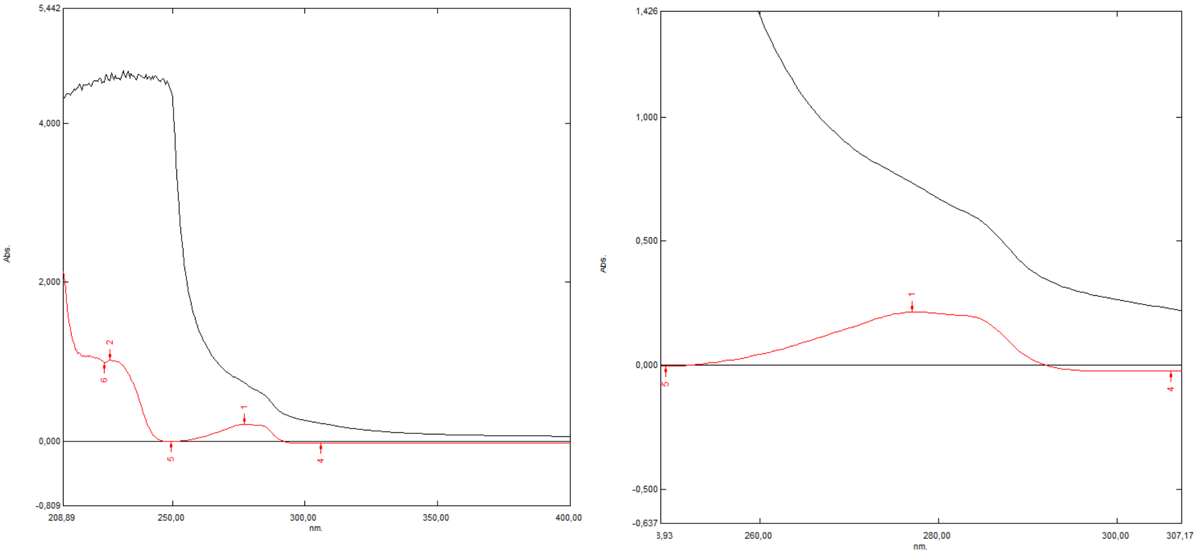


Fig 3.18 Irganox 1425, black curve is at 0 days red curve is after aging 15 days at 60°C, 50% RH. On the right a focus on the characteristic peak zone at 280 nm.

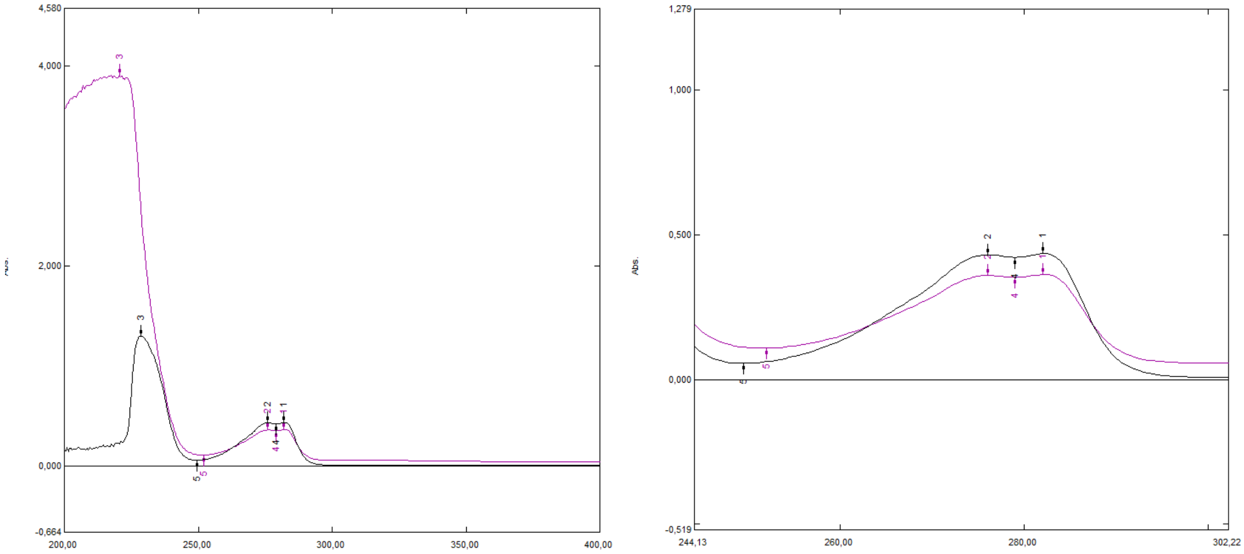


Fig 3.19 Irganox 1010, black curve is at 0 days violet curve is after aging 15 days at 60°C, 50% RH. On the right a focus on the characteristic peak zone at 280 nm.

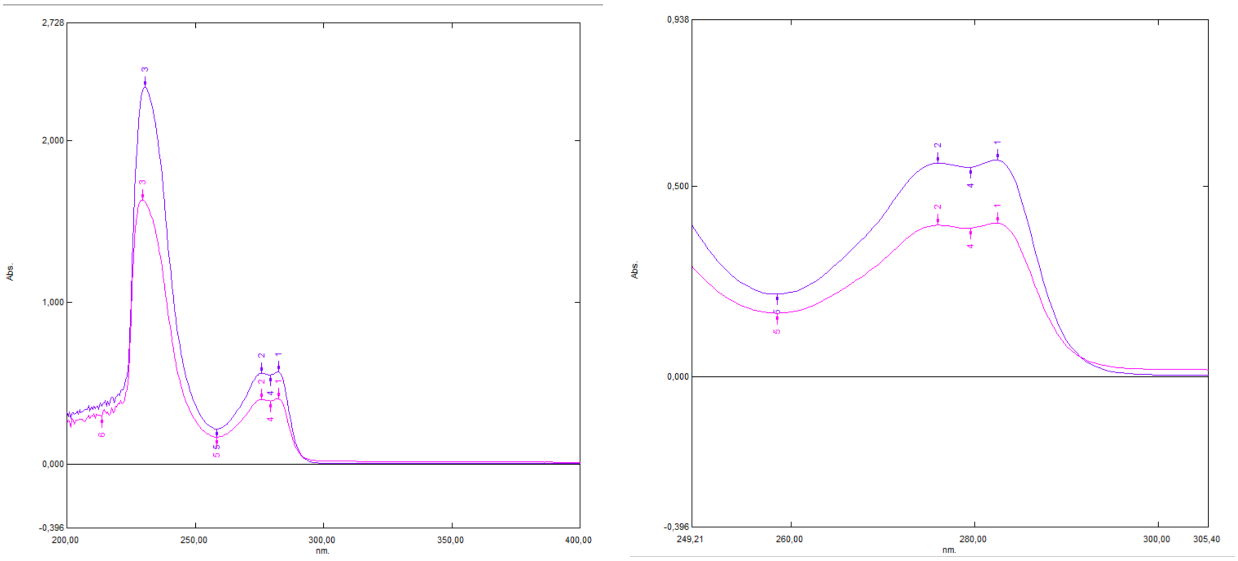


Fig 3.20 Irganox MD 1024, violet curve is at 0 days pink curve is after aging 15 days at 60°C, 50% RH. On the right a focus on the characteristic peak zone at 280 nm.

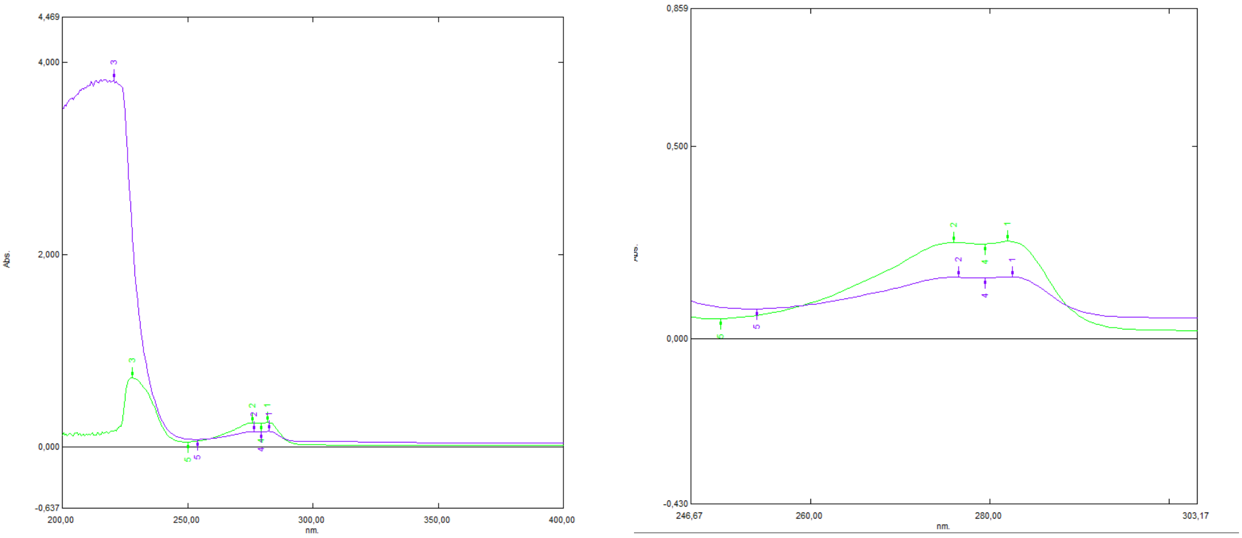


Fig 3.21 Irganox 1076, green curve is at 0 days, violet curve is after aging 15 days at 60°C, 50% RH. On the right a focus on the characteristic peak zone at 280 nm.

As can be observed in the Graphs shown in Fig 3.17, 3.18, 3.19, 3.20, 3.21 in every case the absorbance of the aged additive diminished significantly, thus meaning that the characteristic groups of the hindered phenols were degraded with the photo oxidation. The different peak form between the different additives can be attributed to the chemical structures. It is important to highlight that the change was evident in the values of absorbance, but no significant variation was found in the form of the curve. This means that the degradation process lowered the concentration of the characteristic additive groups, without changing the chemical structure.

3.6.6 PBS from reactor synthesis aging with Irganox MD1024

From the results shown in section 3.6.3 Irganox MD 1024 was the most effective additive to protect PBS from degradation under harsh conditions in terms of temperature and humidity. Different options are then explored in this section, in fact 3 more combinations between PBS with different acidity values from reactor synthesis and Irganox MD 1024. These samples were aged in conditions even harsher than the ones used in section 3.6.3 for the initial screening: 80°C and 38% RH. This choice was made in order to maintain as testing time 15 days, in fact with higher temperature the degradation processes should be faster. Also the examined batches were supposed to be less sensitive to moisture, in fact two of the PBS matrices had significantly lower acidity compared with industrial PBS grade.

PBS1, with low acidity, PBS2, with medium acidity, and PBS 3, with high acidity, were compounded with 0,25% of Organic MD 1024. The samples were extruded and moulded with the same conditions used in section 3.6.3, the Young modulus was tested with DMA analysis, the results of this aging procedure are shown in Fig 3.22, 3.23 and 3.24. An overall increase and change in color was found in all the samples, but without reaching failure, thus confirms that Irganox MD 1024 effectively protects Polybutylene succinate from embrittlement at medium temperatures.

None of the samples underwent failure during the testing period, quantitative results are shown in Tab 3.8

Tab 3.8 Average variations in Young's Modulus for PBS1, PBS2 and PBS3.

Batch	Medium Increase (%)	Medium Increase 0-4 (%)	Medium Increase 4-12 (%)	Medium increase 12-15 (%)
PBS1	29%	15,1	1,2	12,7
PBS2	26%	11,8	7,2	7
PBS3	42%	17,7	10,7	13,6

The medium increase in Young's modulus is significantly higher for PBS3, thus meaning that higher acidity values bring higher sensitivity to the degradative environment. The major part of this increment happened between day 0 and day 4, with a very different kinetic from the degradation process at 60°C. Between day 4 and day 12 no significant change happened, while between day 12 and 15 another significant increase took place. In fact with lower temperature no change was detectable between day 0 and day 8, then a quick increase happened. At 80°C on the other hand the quick increase happened between day 0 and day 4, with almost no detectable changes after that period (changes under 10% are imputable to instrumental errors). The values in modulus reached in this case are lower than the one showed in section 3.6.3, this is imputable to the different acidity values. In fact the change in the aging temperature was negligible compared with the change in acidity value that increased water sensitivity.

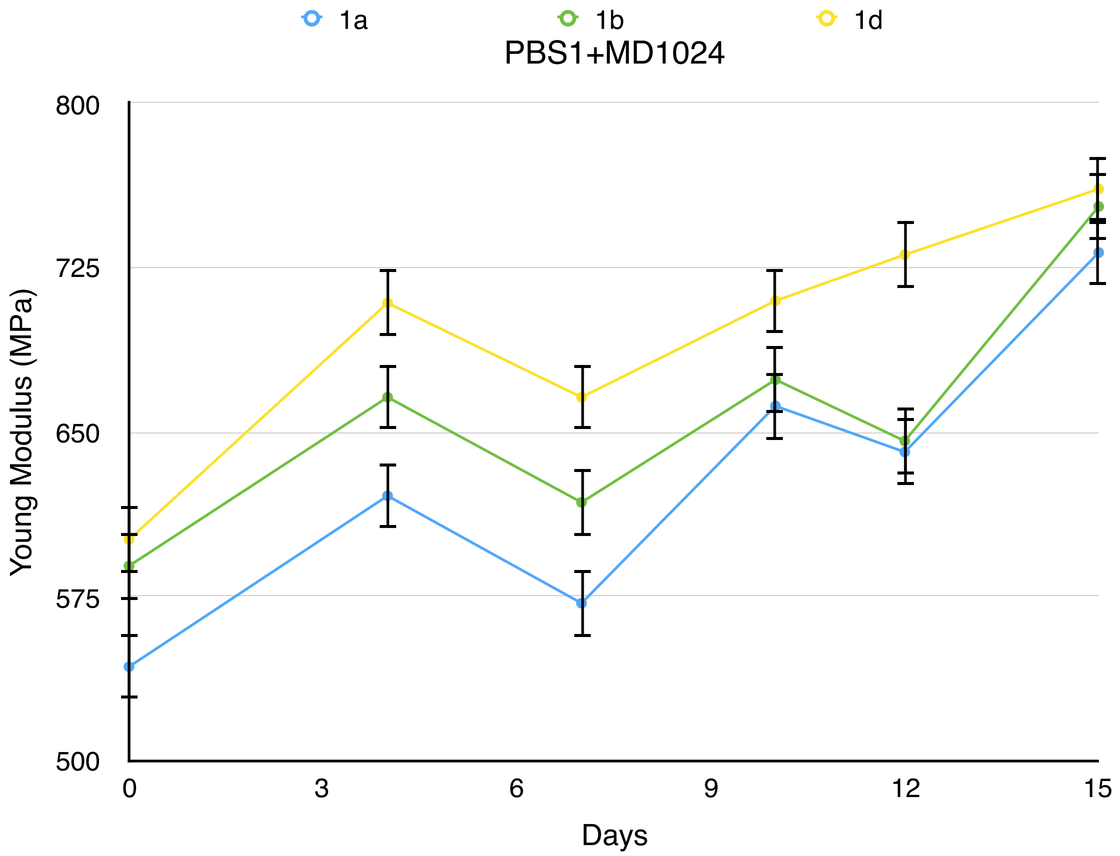


Fig 3.22 PBS1 compounded with Irganox MD 1024, change in Young's Modulus at 4, 7, 10, 12 and 15 days.

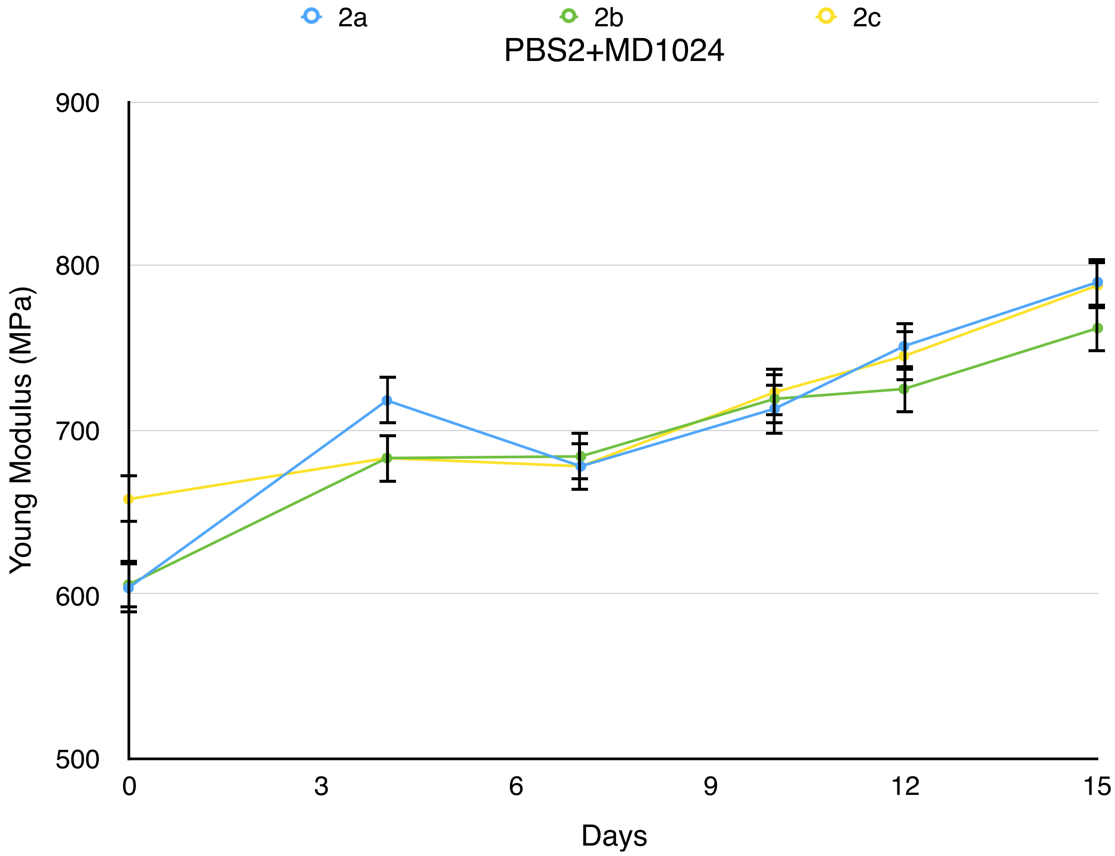


Fig 3.23 PBS2 compounded with Irganox MD 1024, change in Young's Modulus at 4, 7, 10, 12 and 15 days.

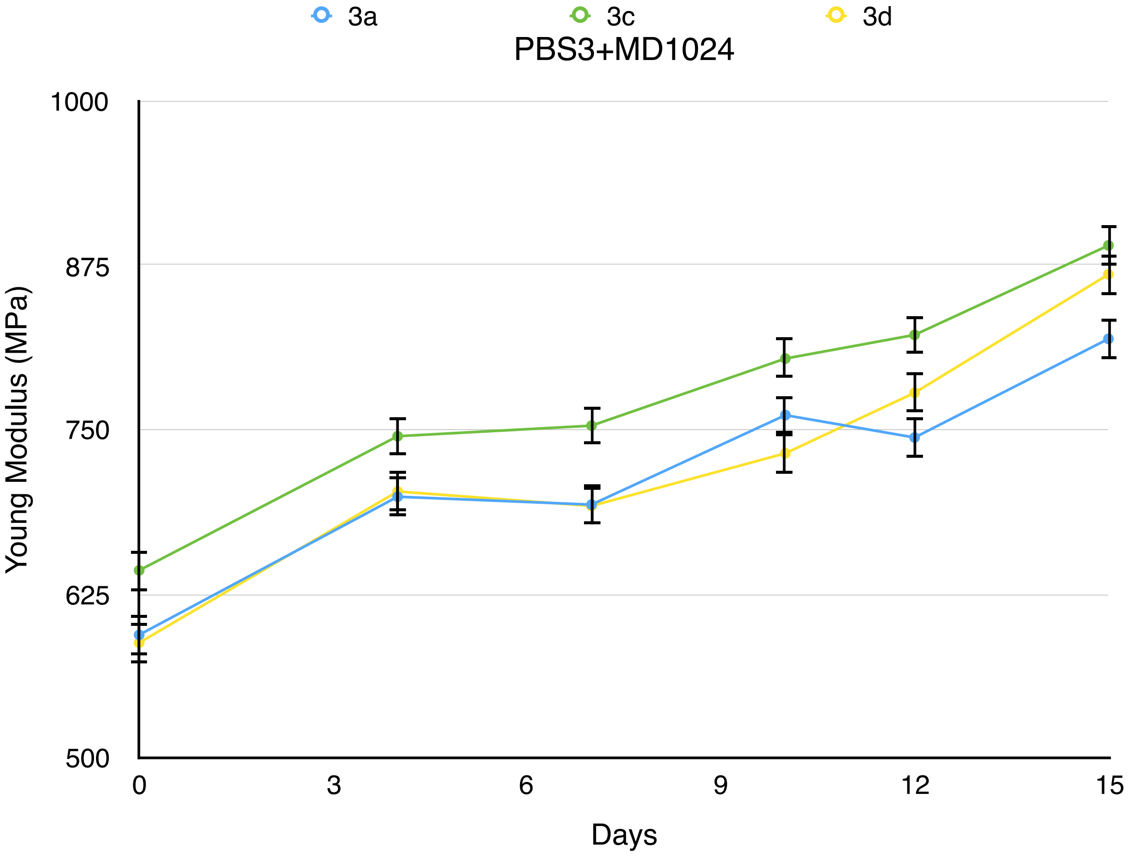


Fig 3.24 PBS3 compounded with Irganox MD 1024, change in Young's Modulus at 4, 7, 10, 12 and 15 days.

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Chapter 4 - Hydrolysis resistance

4.1 Introduction

Hydrolysis is one of the main degradation cause for biodegradable polymers, mainly for the hydrolysis of ester linkages or unstable backbone, this is also the beginning of the biodegradation of polyesters. Different steps are included into the process such as:

- initial hydrolysis of low molecular weight chains, this produces rapidly oligomers
- continued loss of molecular weight with random bond scission and formation of oligomers, with gradual loss of plasticizers
- loss of physical properties such as tensile strength and elongation at break
- weight and volume loss, these low molecular compounds are in fact dissolved into the aqueous medium or digested by microorganisms until the material is degraded essentially to oligomers.

This process brings also loss of esthetic properties with resulting in an opaque and hazy polymer. In the following Fig 4.1 cleavage of the polyester bond because of water absorption is shown for PLA, the same mechanism of molecular weight reduction can be observed for most polyester (1).

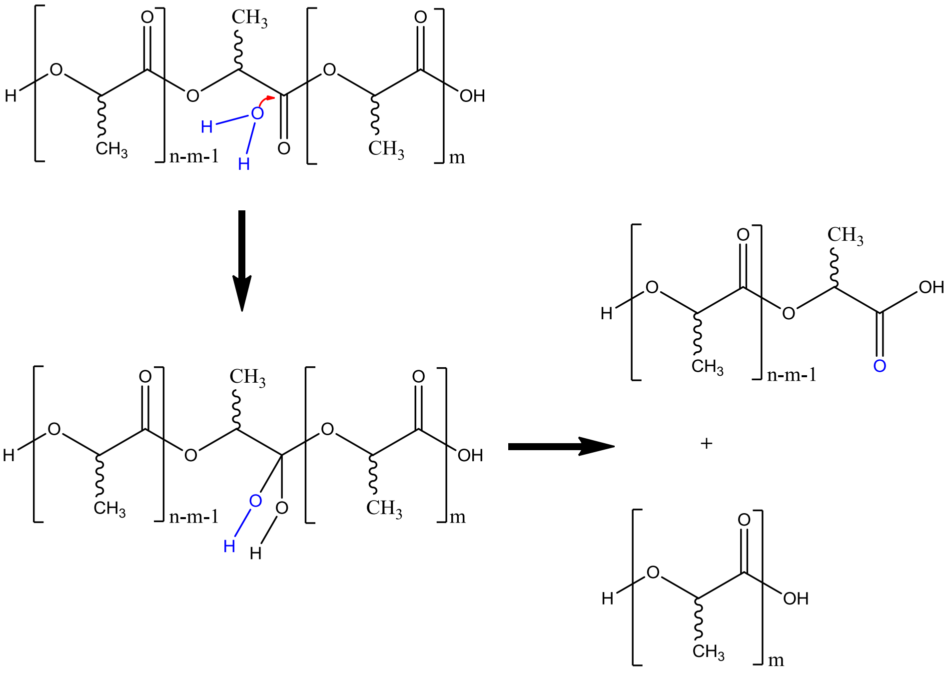


Fig. 4.1 Hydrolytic bond scission in PLA (1).

Hydrolysis starts in the amorphous phase with reduction in molecular weight and formation of oligomers that are water soluble (1). This first degradation doesn't bring any loss of physical properties because the crystalline regions provide the necessary strength, when also those are attacked and hydrolysis starts within the lamellae, loss in mechanical properties occurs. Hydrolysis can take place passively, by chemical reactions, or actively, via enzymatic reaction.

Two main routes are available for the overall degradation of the polyester which include hydrolysis: bulk degradation and surface erosion. In the first case water diffuses faster than the actual degradation reaction rate and the ester hydrolyzable bonds are cleaved randomly, hence the molecular weight decreases homogeneously. When surface erosion occurs the diffusion rate of water is slower than the degradation rate itself which happens just in a thin surface layer, this is an heterogeneous process. Polyesters usually undergo bulk hydrolysis meanwhile anhydrides undergo surface erosion because the chains are more hydrophobic. (2)

Hydrolytic degradation is influenced by several factors such as flexibility of macromolecules, water permeation and diffusion, hydrophilicity, morphology size, form and density of crystallites.

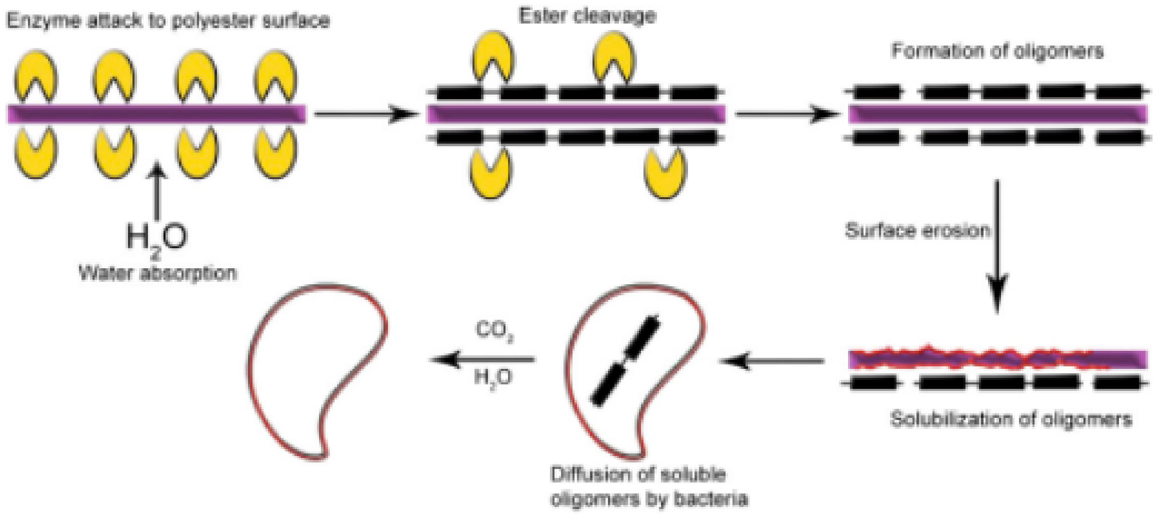


Fig. 4.2 Enzyme catalyzed hydrolytic degradation (3).

Hydrolysis is also involved in enzymatic degradation, as shown in Fig 4.2 enzymes such as lipase are too big to penetrate deeply into the polymer, so they start to act on the surface through its erosion process. The enzymes induce cleavage on the ester bonds thus producing oligomers that have sufficiently low molecular weight to be soluble in water and diffuse into the microorganisms.

4.2 Enhancing Hydrolysis resistance

Some additives are recommended for enhancing hydrolysis resistance, but not much information is available about the real effectiveness of those additives in polybutylene succinate. Carbodiimides are among the most recommended, they contain the carbodiimide group shown in Fig 4.3. They basically react trough the reaction displayed below with carboxylic acid end groups toward amide or ester formation, this lowers the number of hydroxyl end groups thus lowering also water absorption and overall hydrolysis (4).

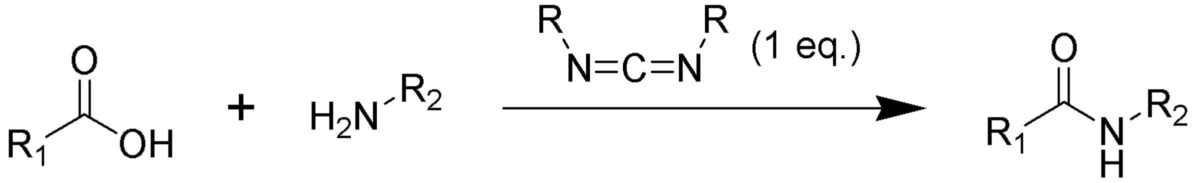


Fig. 4.3 Carbodiimide reaction with carboxyl end groups (4).

They can be used in monomeric form or polymeric form, thus including in the additive longer polymeric chains that will react with the macromolecules.

A change in morphology can work as well: different crystalline morphologies influence the hydrolytic degradation, this is mainly linked to the diffusion rate and the degree of

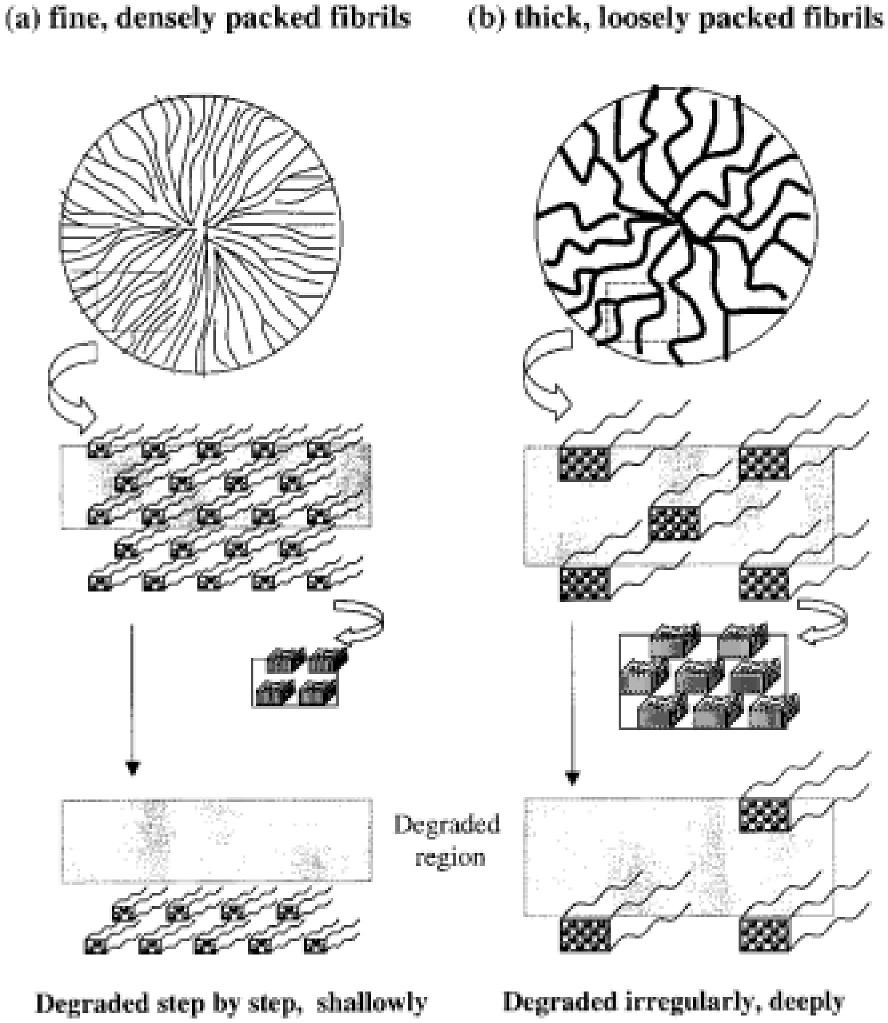


Fig. 4.4 Change in degradation pattern due to different crystallite morphology (5).

permeation of water molecules within the crystallite structures. Even with similar percentages of crystallinity, hydrolytic degradation was slower in melt-quenched samples because fibrils were more tightly packed (5). The different morphology of the crystal regions brought to different hydrolytic degradation, as shown in Fig 4.4. Fine, densely packed fibrils such the ones present in the melt quenched samples led to shallowly and step by step degradation while thick and lovely packed ones brought to deep degradation. Thus can be assumed that with different thermal histories the product will be more or less susceptive to hydrolysis, and a faster cooling rate can help, in some extent, in lowering hydrolytic degradation.

Nanocomposites are also an explored path in order to enhance hydrolysis resistance, in this case the defensive mechanism is a physical one: the insertion of nanostructures, in particular nano platelets lowers water diffusion creating a more tortuous path.

4.3 Polybutylene succinate state of the art

As stated in Succipack project final report (6) hydrolysis resistance is one of the main concerns with polybutylene succinate, whose mechanical properties undergo a dramatic decrease in high humidity conditions. To solve this problem the search for solutions is still open and various options can be found in literature.

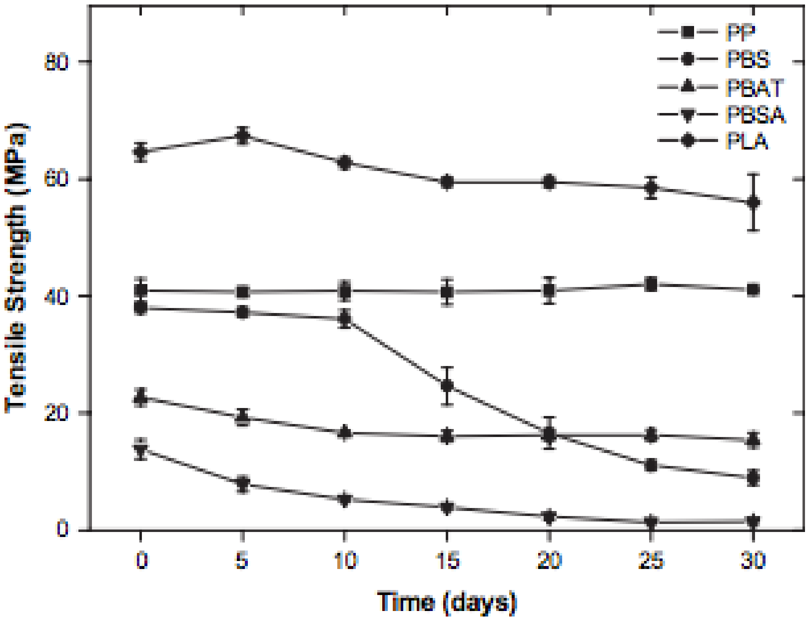


Fig. 4.5 Loss in tensile strength of PBS, PP, PBAT, PBSA and PLA under 50°C and 90% RH over 30 days (7).

As shown in Fig 4.5 in high humidity conditions (7) of 50°C and 90%RH, compared to other polymers such as PP, PLA; PBAT and PBSA, polybutylene succinate is the one that undergone the higher decrease in tensile strength. The decrease over a period of just 30 days for PBS is higher than 50% while for PP, PLA or PBAT is under 10%. During this period, surface hardness increased thus showing an increase brittleness

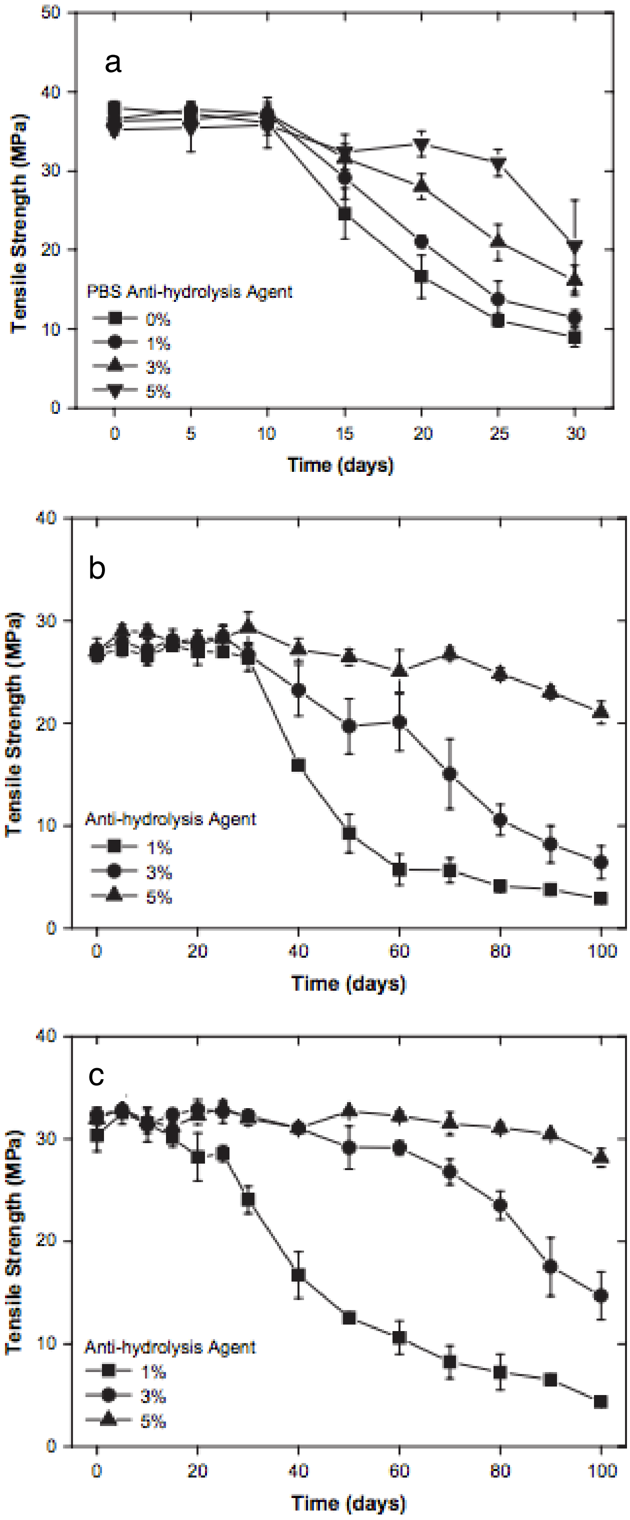


Fig. 4.6 Decrease in tensile strength for PBS and carbodiimide (a), Bamboo flour (b) and wood flour (c) (7).

due to surface erosion of the samples. Before the test procedure the sample surface was smooth and clear. The permanence under high humidity conditions brought random degradation with the creation of cavities, voids and a rough surface.

Several examples about Polybutylene succinate nanocomposites are present in scientific literature and has been presented in chapter 1.15, also using Cloisite 30B that is the one used in the present work. In particular Cloisite 30B is also reported to be the most compatible one, with higher degree of intercalation (8). Nano composite with organic fibers were also proposed (coconut, sisal, bagasse and curaua), but they increased water uptake in different extent because of their hydrophilic nature. This was also related to the dispersion and overall compatibility between the polymer and the fibers, in fact ,with less hydrophylic fibers there was not intimate contact with the polymer matrix, thus creating voids that enhanced water absorption (9)

Kim et al used Bamboo flour and wood flour as natural fillers to enhance hydrolysis resistance under 50°C and 90% RH in polybutylene succinate, comparing them with the effects of a carbodiimide (7). As shown in Fig 4.6 all the proposed nanocomposites had an effect in reducing hydrolysis, in fact the reduction in tensile strength over time was lower with increasing presence of anti-hydrolysis agent. In Fig 4.6 a the effect of carbodiimide is shown over 30 days, with a higher percentage of additive (5%) the lower decrease was obtained, comparable results were found with bamboo flour (b) and wood flour (c). 5% of wood flour revealed as the best option, over 30 days and 100 days also, with a negligible decrement in tensile properties. Regarding the increase in surface hardness it was decreased when anti-hydrolysis agents were added to the biopolymer, hence reducing surface brittleness.

Other organo modified layered silicates have been investigated to increase hydrolysis resistance in PBS, the results obtained were in most of the cases an increase in the biodegradation rate of the nanocomposites (10). This acceleration is a consequence of the nature of the nanofiller, mainly its higher hydrophilicity increases the water uptake more than the tortuous path created by the platelets lower it. The clay addition also lowered the overall crystallinity, increasing the amorphous regions and increasing also the penetration of water molecules. TiO_2 and SiO_2 nanoparticles were also used for nanocomposites, in this case the degradation was inhibited because silica and titania inhibit the diffusion and absorption of the enzymes.

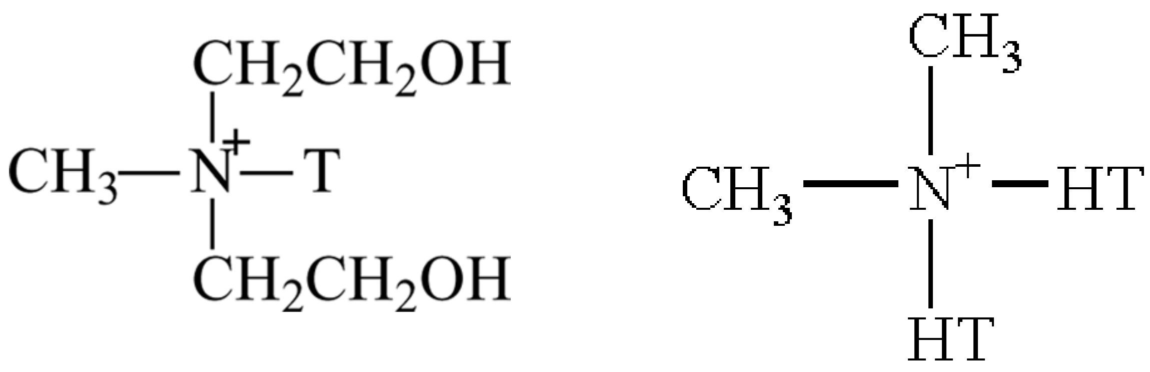
4.4 Materials used

4.4.1 Talc

Talc is a clay mineral that in this case was used as a reference material for nano composite creation, in order to compare it in terms of dispersion and distribution with the organo-modified cloisites. It is composed of hydrated magnesium silicate, the lattice can be monoclinic and triclinic; the small crystals are arranged in folia that have perfect basal cleavage. With Mohs hardness scale it is classified under 1, in fact it can be scratched by one finger nail (11).

4.4.2 Cloisite 30B

Cloisite 30B is an organomodified montmorillonite with metal tallow bis-2-hydroxyethyl quaternary ammonium salt. (12). In Fig 4.7 the structure of the salt modifier is shown.



$$CH_3-\overset{\displaystyle CH_2CH_2OH}{\underset{\displaystyle CH_2CH_2OH}{N^+}}-T \qquad CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle HT}{N^+}}-HT$$

Fig. 4.7 The left structure is the salt modifier in Cloisite 30B and the left one is the modifier for Cloisite 20A (12) e (13).

4.4.3 Cloisite 20A

Cloisite 20A is an organomodified montmorillonite with dimethyl dehydrogenated Tallow quaternary ammonium. (13) In Fig 4.7 the structure of the salt modifier is shown.

4.4.4 CRODA Pripol 1009

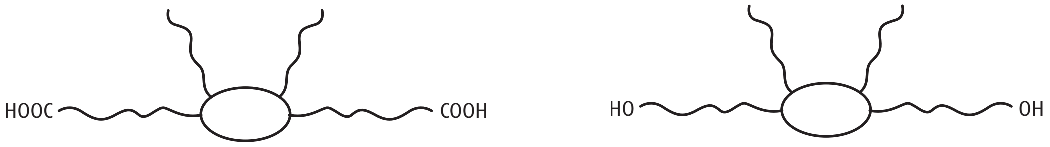


Fig. 4.8 Pripol 1009 structure (14).

Croda's Pripol is a branched C36, available in two forms: a dicarboxylic acid and a diol, as shown in Fig 4.8 (14), due to the long carbon chain it brings excellent hydrophobicity. It is made from natural fatty acids, with 100% of renewable carbon content. The dimer furnished is UV stable and has high purity, it is recommended for polyesters like PET and PBT, it comes in the form of a viscus clear liquid. Blending with PET and PBT brought several advantages such as:

- Enhanced hydrophobicity: it reduces water absorption, accelerates drying before processing and improved hydrolytic stability and chemical resistance.
- Improves flexibility acting as a plasticizer, reduces stress and strain after moulding
- Improves melt flow properties

4.5 Experimental Overview

New ways to improve polybutylene succinate resistance to hydrolysis were explored, in particular the use of nanocomposites or fatty acids. Two mechanisms were then involved in this expected change in properties, in the first case a physical one were the platelets created a more tortuous path for water diffusion, in the second case a chemical one was involved, the additive should react with condensation reactions with the end hydroxyl groups of PBS, lowering their concentration hence water absorption and sensitivity.

The initial step was to individuate the most compatible clay in terms of dispersion and distribution, thus three inorganic layered structures were compounded with the polymer using the conditions mentioned in Cap 3.6. Cloisite 30B, Cloisite 20A and talc were added at 5 wt% to industrial PBS. Talc was used as a reference, in fact it wasn't expected to disperse well in the polymer. The samples were observed with SEM and Cloisite 30B was chosen as the most compatible clay.

Then water absorption with ASTM D570-98 was tested for three samples of industrial, high acidity PBS; the polymer itself, and then Pripol 1009 and Cloisite 30B were added into the extrusion process. This step was useful in order to determine if the additive would be able to react efficiently during extrusion with the polymer.

Then the same water absorption procedure was used to compare PBS from reactor synthesis and low acidity value, with clay, Pripol 1009, Pripol 1009 and clay, compared with PBS from reactor synthesis with Pripol added in the reactor and clay added during the extrusion process.

4.6 Improving PBS hydrolysis resistance

4.6.1 PBS Nanocomposites observation

Sample preparation

In order to understand the interactions between the PBS matrix and the fillers added during extrusion a cleavage fracture surface was needed. Usually polymer's fractures involve a certain degree of plastic deformation, that in this case was to be avoided. The samples were then cooled in liquid Nitrogen and broken with an impact load to induce fragile fracture. After selecting the surfaces with the right orientation (perpendicular to the direction of extrusion, in order to see the possible filler orientation) the samples were placed on the specimen and stopped firmly with conductive tape. The final step was the coating with a thin layer of Au, in order to have a conductive surface on which the electrons can be dispersed.

Sample Observation

Many different types of nanocomposites can be created using clays, in order to improve polymers properties, especially with packaging applications. The best filler was to be determined in order to compare it with simple polymer and additive plastic. The aim with nanocomposites, that can help enhancing hydrolysis resistance, is to diminish water permeability adding a component that is less hydrophilic or that can hinder the diffusion paths to water molecules. For clays, since they are highly polar structure the supposed mechanism is the second one; thus achieving high distribution and dispersion is fundamental. Three samples were explored and observed using SEM imaging, one reference with talc powder and two options for clay. The samples observed in the first stage were:

- PBS extruded @ 180°C, 100 rpm, 5 minutes
- PBS extruded + 5% talc
- PBS extruded + 5% Cloisite30B
- PBS extruded + 5% Cloisite20A

Fig 4.9 shows the PBS matrix, which undergoes a fast degradation under the electron beam so that rising to magnitudes higher than 2500x was difficult without compromising the sample. The observation of the nano composites was made at 2500x and 1000x to highlight the distribution and the dispersion of the filler.
In Fig 4.10 the talc nano composite can be observed, confirmed in the composition by the presence of Mg and Si with the EDS analysis, the particles are hence well distributed, but not well dispersed. There are residue conglomerates, made of little

lamellae. To investigate the filler dispersion an EDS analysis was conducted of the matrix in the zones in which there was no evident residual particles, in the case in which there were present the characteristic elements of the filler (see Chapter "materials used") it therefore would have been well dispersed. In the case of the talc no evidence of Mg and Si was found in the matrix, Cloisite30B was the only case in which Silicium was found also in the matrix.

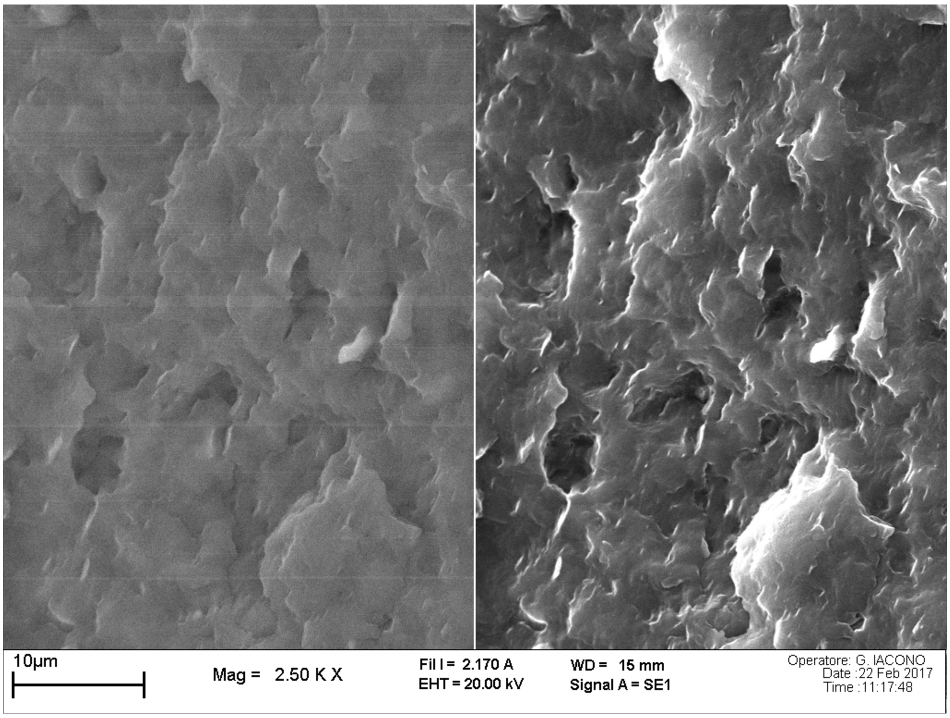


Fig 4.9 SEM images of PBS surface 2500x, on the left is the image obtained with backscattered electrons and on the right with EDS analysis.

The presence of Nitrogen was not reliable as an indicator of dispersion because the atomic number of the element is too low to allow its detectability with the X-ray detector used. The further analysis of CLO30B composite with Backscattered electrons allows to see with higher contrast the two different phases present in the composite, (the clearer is the nano clay and the darker the polymer). As seen in the picture the nanoclay conglomerates are also present and visible under the surface layer, thus the bond between the matrix and the filler is strong. The morphology of the composite with CLO20A is more inhomogeneous than the one with CLO30B, with more residual conglomerates in the matrix.

In the case of CLO30B the dispersion and distribution of the nano fillers were the best between the analyzed cases. As displayed in Fig 4.10, at 1000x the structure of the composite is homogenous (hence the processing conditions are optimal for the formation of the composite) and there are not many residual conglomerates. Due to this observation Cloisite 30B is the chosen filler to be used to try to enhance PBS hydrolysis resistance.

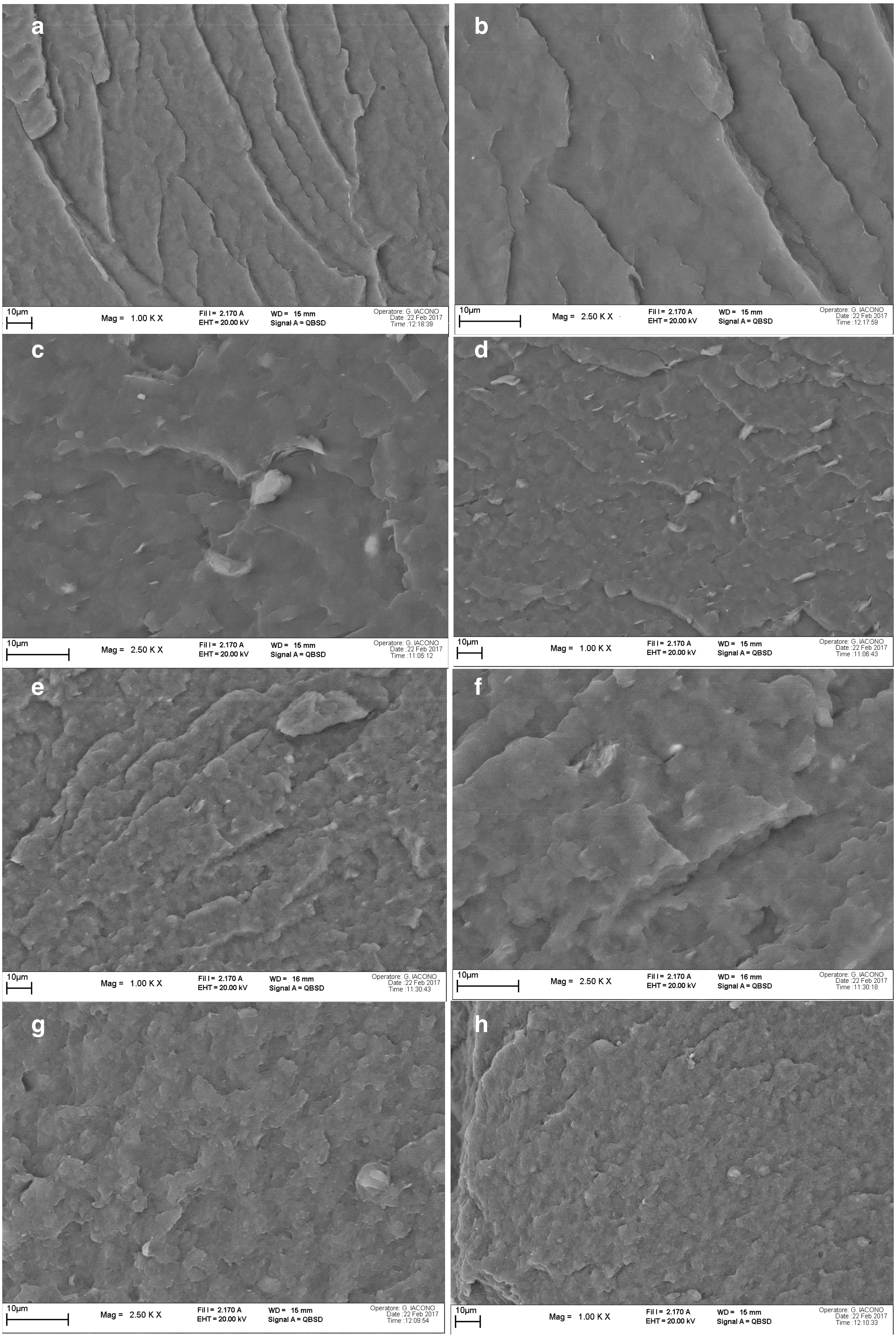


Fig 4.10 SEM images of pure PBS (a,b), PBS and talc (c,d), PBS and CLO30B (e,f), PBA and CLO20A (g,h). On the left 2500x and on the right column images are taken at 100x.

4.6.2 Observation of PBSp nanocomposites

PBSp nanocomposites with Cloisite 30B were also observed with SEM imaging in order to investigate how the creation of anhydride groups influenced the formation of the nanocomposite. Has shown in Fig 4.11 Cloisite is heavenly distributed but not dispersed, little platelets are still visible. From the element analysis the typical elements of phyllosilicates can be found in the matrix and in the brighter platelets. Thus meaning that the clay has been partially dispersed in the matrix, but not completely, residues can still be seen. These conglomerates are all oriented on one direction, the one in which the shear stress applied from the extruder was higher. From picture 4.11 (c) the homogeneous distribution can be appreciated, while in Fig 4.11 (a) the platelets alignment is shown.

In picture 4.11 (b) cubic structures can be seen, these are salt particles, derived from the water absorption procedure conducted on the sample before it was observed with SEM imaging. With EDS analysis Potassium and Calcium were found, confirming that the cubic particles were residues of the water presence.

The presence of Pripol 1009, added during synthesis lowered the compatibility between the polymer matrix itself and the clay. This is readily understood comparing Fig 4.11 to Fig 4.10, when anhydride groups weren't included in the chains the dispersion was higher. The reaction with the fatty acid decreased the hydrophilicity of the polymer, thus resulting in

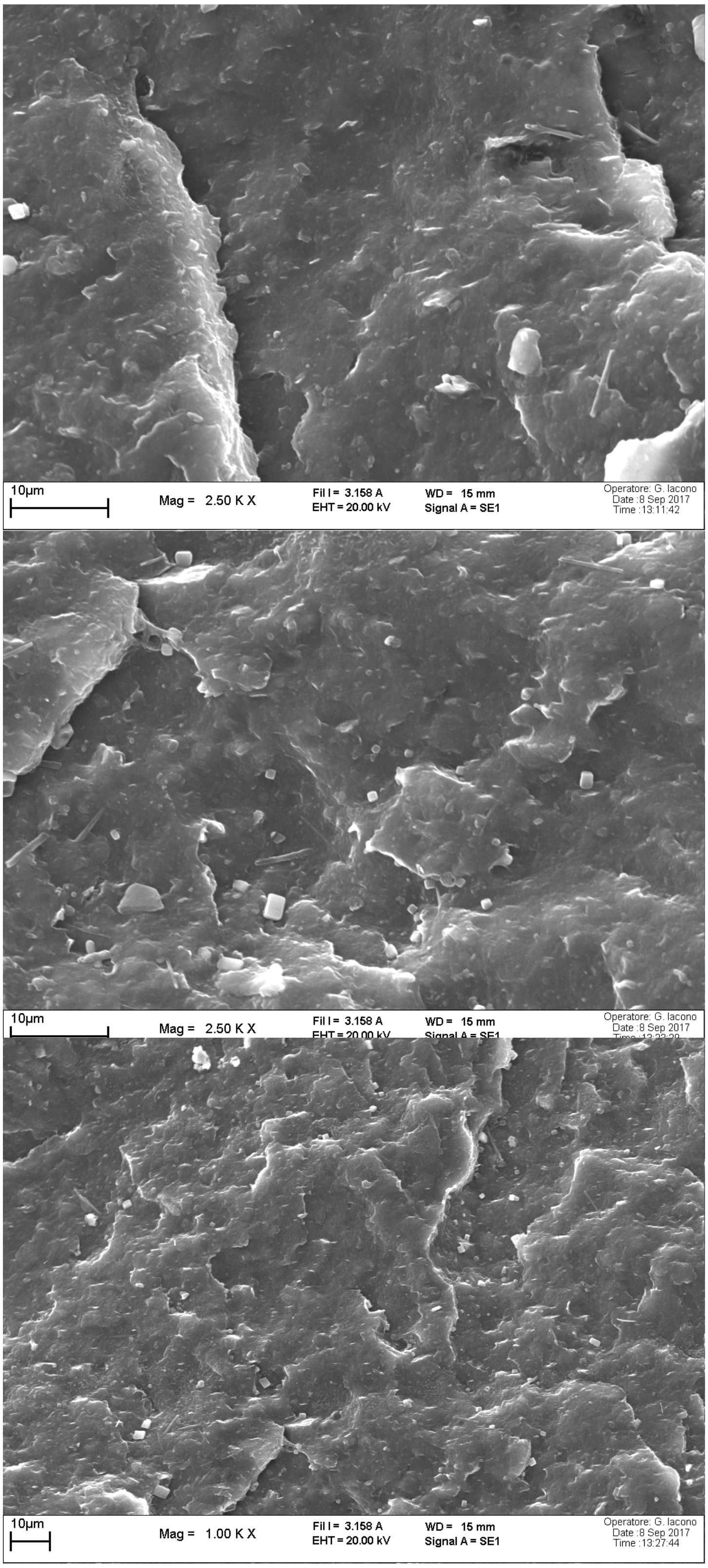


Fig 4.11 SEM images of PBSp compounded with Cloisite 30B, (a) and (b) are taken at 2500x and (c) at 1000x.

lower compatibility with the nanofiller.

4.6.3 Water Absorption with industrial PBS

Three plastic-additive combinations were prepared, to investigate two different additives and their influence on water absorption and hydrolysis resistance, Cloisite30B and Pripol 1009, kindly supplied by Croda Coatings and Polymers.

The specimens were prepared with the micro twin extruder, 100 rpm for 5 minutes at processing temperature of 180°C, and then moulded with the platen press at 180°C under 100 bar. The three combinations of polymer additives were:

Tab 4.1 Industrial PBS and additive compounding.

Sample N°	Polymer matrix	% Additive	Additive (g)	Polymer (g)
1	Industrial PBS	-		18
2	Industrial PBS	3% Propil	0,51	18
3	Industrial PBS	5% Cloisite30B	0,85	18

The water absorption was measured with the procedure described in ASTM D570-98.

For each one of the mixture polymer-additive, 3 samples 60x60x1mm were moulded with the two plates press, in order to have a range of different values and a statistical analysis on the results. The samples containing CLO30B were the darker ones, because of the presence of the clay. The samples with Pripol additive remained sticky when touched with bare skin, but didn't have any kind of adhesion on the metallic mould so they were easily pulled off. These were also the ones to present

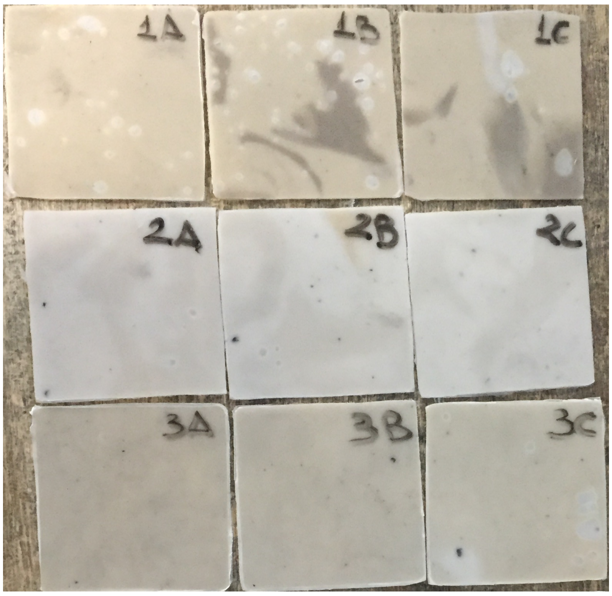


Fig 4.12 Industrial PBS samples for water absorption, (1) is the polybutylene matrix itself, (2) is PBS compounded with Pripol, (3) is industrial PBS compounded with Cloisite 30B.

less visible voids, followed by CLO30B nanocomposites and the polymer matrix itself which had higher void concentration.

As shown in Fig 4.12 the samples containing Pripol assumed a pale white color and were the ones with less voids and cavities, thus meaning that the fatty acid increased the overall processability. The samples with CLO30B were the darker ones, because of the presence of the clay, they also had less voids in comparison with polybutylene succinate without fillers. Adding the nano filler decreased mould shrinkage, allowing better processability with the compression moulding machine.

Firstly the 18 samples were dried at 50°C for 24h, then cooled down in the dryer for 2 hours at 0% RH. They were then weighted and immersed in distilled water for 24h, then they were dried using absorbent paper and weighted again, after some minutes. This little interval of time was necessary for the samples to stabilize their weight, in order to let superficial water to evaporate and reach equilibrium with the surrounding atmosphere. They were dried again at 50°C for 24h, then cooled down in the dryer for 2 hours at 0% RH and weighted again in order to calculate any weight loss in water by extraction. The results, as average value, are shown in the following Table and Graphs, just one specimen (for PBS1) was eliminated from the data analysis because of its high concentration of voids the resulting value were far from the others.

Tab 4.2 Industrial PBS Water absorption and weight lost after immersion

Sample	Weight after dryer (mg)	Weight after Water (mg)	Final weight after dryer (mg)	Gained weight after water immersion (mg)	Lost weight in water(mg)
PBS3	4256,4	4296,3	4254,1	39,9	2,26
PBS3+Propil	4147,6	4202,2	4148,2	54,6	2,9
PBS3+Clo30B	4264,5	4308,5	4262,3	44	2,23

From the graphs shown in Fig 4.13 and data showed can be deduced that the additive and the clay didn’t act as expected, in fact water absorption was enhanced. Adding the organo-modified clay and Propil dicarboxylic acid increased plastic hydrophilicity, also because the additive acted as a plasticizer, lowering the crystallinity of the matrix. Regarding Cloisite 30B, it increased water absorption, mainly because of its hydrophilicity and because it disturbed the polymer’s crystallization process when cooled.

The second weighting procedure allowed us to calculate if there was any weight loss during water immersion, due to the fact that some components were extracted by water (oligomers and other small molecules). As is shown in the graph the weight loss is higher for PBS with Pripol because the fatty acid acted as a plasticizer and it was easier for water to extract low molecular weight compounds.

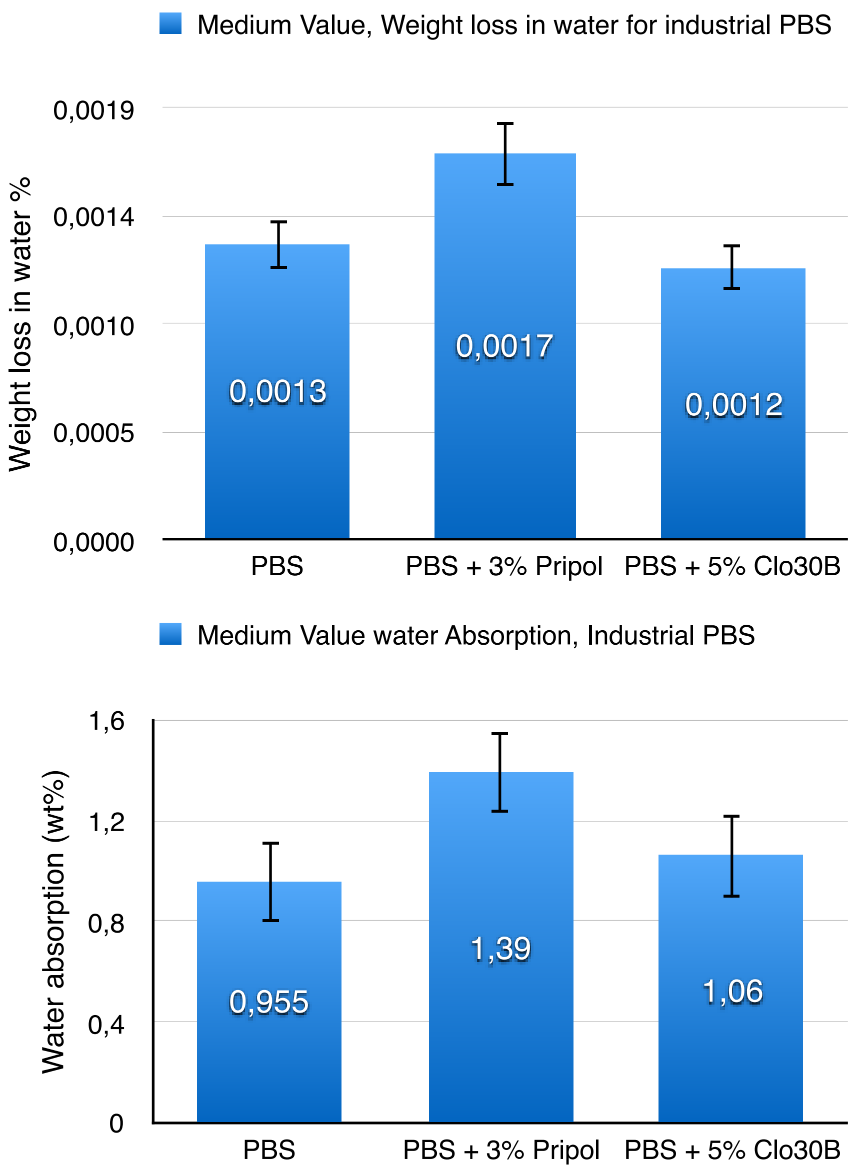


Fig 4.13 Graphs obtained for water absorption and weight loss in water for Industrial PBS compounded with Pripol 1009 and CLO30B.

These results shows that Prypol didn't lower water sensitivity because it didn’t react with polybutylene succinate during extrusion, it simply acted as a plasticizer thus enhancing hydrolysis. Also the results with Cloisite 30B were not positive, hence this clay is compatible with PBS but its addition results in a higher water sensitivity. Therefore a new route was explored to lower water absorption, also using Pripol, in order to obtain the reaction it was added during reactor synthesis.

4.6.4 Water absorption of PBS from reactor synthesis

Six more plastic-additive combinations were prepared, to investigate how these additives influenced different polymer matrices on water absorption and hydrolysis resistance, Cloisite 30B and Pripol 1009 were also used. Polybutylene succinate was produced via reactor synthesis this time, PBS1, with low acidity was used and Pripol and Cloisite 30B were added during extrusion (for the polymer properties refer to

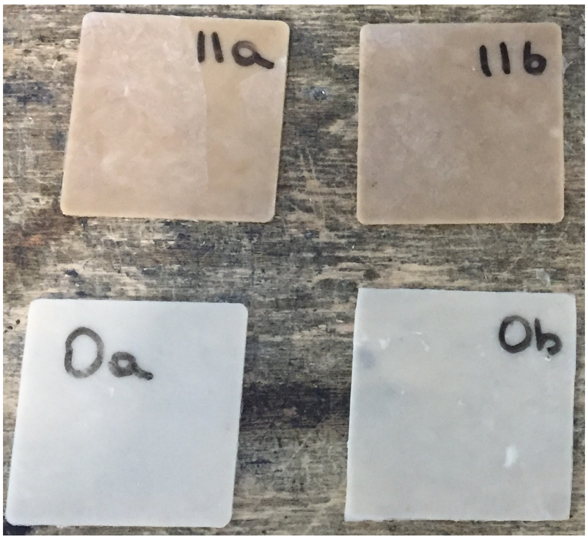


Fig 4.14 Picture of PBS from reactor synthesis, samples 0 are PBS with Pripol added in synthesis, samples 11 are PBS1, with low acidity values.

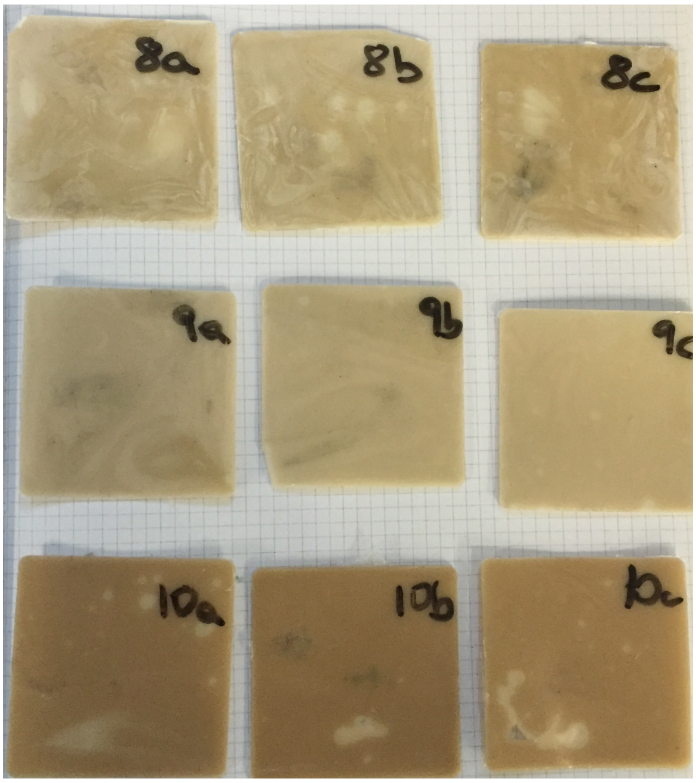


Fig 4.15 Picture of PBS from reactor synthesis, with low acidity and without Pripol. Samples 8 are PBS1, Samples 9 are PBS1 with Pripol extruded, Samples 10 are PBS1 with Cloisite 30B extruded.

chapter 2.5). Pripol was also added during reactor synthesis to allow condensation to happen thus exploiting the additive potential, PBSp was obtained.

As shown in Fig 4.14 and Fig 4.15 there is a great difference in the appearance of PBS samples. In Fig 4.14 the difference between samples of PBS 1 versus PBSp can be appreciated; as it happened with the extruded samples, adding Pripol 1009 brought a pearly white color to the samples and increased processability. Samples 0 have in fact less voids than samples 11, that are also darker.

In Fig 4.15 the different compounding choices are shown, PBS1 with Pripol (9) is the one which presents the lighter color and less voids, PBS1 with CLO30B is the darker one (10) and PBS1 itself has the higher percentage of voids. These behavior didn't change with less acidity and a polybutylene succinate that derived from reactor synthesis, versus the industrial one considered in previous paragraph.

PBSp was tested in the extruded form and not in the processed form, in fact having the additive already inside the polymer itself would shorten the processing timing and extrusion could be unnecessary also in some cases. Cloisite 30B was also added to PBSp to investigate the combined effect of the nano composite and the additive.

The specimen were prepared with the micro twin extruder, 100 rpm for 5 minutes at processing temperature of 180°C, and then moulded with the platen press at 180°C under 100 bar. The six combinations of polymer additives were:

Tab 4.3 PBS1 and PBSp with additives

Sample N°	Polymer matrix	% Additive	Additive (g)	Polymer (g)	State of the polymer
1	PBS1	-		18	Extruded
2	PBS1	5% Cloisite30B	0,85	18	Extruded
3	PBS1	3% Pripol	0,51	18	Extruded
4	PBSp	-		18	Not Extruded
5	PBSp	-		18	Extruded
6	PBSp	5% Cloisite30B	0,85	18	Extruded

For each one of the mixture polymer-additive, 3 samples 60x60x1,5mm were moulded with the two plates press, in order to have a range of different values and a statistical analysis on the results. Also in this case the samples containing clay were the darker ones and those of PBSp were the whiter. The water absorption procedure was the same of that indicated in ASTM D570-98.

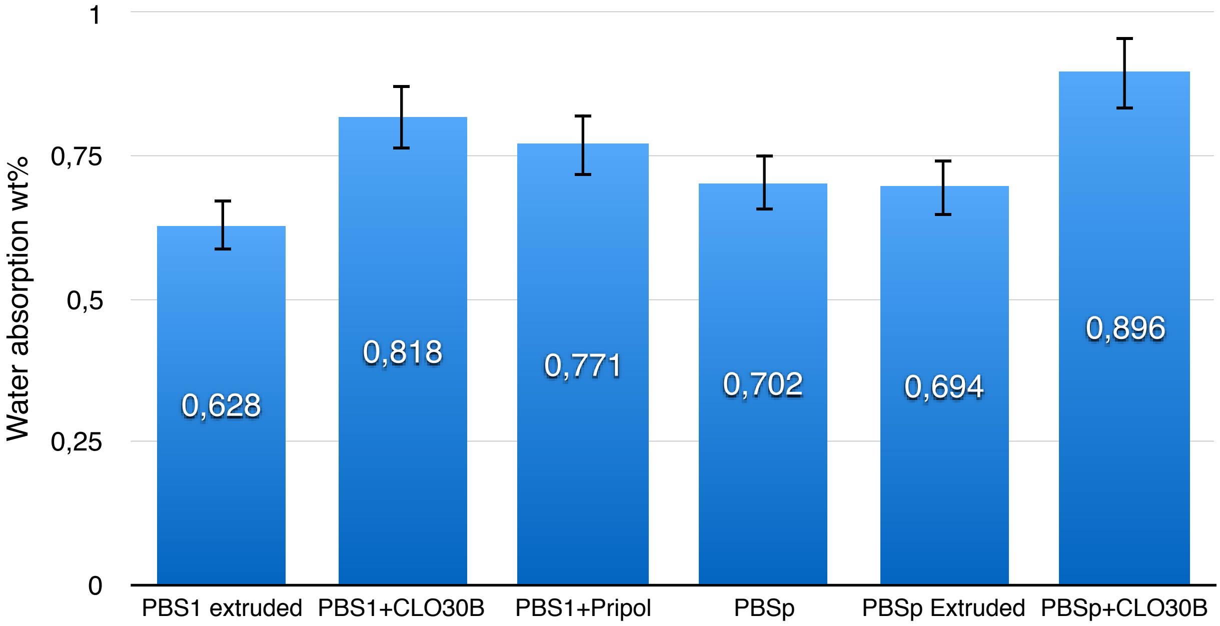
Here following the collected data for the six samples:

Tab 4.4 PBSp and PBS1 water absorption and weight lost in water

Sample	Weight after dryer (mg)	Weight after Water (mg)	Final weight after dryer (mg)	Gained weight after water immersion (mg)	Lost weight in water(mg)
PBS1	5916	5954,4	5914,6	48,5	1,37
PBS1+CLO30B	5488,1	5530,2	5487,73	42	0,4
PBS1+pripol	5591,4	5630,6	5590,6	39,3	0,77
PBSp	5764,9	5804,9	5763,8	40	1,1

Sample	Weight after dryer (mg)	Weight after Water (mg)	Final weight after dryer (mg)	Gained weight after water immersion (mg)	Lost weight in water(mg)
PBSp extruded	6081,2	6119,3	6080,7	38,1	0,53
PBSp + CLO30B	5952,6	6006		53,4	

As shown in the graphs in Fig 4.16 the addition of Cloisite 30B during the extrusion increased water absorption, its high hydrophilicity contributed to rise water sensitivity. The same effect had the additive during extrusion, Pripol didn't react with Polybutylene succinate thus increasing the overall number of hydroxyl end group therefore water sensitivity. The presence of anhydride groups created with Pripol added during synthesis didn't lower sensibly water absorption compared with PBS1, the polymer with lower acidity. From the characterization of the two batches PBS has an acidity of 12 meq/Kg and PBSp of 21meq/Kg, the slightly higher water absorption can be then attributed to the higher concentration of hydroxyl groups. No difference can be spotted between PBSp extruded or not extruded, thus meaning that the overall degradation resulting from one extrusion cycle is low.



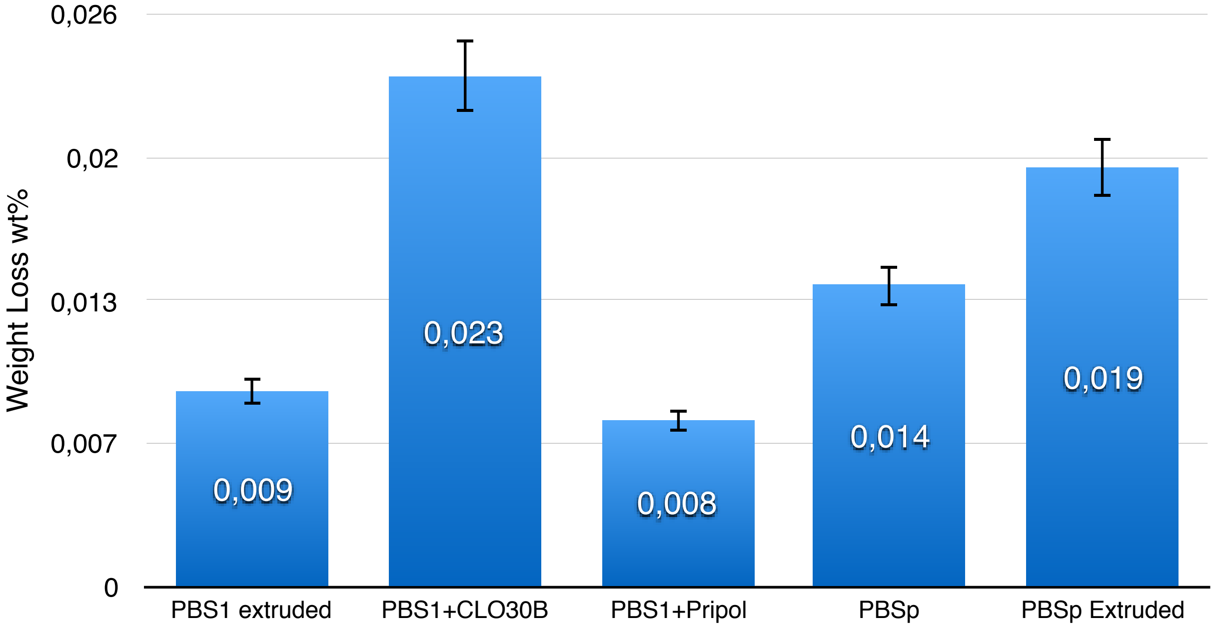


Fig 4.16 Graphs obtained for water absorption and weight loss in water for reactor synthesis PBS compounded with Pripol 1009 and CLO30B and also cross linked with Pripol.

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Chapter 5 - Results and Conclusions

Multiple solutions for enhancing Polybutylene succinate resistance to thermal degradation, aging and hydrolysis were explored. PBS is a promising polymer in the field of packaging applications, but its development is still under research. Thermal stabilization and hydrolysis resistance is thus fundamental for its industrial implementation.

Not many results were available in literature regarding PBS compounded with the most used additives for thermal stabilization used for polyesters, thus an initial screening was necessary. During this aging procedure, that took over 15 days on industrial PBS, under 42% RH and 60°C, the most compatible and hence efficient additive was found. Irganox 1010, 1076, 1425, 1330 and MD1024 were testing, Irganox MD 1024 resulted as the best choice. The additive was the only one to prevent failure because of sample embrittlement. Irganox MD 1024 was also chosen for further investigation. It was compounded with three grades of Polybutylene succinate derived from reactor synthesis, then aged for 15 days under 80°C and 38% RH. The influence of different acidity value, was explored and it was that for higher acidity value water sensitivity increase is significantly higher than for lower acidities.

Furhter investigation is needed for exploring how the different values of acidity influence the degradation process in the long run, aging the samples until failure occurs. Other, longer, aging procedures are needed, to fully investigate the additives effect on PBS. Also a clear picture of the degradation kinetic is needed, as shown by these results, temperature and relative humidity are important factors that need to be fully addressed.

Various polybutylene matrices, with Irganox MD 1024, 1330 and Pripol 1009 added during extrusion or during synthesis, were aged at room temperature and different RH values over a period of 45 days. No clear trend was found, this is probably linked to the period of time on which the samples were tested, too short for the degradation to occur on a significant extent. Changes in the tested parameters occurred just in those samples that had the higher sensitivity to moisture, at higher percentages of RH. In this case further investigation is needed to fully investigate how the different plastic matrices produce degrade over longer periods of time. In particular three interesting options were compared: PBS with Irganox 1330 added during synthesis or during extrusion and Irganox MD 1024 added during extrusion. It is interesting to evaluate how the additive efficiency varies within these options.

Hydrolysis resistance is another important drawback for polybutylene succinate, in this work some possible alternatives were explored, in particular the addition of canonically to obtain nanocomposites and of a dimeric fatty acid, Pripol 1009. The presence of the ester group brings high sensitivity to water presence and hydrolysis in the polymer matrix. The additive and the nanofiller were extruded with the polymeric matrix, then water absorption was tested. Both the tested options resulted in higher water retention, thus meaning that these alternatives aren't effective in the case of low acidity PBS from reactor synthesis. The use of nano clays and also of the fatty acid increased the overall hydrophilicity of the polymer, the expected increase in barrier properties wasn’t found. Interesting future research can investigate the effect of additives and filler on different PBS grades.

Appendix - Techniques used

1 - Titration

Titrimetry is a laboratory technique used for chemical quantitative analysis to determine the concentration of an unknown analyte, in the present work acid-base titration was used to determine the acidity value of different PBS matrices in terms of meq/kg. The reagent is a prepared standard solution and then mixed in determined volumes with a solution with known concentration of the analyte. Titration with polymers can be used if the molecular weight is not too high (1) to identify the concentration of end groups thus can be correlated with the average molecular weight.

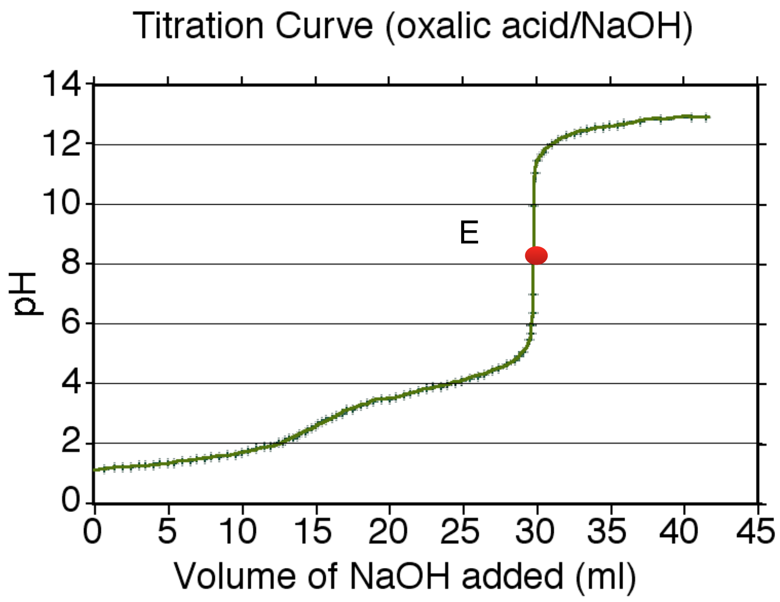

Fig A.1 Typical titration curve of oxalic acid titrated with NaOH to identify the equivalent point. (2)

The curve obtained with the analysis displays the volume of titrant added versus the change of pH of the solution, a typical path is shown in Fig. A.1. This variation can be measured using an indicator that usually is a weak base or acid added to the analyte that changes color when the equivalence point is reached. Otherwise in potentiometric titration an electrode is used to measure the potential variation (Volt) in the analyte. Two electrodes are used, a reference electrode and the indicator electrode immersed in the analyte. The reference electrode, usually hydrogen or silver chloride electrodes (3), is immersed in the half part of the cell created by the two solutions that remains constant in potential. The indicating electrode is dipped in the analyte solution, whose value of pH changes with the addition of the titrant, thus changing also voltage values.

With the addition of the base NaOH the pH of the solution increases, slowly at first then with a sudden growth when the equivalent point is reached (point E in Fig. A.1). The point of inflection in the curve indicates the volume of titrant solution added to neutralize the chosen analyte, with this information the polymer acidity can be calculated.

2 - Melt Flow Index

Melt flow index a measure of the polymer fluidity under pressure, an inverse measurement of the polymer viscosity. This measure is widely spread in polymer testing technologies because it is easy to handle and quick to perform, there is no need of additional solvents of additional equipment and can be executed with the same drying condition and temperature present during the polymer processing.

The polymer melt is extruded at high temperature trough a standard nozzle under a determined weight to assure enough shear stress for the extrusion process, the fluidity value is given in grams of material extruded in a given time, usually 10 minutes, this is called the MFI (melt flow index). The piston can be loaded with different weights, the standard used in this work is 2,16 kg and a cylinder temperature of 190°C, with three hours of drying at 80°C, these conditions are used because of their similarity to the processing conditions used later during extrusion and moulding.

Fig. A.2 Melt Flow Index (4)

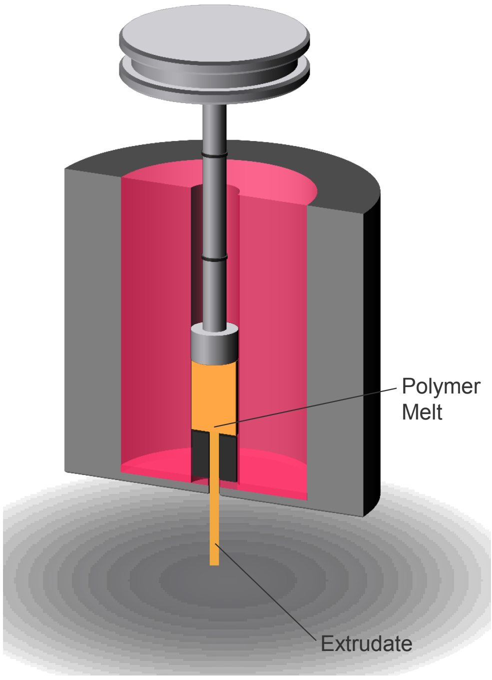

Fig. A.3 Melt flow index apparatus schematization (5)

4 to 5 grams of material is inserted into the heated barrel, then is properly pre-pressed to avoid the formation of air pockets. Preheating of the sample can follow

this first step with specific time periods, then the specific weight is applied trough a piston, 2,16kg is the standard used more often. The weight exerts pressure on the melt, thus generating shear forces that extrude the polymer through the nozzle. At fixed time intervals the melt is cut and then weighted, calculating the main value between at least five measurements is necessary to have a reliable measure of MFI (1).

Small changes in the polymer mechanical properties and molecular weight can be spotted using this analytical technique, thus MFI was readily included in this work. With Melt flow index is not possible to obtain the full diagram of polymer viscosity versus shear rate, just several single points can be calculated.

3 - Solution Rheometer - Inherent viscosity

A polymer dissolved in a solvent enhances its viscosity, the extent of this effect can be related to the molecular weight; the higher the Mw is, the more viscous the solution will be. In fact with bigger macromolecules the resulting secondary forces are higher thus reducing the mobility of the solvent molecules.

This measurements are carried out according to ASTM D2857-87 to determine the dilute solution viscosity of polymers. The practice is applicable to all polymers that dissolve completely without chemical reaction or degradation to form solutions that are stable with time in a temperature range between room temperature and 150°C. Results can be expressed in terms of specific viscosity, intrinsic viscosity, reduced viscosity or relative viscosity, expressed in the following formulas. In macromolecular chemistry the most used are reduced and intrinsic viscosity (6, 7).

Relative viscosity

$$\frac{\eta}{\eta_0} \approx \frac{t}{t_0} \quad (1)$$

Specific viscosity

$$\frac{\eta - \eta_0}{\eta_0} \approx \frac{t - t_0}{t_0} \quad (2)$$

Reduced viscosity

$$\frac{\eta - \eta_0}{\eta_0 \cdot c} = \frac{\eta_{spec}}{c} \quad (3)$$

Intrinsic viscosity

$$\lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 \cdot c} = [\eta] \quad (4)$$

The measurement of intrinsic viscosity is a reliable test that involves the use of solvents, this requires special attention for health and safety and specialized employees.

The information provided by the procedure can help in the molecular characterization of the polymer, viscosity is dependent on molecular weight distribution, chain ramifications and other parameters correlated with the polymer characteristics. The relationships that correlate viscosity depend upon many variables influencing this molecular size of dissolved polymer, such as temperature and solvent type. Varying the type of solvent also the interaction with the macromolecules is different, in particular the swelling can be higher and slow down the flux, the viscosity will then be higher.

$$F_v = \frac{V}{t} = \frac{\pi R^4 \Delta p}{8\eta L} \qquad (5)$$

With Poiseuille law, displayed above, the time of efflux can be directly correlated with the value of viscosity that is then commutated to intrinsic viscosity using the solvent value of viscosity and the concentration of the solution. The value of intrinsic viscosity is particularly valuable because it doesn't depend on the concentration. As displayed in Fig. A.4 the values of reduced viscosity are influence greatly by the concentration solution, in order to have comparable values we need to consider the limit at infinite dilution.

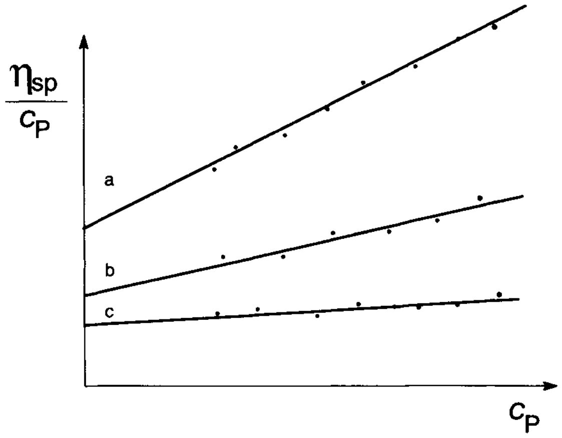

Fig. A.4 Evaluation of intrinsic viscosity and reduced viscosity with different values of concentration for a high molecular weight polymer (a), medium molecular weight (b) and low molecular weight (c). (1)

Thanks to the following relationship the elution time and the viscosity can be related, so a simple Hubbelhode viscosimeter can be used. At first the solvent characteristic efflux time shall be determined in the viscosimeter, in a thermostatic bath, with 0,1°C of tolerance. 10-15 cc of solvent is the average quantity used, the procedure may vary with different operators so it’s recommended that each one measures its own time, at least five times and then considering the average value.

4 - Differential Scanning Calorimetry

Differential scanning calorimetry, or DSC, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. This technique is widely used for the characterization of polymer samples to identify their physical and chemical transformation such as: degradation, melting, glass transition, phase transitions, etc. Both the sample and reference are maintained at the same temperature, which increases at a constant rate, throughout the experiment.

Fig A.5 Q20, TA instruments, DSC module. (9)

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic, for example crystallization is exothermic and melting is endothermic, it requires more heat to complete the transformation from solid to liquid state. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions (8).

DSC may also be used to observe more subtle physical changes, such as glass transitions. It is widely used in industries as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. Also chemical reactions such as oxidation and degradation of the sample can be observed.

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. Depending on the type of instrument the exothermic transition can be measured as an positive or negative peak. Integrating the peak area is also useful to calculate the transition hentalpy. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Glass transitions appears as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs.

A thermocouple is located symmetrically between the sample and reference sensor platforms, and acts as an independent measurement and furnace control sensor. An array of nickel cooling rods that connect the silver furnace with the cooling ring: this design produces superior cooling performance over a wide temperature range, higher cooling rates and agility from heating to cooling operation (30).

The samples are prepared with: Tzero DSC Sample Encapsulation Press, sample preparation is fundamental to achieve good results. The Tzero press crimps and seals hermetically the sample in a wide variety of materials. The die sets are magnetically attached with no tools or user adjustments required. In addition, each die set is color-coded to the box containing standard aluminum or hermetic pans.

DSC provides rapid and precise determinations of transition temperatures using minimum amounts of a sample. Common temperature measurements include: Melting, glass transition, thermal stability, oxidation onset, cure onset, polymorphic transition, crystallization, solid-solid transition.

The graph in Fig. A.6 shows typical shapes for the main transitions observed in DSC. DSC is an excellent tool for determining the thermal history of a polymer sample. The sample can be subjected to a “heat-cool-reheat” cycle and a comparison can be made between the two heating cycles. By comparing the first heating cycle (unknown

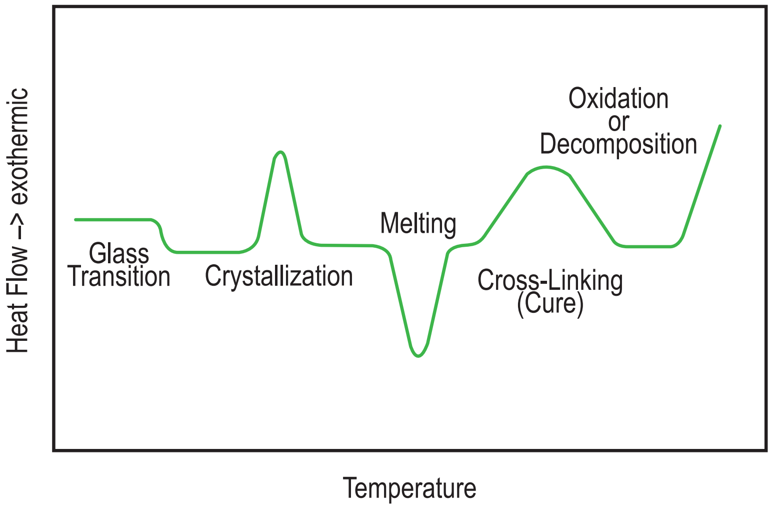

Fig A.6. Typical DSC curve for polymers. (9)

thermal history) to the second heating cycle (known thermal history), information can be derived concerning the original morphology of the material. This can be useful in troubleshooting problems in performance or processing conditions (11).

5 - UV-Visible Spectroscopy

UV-Visible spectroscopy is based on Lambert Beer law that states that the attenuation of a beam of light trough a sample is related to the concentration of the chromophore and the width of the sample. Uv-Visible spectrophotometer from Shimadzu was used. The law ca be expressed as below in equation (6):

$$A = -\log(I_1 / I_0) = \varepsilon c l \tag{6}$$

Where A is the absorbance, I_1 and I_0 are the intensities of the out coming ray and incident ray respectively, ε is the extinction coefficient, c the concentration and l the thickness of the sample.

When chromophore molecules absorb light in the UV-Visible range, this energy induces electronic transition between electronic levels (π to π* excitation for example) or chemical bond vibrations (stretching, scissoring etc.). This results in an energy decrease in the incident beam trough the solution it self. Lambert Beer law is valid just under certain conditions such as: the solution has to be homogeneous and not turbid, the attenuators must not influence each other, thus a diluted solution is needed (12).

The spectrometer has a radiation source that emits in the wanted range, usually deuterium and hydrogen lamps are used, the generated beam passes trough a prism, a monochromator if needed and then it goes trough the sample. A detector collects and amplifies the informations about the decrease in intensity of the beam, they are analyzed for all the desired wavelengths and used to determine the spectrum (13).

This type of spectroscopy is very important for polymer characterization, ultraviolet and visible light in the range from 185 nm to 760 nm is used (13). The instrument records the ratio of light transmitted trough a sample or the percentage of intensity extinction of the initial beam, absorption versus wavelength spectra are then produced. From the obtained spectra the characteristic chemical group contained in the polymer structure can be determined comparing the trace with tabled values for the specific chemical groups. For example, the double bond between two carbon atoms at 170nm, the triple bond at 180 nm and the carboxyl group at 290 nm and 180 nm. When considering these wavelengths neighboring atoms must be taken into account, they can affect where the group absorbs thus shifting the predicted peak.

These measurements are carried out on diluted solutions, often on chromophores, this is necessary in order to have a behavior that can be modeled under Lambert

Beer law. Quantitative analysis can be performed, such as relative or absolute quantity of certain chemical groups present, basically their concentration in different samples. Qualitative analysis can also be useful, such as which chemical groups are contained and how they can change in time or with harsh aging conditions, or it can also detect impurities. Obviously just groups that absorb in Uv-Visible range can be analyzed, thus limits the types of polymers that can undergo this kind of analysis.

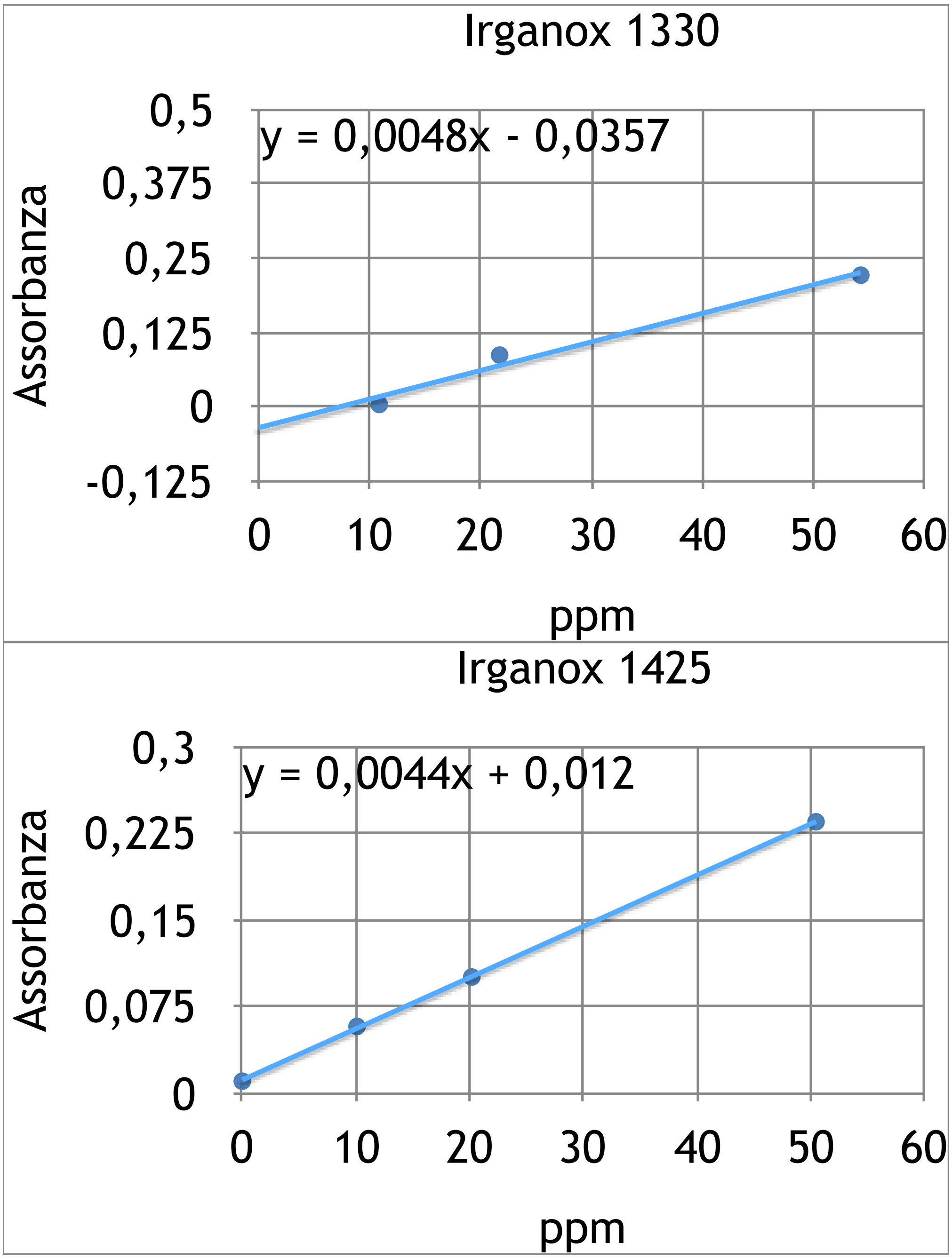

Fig A.7 Calibration Curves for Irganox 1330 and Irganox 1425.

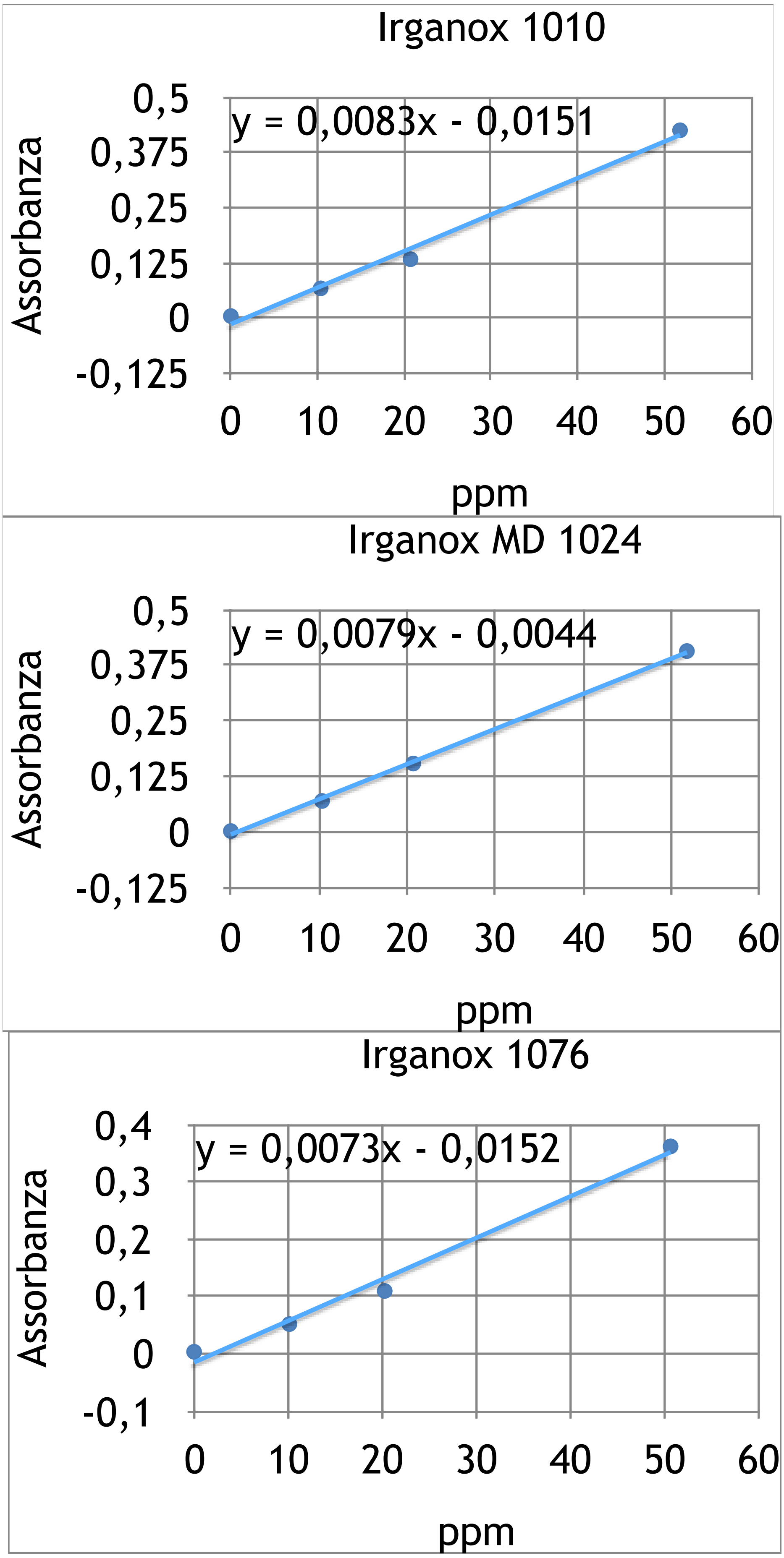

Fig A.8 Calibration Curves for Irganox 1010, 1076, MD 1024.

Calibration

Initially this technique was used to investigate the real quantity of additives present in the matrix after the first blending, due to the difficulties in the filling procedure and how the spectra changed after the accelerated aging procedure. Firstly the calibration diagrams were compiled for Irganox 1010, 1076, 1425, MD1024, 1330, then the spectroscopy was conducted on the polymer blends, ideally containing 0,25% and 0,5% of each additive respectively. But when approaching the analysis of the quantity within the polymer, interaction between the additive and PBS itself kept the analysis to be completed and a precise calculation of the additive real quantity was not achieved.

Solution with 1000ppm concentration were made; Irganox 1010,1076, MD 1024,1330 were diluted with dichloromethane, Irganox 1425 was diluted in methanol, these solutions were stored in order to avoid the possible degradation carried by sun light. From the mother solution, with sequent dilution, solutions of concentration 50 ppm, 20 ppm and 10ppm were produced for each additives. This solutions were analyzed with the UV-Visible spectrometer in the range 200-400 nm, the characteristic peak of the different additives, was approximately at 280 nm. From the intensity value at 280 nm and 350 nm of the different solutions and the solvent the calibration diagrams were compiled, with the results showed above in Fig A.7 and A.8.

6 - Micro Twin Screw Compounder

The Micro twin screw compounder (MC 15), produced by Xplore group, has a capacity of 15 cm^3 and offers a maximum torque of 12 Nm/screw. The screws can be used in co-rotating rotating mode and it's linked with nitrogen supply to assure an inert atmosphere for the most sensible polymers. this was of extreme use with PBS, in fact it is extremely sensitive to moisture when processed. As it can be seen in Fig A.9 we can easily identify the fundamental components:

1) the engine, generating the torque
2) the twin screws
3) the cavity where compounding takes place
4) the cooling system
5) the slot where the filling system can be housed
6) the touch screen with all the technical informations
7) the basement
8) output die

The software used with this machine gives as output different informations versus time, such as torque, temperature profile, screw speed, nozzle temperature (14). In this case the torque profile is the most important data needed, in fact analyzing it the degradation of the material, can be deduced. As input the operator must insert the temperature profile, there are six different thermocouples and the temperature of the three levels (input, mid-screw and output) can be chosen, also the maximum torque given by the screws and the processing time.

Fig A.9, Microtwin extruder (14).

After cleaning all the components that will be in contact with the polymer to avoid contamination, the screw are lodged in their slots and the chamber closed tight with six screws. Then the heating of the core parts starts until all six thermocouples reach

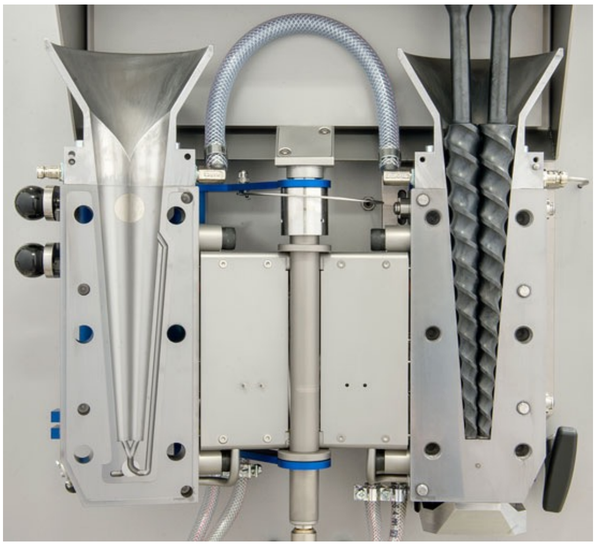

Fig A.10, Microtwin extruder insight (14).

duty temperature, the six screws are tighten again to avoid the presence of little voids due to thermal expansion, in which the fluid matrix can infiltrate. The nitrogen flux is

opened and the loading part is inserted in its slot (5). To calculate the quantity of matrix needed we can correlate its density with the maximum hold volume of the chamber, connecting also the right percentages of additives.
During the filling the screws maintain 30 rpm to let the matrix soften and reach the processing temperature. When the camber is full starts the processing, during which the matrix and the additives are compounded, then flipping the lever the polymer is extruded in a thin cylinder.

7 - DMA - Dynamic Mechanical analyzer

Dynamic mechanical analysis (DMA) is the technique of applying a cycling stress or strain to a sample and analyzing the response to obtain phase angle and deformation data. These data allow the calculation of the damping or tan delta (δ) as well as modulus and viscosity data. Two approaches are used: forced frequency, where the signal is applied at a set frequency, which is the one used in the PBS characterization, and free resonance, where the material is perturbed and allowed to exhibit free resonance decay (15). It is estimated to be 100 times more sensitive to the glass transition than differential scanning calorimetry (DSC), and it resolves other more localized transitions that are not detected in the DSC. In addition, the technique allows the scanning of a material's modulus and viscosity as a function of temperature, strain, or frequency. DMA is a very important tool in the modern polymer laboratory.

If a constant oscillatory load is applied to a sample, the sample will deform sinusoidally as well. This two sinusoids, the load and the resulting deformation, will be reproducible if the material is deformed within its linear viscoelastic region, thus is fundamental to remain in the elastic deformation region (16). The resulting strain wave shape will depend on the ratio between the viscous and the pure elastic behavior that the polymer has. The two extremes of the material's behavior, elastic and viscous, provide the limiting extremes that will sum to give the strain wave.

The material at the elastic or Hookean limit will respond elastically with the oscillating stress, without phase lag, completely in phase with the applied stress. The viscous limit was expressed as the stress being proportional to the strain rate, this curve has a certain phase lag from the stress curve. The material's behavior lies between these two limits, so the curve is an intermediate between the two cases. The difference between the applied stress and the resultant strain is an angle, δ. So the elastic response at anytime can now be written as:

$$\varepsilon(t) = \varepsilon_0[\sin(\omega t)\cos\delta + \cos(\omega t)\sin\delta] \qquad (7)$$

This equation can be separated into the in-phase (elastic, sinusoidal curve) and out-of-phase strains (viscous, co-sinusoidal curve) that corresponds respectively to the storage modulus and the loss modulus.

Dynamic Mechanical Analysis (DMA) is a technique that is widely used to characterize a material's properties as a function of temperature, time, frequency,

Fig. A.11 Dynamic mechanical analyzer (17)

stress, atmosphere or a combination of these parameters, the machinery is shown in Fig A.11.

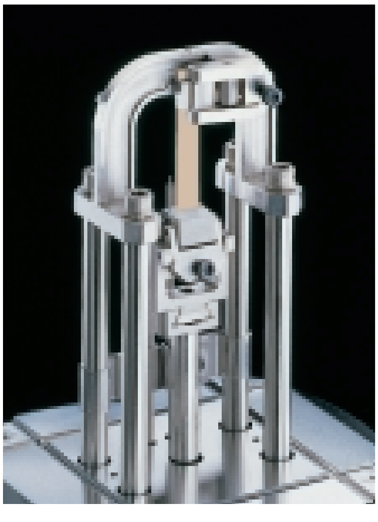

Fig. A.12 Tension clamp (18).

The instrument can apply a maximum force of 18N, with a measured modulus range from 1 kPa to 3000 GPa and a precision of 1%, in a temperature range from -150°C to 600°C. The frequency range may vary from 0,01 Hz to 200 Hz, the heating rate can be as higher as 20°C/min and the cooling rate can be up to 10°C/min (17). Useful information for polymer's characterization that can be derived from this analysis are: storage modulus, loss modulus, tan delta, temperature, sample stiffness, creep compliance, relaxation modulus.

The Q800 features a variety of sample clamps that provide for multiple modes of deformation. In Tension mode, the sample is placed in tension between a fixed (the one above) and moveable clamp (the one underneath) as displayed in Fig A.12. In oscillation experiments, a small static force is applied in order to prevent buckling.

8 - Compression Moulding Machine

Laboratory compression moulding machine is used in the manufacturing of polymer sheets for optical and physical tests of moulded forms. Depending on the requirements, these machines are also suitable for composites, components or for embossing. Platen Press P200 E (Collin) was used (19). The upper plate is fixed, meanwhile the lower one is moveable, lower platen, these presses cover a range of pressure up to 500 bar.

Fig A.13 Compression moulding machine (20).

This type of press allows the processing of materials within a temperature range from 20°C to 300°C. It has electrical heating and water or under pressure air cooling.
As shown in Fig A.13 there are different parts:

1. pressure switch
2. power switch
3. control panel, from here the temperature can be adjusted and the two plates can be opened or closed.
4. four tie bars
5. bottom moving platen with built-in, double-acting hydraulic cylinder
6. top platen
7. safety door, when open the press doesn’t close the two platens.

A system of pressure accumulators reduces pressure peaks and guarantees a constant level of pressure. The control is semiautomatic by preselecting pressure, pressing and cooling time (21).

9 - SEM and EDS analysis

A scanning electron microscope is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons (22). These are high cost devices and require measurements to be under vacuum, to avoid electron interaction with gas particles. The samples must be conducting and, hence, a biological or non conductive sample must have a gold layer deposited on its surface if it is to be investigated, as in our case with the polymer matrix.

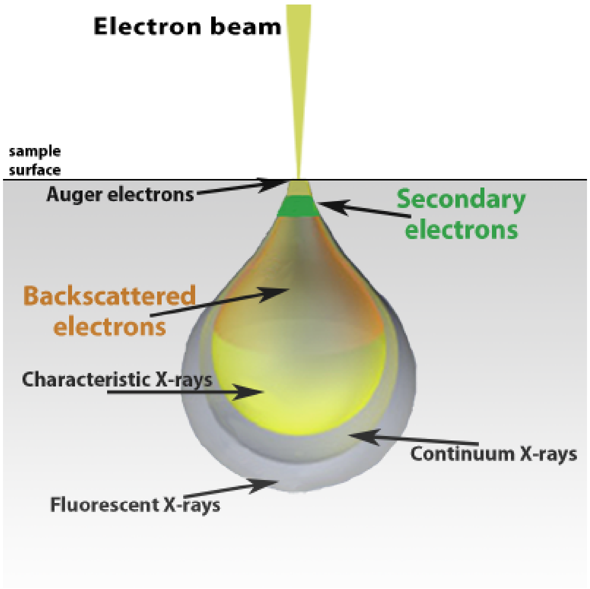

Fig. A.14 Schematization of the interaction between the electron beam and the sample surface (23).

This surface technique enables the operator to analyze the very first layers of the material, as we can see from Fig A.14 (23).

The energy carried by secondary electron is dissipated with the production of several signals such us the ones displayed in Fig A.14 such us Backscattered electrons, secondary electrons, x-rays and auger electrons. Secondary electrons and backscattered electrons are commonly used for imaging: the first ones are used to detect the sample surface morphology, on the other hand backscattered are used to investigate different chemical compositions such as in different phases.

The SEM is critical in all fields that require characterization of solid materials, also because most applications require minimal sample preparation.

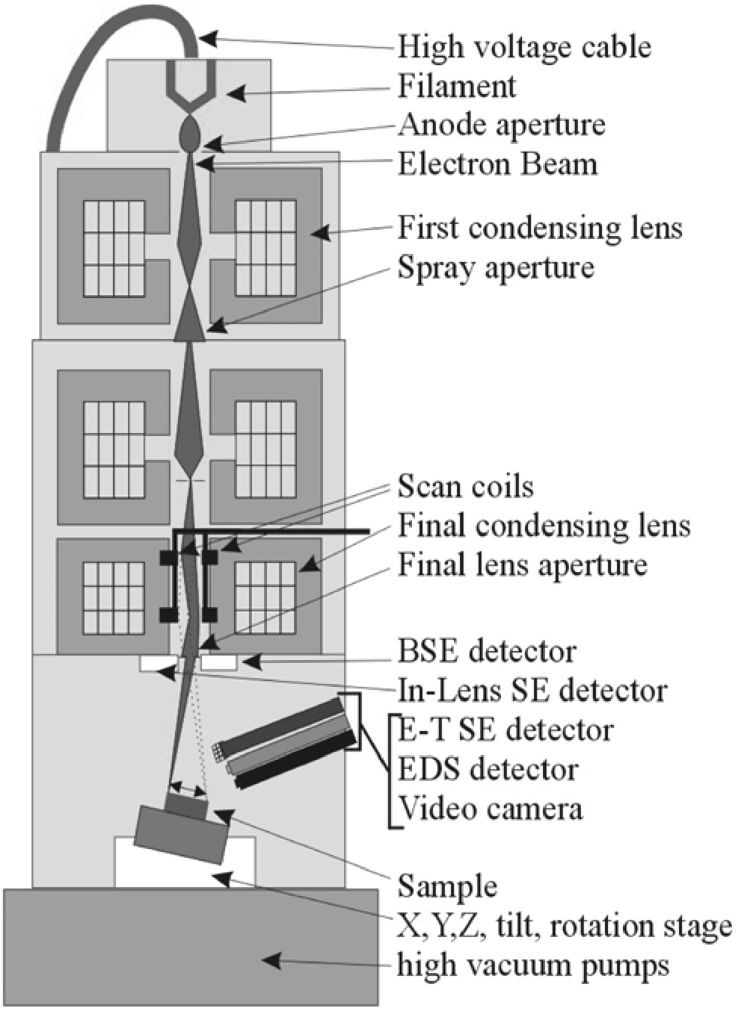

Fig A.15 Schematic illustration of a Scanning electron Microscope. (22)

The SEM consists of a column which houses the filament (which is the electron source), electromagnetic lens, and the beam scanning coils. At the base of the column is the sample chamber, which is linked to the vacuum pumps, that contains the stage and detectors. A portion of each signal travels in a direction such that it enters a detector as shown in fig A.15.

The EDS analysis, Energy Dispersive X-ray Spectrometry, uses of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied (24).

This technique can be combined with the SEM (equipped with an X-ray detector) to obtain a clearer view on the different phases present in the samples, thus recognizing the chemical elements contained. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$), as it was in our case. Qualitative analysis involves the identification of the lines in the spectrum, this kind of spectra can be obtained quickly. Quantitative analysis entails measuring line intensities of the spectra for each element in the sample and for the same elements in calibration Standards of known composition.

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