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Natural Polymers and Additives in Commodity and Specialty Applications: A Challenge for the Chemistry of Future

Mario Malinconico, Pierfrancesco Cerruti, Gabriella Santagata, Barbara Immirzi*

Summary: Polymers which are biodegradable in vivo and in the environment, especially those of natural origin, are perceived by the public as a valuable alternative to non biodegradable plastics. However, biodegradability, although important, cannot be the only driving force for the market acceptance of so called "green" plastics and chemicals. The applications of traditional oil-based plastics and plastic additives span from commodities to specialties, due to their performances and sometimes affordable costs. Can naturally derived polymers and additives face the challenge of petro-plastics and chemicals? Can we use the experience acquired in the so-called "plastic age" to tailor the performances of natural polymers and polymer additives for a demanding technological world? Several experiences on the processing of natural biodegradable polymers and on their formulation with additives coming from natural sources to obtain modified plastics, blends or composites are reviewed.

Keywords: biodegradable polymers; natural additives; poly(3-hydroxybutyrate); rheology; thermal properties

Introduction

For more than fifty years, plastic polymers have been the most practical and economical solution for packaging applications, replacing more traditional materials such as paper, glass and metals in many packaging applications, due to their low cost, low density, resistance to corrosion, ready availability; excellent optical, mechanical, and barrier properties, heat sealability, resistance against water and grease and ease of processing. In fact, packaging accounts for approximately 40% of all plastic consumption.

However, nowadays the biggest environmental problem around plastics is their low recycling percentage. Whereas metal is recycled for 35%, paper for 30% and glass for 18%, plastic only reaches 3–4%. In the case of plastics the other options are energy recovery and landfill disposal, and in the specific case of Europe it can be said that around 50% plastics is not recycled, hence not valorised. These percentages acquire a scaring dimension if transformed into tonnes of materials. In Europe, consumption of thermoplastics reached nearly 40 million tonnes in 2006. Of these quantities the 27,4% was used in rigid packaging and the 20,7% in flexible packaging. Globally, in recent years thin wall packaging (TWP) has become an increasingly well delineated sub-segment of the rigid plastics market in Europe, which accounts for over 2.5 million tonnes of thermoplastics. So, environmentalists have urged replacement of plastics with materials from renewable resources, because plastic films are neither totally recyclable nor biodegradable and may cause serious environmental and waste disposal problems. Although high development costs and lack of available alternative

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Institute on Polymer Chemistry and Technology, ICTP-CNR, Via Campi Flegrei, 34–80078 Pozzuoli, Naples, Italy
E-mail: Mario.malinconico@ictp.cnr.it

products limited progress in this direction, recent explosions in prices of petroleum products have brought this problem to the forefront again, emphasizing the limited nature of the crude oil resources and providing compelling economic incentive for the exploration of renewable alternatives based on bioplastics. In consequence, the plastics industry is putting more and more emphasis on the use of renewable raw materials.[1]

For biodegradable resins to compete with non-biodegradable synthetics, the critical mechanical, optical, and/or barrier properties for the intended application must be matched. This is especially difficult in the case of moisture barrier properties, because no biodegradable polymer approaches the hydrophobic character of synthetic polymers such as LDPE. Because of their inherent hydrophilic nature, biodegradable polymers are usually poor moisture barriers (high Water Vapour Permeability WVP). They are, however, naturally good oxygen barriers at low Relative Humidity (RH), but oxygen permeabilities increase exponentially as RH increases. Addition of micro- and nanofillers are considered in order to increase barrier properties.

Nonetheless, development of economically viable biodegradable polymers for packaging, requires the use of conventional synthetic polymer packaging conversion technology.

Non-edible, polymeric materials available for bioplastics formulation include certain cellulose-based products (e.g., cellophane), microbial polyesters (e.g., polyhydroxybutyrate/valerate copolymers produced by bacteria), biodegradable synthetic polymers (e.g., polylactic acid produced from lactic acid fermentation) and combinations of starch with biodegradable synthetic polymers (e.g. Mater Bi). Natural polymers or polymers derived from natural monomers offer the greatest opportunities, since their biodegradability and environmental compatibility are assured. In the present paper, starting from a literature analysis of recent advancements in the field of polymers and additives for sustainable plastics technology, some examples coming from our experiences will be outlined.

State-of-the Art of Packaging and Biopolymers

Considering the different options for packaging, these are the most representative in the market:

- **Paper or pulp-based materials**, ranging from wrapping paper, cartons boxes, disposable cups and plates, bags and envelopes to corrugated cardboard used both for primary and secondary packaging;
- **Glass**, is by weight the most common form of packaging waste, making up to 6% of the total weight of the household bin. Glass fights for increase sales in front of plastics. Glass is inert, there is no migration of components to the food and there are no alterations of taste caused by these substances, it is a perfect barrier to atmospheric oxygen, avoiding rancidness and changes of colour, but however can break. The small splinters being undetected present a great hazard to consumers and the industry spends great efforts to avoid any fragmentation.
- **Plastic materials** (mainly commodity resins such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephtalate (PET) and polyvinyl chloride (PVC) have gained ground because of their lighter weight, for being unbreakable and requiring less energy in production. Developments of multi-layer systems, i.e. PET with polyethylene-*co*-vinyl alcohol (EVOH) barrier are used as gas barrier in food packaging in order to avoid oxygen entering into the packaging and to avoid modified atmosphere to leave outside.
- **Metallic cans** are widely used for packaging of pasteurized and sterilized food. Aluminum is most commonly used as material for beverage cans, foils and laminates and its recycling rate is

high as aluminum has a strong scrap metal value. Steel is widely used for packaging of food, beverages and industrial goods such as paints and aerosols. The implementation of the Packaging Regulations has increased recycling as all steel packaging, such products as steel drums and bale wire are now subject to recycling. They present corrosion with acidic media. Metal ion release was drastically reduced by internal coating of the cans with layers of varnish. The wrong varnish can also create a high level of bisphenol A diglycidyl ether (BADGE) leakage.

Despite of their origin, bio-based polymers are not necessarily always biodegradable, whereas biodegradability[2] and compostability[3] are properties caused by the special molecular structure of such polymer materials, and do not depend on the raw material source. In this respect, it is emphasized that this functionality comply with the EU norm EN 13432, as clearly defined in the "basics" of the Industry Self commitment for biodegradable and compostable polymer products" from 2004, officially acknowledged by Directorate General Enterprise and Industry of the EU-Commission. To date, significant technological development has been achieved to produce biodegradable materials for packaging applications with comparable functionalities to those of traditional oil-based plastic packaging.

▶Biodegradable packaging decomposes in 2 years. Traditional non-biodegradable packaging takes more than 200 years to return to the earth and creates harmful greenhouse gases when burned.[4] The requirement of full compostability in 90 days must be fulfilled (EN 13432). This norm is used by the European Bioplastics Association to approve plastic products if the marketer advertises the product to be "compostable" or "biodegradable". Last but not least, only 45% comes from renewable sources, while 55% are still petrochemicals. Composting could produce humus in arid-zones as an additional advantage as fertiliser and substrate in soil. Opening up these composting systems for biopackaging, is another way of closing the loop for these innovative packaging solutions. In addition, composting systems are economically very competitive compared with incineration.

Rising to this challenge, several research groups as well as industrial companies worldwide are now developing new eco-friendly packaging solutions to exploit the 'ecological' advantages of biopolymers in applications such as food packaging. The past decade has seen rapid growth of new materials from renewable resources. Biopolymers directly extracted from biomass (e.g. proteins, polysaccharides, lipids) or from microorganisms (e.g. polyhydroxyalkanoates), as well as some produced by classical chemical synthesis, e.g. polylactic acid (PLA), have been used to develop new structures for biomedical applications such as tissue engineering and organ regeneration.[5] Development of food packaging applications from biopolymers has lagged behind medical materials due to high cost, low strength, and poor water resistance.

▶ Starch-Based Polymers. Starch is an abundant, inexpensive, renewable, and fully biodegradable natural raw material. However, the hydrophilic character of starch leads to poor adhesion with the hydrophobic polymer in starch-polymer blends. In spite of its relative weakness and melting point at about 60 °C, that is too low for many applications, starch is the most commonly used and lowest-costing ingredient of all biodegradable polymers. The starch can be derived from corn, potatoes, and rice. According to the manufacture methods there are:

- Surface-Modified Starch Additive: Starch is treated with a small amount of an unsaturated fat or a fatty acid oxidizing agent, such as vegetable oil.
- Gelatinized Starch Additive: Gelatinized starch is used in films of polyethylene-*co*-acrylic acid (EAA) and in a

mixture of EAA and low density polyethylene.

- Thermoplastic Starch Materials: They contain 70–100 percent starch as the base for the polymer. They have great water-solubility and are very easily consumed by microorganisms. They are indicated for mulch films, bags for animal feed and fertilizer, and products that will end up in water.

Recent innovations in the field of biodegradable plastics are:

- Amcor, together with Plantic Technologies develop a biodegradable, flexible plastic packaging for confectionery.
- NatureWorks, a Cargill daughter released a polymer from corn starch, the polylactic acid.
- Danisco has produced a biodegradable plasticiser from hardened castor oil and acetic acid.
- Stanelco markets a natural, biodegradable food packaging material based on starch.
- BASF launched Ecovio plastic, a biodegradable plastic made up of 45% PLA from NatureWorks together with biodegradable plastic Ecoflex to make carrier bags, compostable can liners, mulch film, food wrapping, and for other applications.
- Companies have been using PLA plastics as packaging for foods like organic milk in US, such as Naturally Iowa. Retailers like Delhaize in Belgium and Auchan in France have also been testing PLA for various food packaging.
- Introduction of biodegradable packaging in supermarkets: searching for alternatives to petroleum-based packaging. Supermarket chains Sainsbury from UK and Delhaize from Belgium move its private label products to biodegradable packaging in an effort to reduce rubbish collected for landfill.
- Onwulata and Seiichiro Isobe[6] combined whey protein isolate (a byproduct of cheese production), cornstarch, glycerol, cellulose fiber, acetic acid and the milk protein casein, creating a biodegradable plastic product that can be mixed with polyethylene.
- Novamont, Italy, is closing the loop to all-renewable starch based formulations by a biorefinery approach to the synthesis of aliphatic polyester components in their formulation. So far, the polyester combined to the gelatinized starch was of fossil origin, while recently they have started to obtain it from crop oils, transesterified and functionalized in order to make them suitable for melt processing. A production capacity of 60.000 tons is being reached.

Nowadays, several companies such as Novamont, Biomer, Metabolix, Cereplast, NatureWorks, Plantic, etc. offer biopolymers in their portfolio, especially polylactides and starch-based. Although there are many possibilities to use biopolymers, polylactic acid and starch are the most used ones. Studies with other biopolymers have been carried out, but the possibilities of these polymers are not exploited at commercial level enough.

▶ In general terms biopolymers are either strongly plasticized by moisture sorption or have, like PLA, medium barrier properties to gases, vapours and hydrocarbons. In this context, functional nanoadditives with tailor-made and harmless modifications can have a significant potential to enhance mechanical and barrier properties.[7,8] Nanoclays as montmorillonite or hectorite are classically used to improve strength and stiffness of biodegradable polymers, and to reduce their gas/water vapour permeability.[9] Rare works can be found on the incorporation of carbon nanotubes (CNT) into a biodegradable matrix and none reports the use of such compounds for sensing (i.e. humidity sensing).

State-of-the Art of Agri-Food Processed Bio-Waste

At present, drying of food waste after processing represents the most known approach to produce fertilizers. By means of modern biotechnologies, it is possible to manipulate these residues to convert them in potential resource with high added-value. The improvement of chemical, physical and organoleptic properties of final products and the reduced amount of effluents have a positive effect on economic and environmental aspects.

Among several biotechnological products, polysaccharides are of considerable interest, since, regardless their concentration, they are fundamental as gelling agents used to thicken and stabilize liquid solutions, emulsions, and suspensions. For example, from tomato processing waste (Italy being one of the major European manufacturer), it is possible to recover up to 20 wt.% of polysaccharides with noticeable filming and gelling properties.

The biopolymers present in some by-products of agri-food processes show the ability to interact with other polymers such as proteins, lipids, and polysaccharides as well as modifying their characteristics. More specifically the electric charges, the linear or branched structure, the presence of non-carbohydrate substituents influence the chemical and physical properties of polysaccharides and their interactions with other biopolymers.

Most of polysaccharides come from plant membranes, determining the rheological behaviour of fruit and vegetables juice and puree. This effect is very important in order to characterize and standardize the final product, and also to optimize the technological parameters, since they are strictly related to the fluid-dynamic features of products to be processed, that can vary during the transformation procedure. Rheological properties can be affected by the pectin content, by their polymerization and esterification degree, by their cellulose, hemicellulose and oligosaccharides content, which contribute all together in determining the consistency, viscosity and branching level of the material.

Some factors influencing the final results, other conditions being equal (cultivation, maturation and so on) are calcium ion concentration, the thermal treatment, the pH value, the molecular weight and the degree of esterification of pectin substances of fruit texture. The addition of calcium increases the consistency because it reduces the effect of structural and physiological disorder caused by operations applied for conversion of fresh food into preserved food. From a chemical point of view, the reduction of structural disorder due to the presence of calcium has been explained as a consequence of association of low esterified pectin with calcium ions, forming contact zones able to create highly branched polymers. Thus the final product shows higher viscosity.

State-of-the Art of Nanoparticles in Packaging

Modern packaging protects food, increasing shelf life and safety. It also makes distribution possible over long distances. Its closures are made to avoid any undesired alterations after production. Foodstuffs of animal and plant origin may present intrinsic hazards due to contamination by micro-organisms. Microbiological contamination refers to the presence of one or more various bacteria, yeasts, mould, fungi, protozoa or their toxins and by-products, which could adversely affect the product or consumer's health and safety. A well-known example of a microorganism that can be dangerous is salmonella. When food is contaminated with salmonella or other dangerous micro-organisms, it poses a risk to human health. The most common methods used either to kill or to reduce the growth of microorganisms are the application of heat, the removal of water, the lowering of temperature during storage, the reduction of pH, the control of oxygen and carbon dioxide concentrations, and the removal of the nutrients needed for growth. The use of chemicals as preservatives is strictly regulated by governmental agencies such as the Food and Drug Administration (FDA) in the US.

Nanoparticles can be used as drug carriers in order to promote the compatibility of antimicrobials with the plastic material. This approach is inspired by new nanotechnologies used to obtain reinforced polymers which have received much attention in both scientific and industrial areas, due to their enhanced mechanical and barrier properties as well as flame resistance. Organoclays are normally obtained by replacement of the inorganic exchange cations in the galleries of the native silicate clay by alkylammonium surfactants, which favour the compatibility between the surface chemistry of the clay and the hydrophobic polymer matrix. This replacement expands the clay galleries facilitating the penetration of the antimicrobial and then its dispersion through the polymer matrix during the melt extrusion. Moreover, the lamellar structure could protect the active molecules from degradation. Small amounts of nanosized filler (max 5 wt.%) are sufficient to increase materials properties and guarantee antimicrobials activation.

The most common and used nanoparticles are lamellar silicates, however, nanofillers with different aspect ratios are now commercially available, nanosized in either three dimensions (particles: silica, polyhedralsilsesquioxanes (POSS), etc.), two dimensions (tubes, e.g. carbon nanotubes and nanofibres, needle-like clays, wiskers, etc.), or one dimension (lamellar inorganics: phyllosilicates/clays, hydrotalcites, phosphates, etc.).

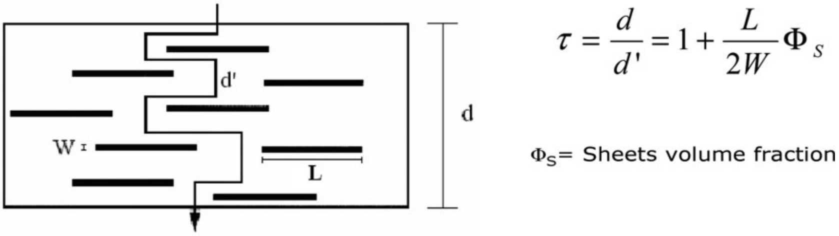
Layered clay type silicates are among the most useful nanoparticles in packaging. The most commonly used lamellar silicate are in the group of aluminosilicate partially substituted by Mg or Li (phyllosilicates) including the well-known montmorillonite. The influence of layered nanoparticles on gas and liquid permeability is considered especially convenient for reducing water vapour permeability and oxygen transfer. At a molecular level the diffusion path length is increased by filler non-permeable sheets that maximise path tortuousness (τ) as seen in the following Scheme 1.[10]

Besides, these materials commonly called nanoclays offer additional benefits. Typical improvements obtained by adding low amounts of nanofiller to a polymer matrix are the following:

- Reduced Gas Permeability (lamellar nanocomposites)
- Modified Thermal Degradation
- Preserved Optical Transparency
- Increased Elastic Modulus
- Condensed Phase Catalysis
- Increased Solvent Resistance

Moreover, they can incorporate the appropriate chemical modifications and provide "planar platelets" to aid in the formation of a continuous exterior layer with bacteriostatic effect at the plastic surface.

However, it is necessary to achieve a good dispersion level of the nanoclay into the polymer to behave as a nanocomposite. So far, many methods are used to obtain a good dispersion of the inorganic compound into the polymer.[11–14] In the melt-compounding method, polymer nanocomposites can be prepared by conventional compounding techniques (twin-screw extruder and melt compounder). If the compatibility between the polymer chains and the organic modification of the



Scheme 1.
Increased diffusion path length by the presence of oriented sheets (nanofiller).

nanoparticles is sufficiently high, polymer chains penetrate into the galleries of the layered minerals, and intercalation or exfoliation of the layered clay can occur. The solution-blending method consists in dissolving the polymer and the organically modified clay in a common solvent and subsequent removing of the solvent.

Case Study: The Effect of Pomace Extract on Thermal and Processing Stability of Poly(3-Hydroxybutyrate)

PHB belongs to the family of polyhydroxyalkanoates (PHAs), which are biodegradable polyesters synthesized by several bacterial strains as carbon and energy reserve.[15] PHB is a biodegradable, hydrophobic thermoplastic polyester, with a crystalline fraction of about 50%[16] melting and glass transition temperature around 170 and 5 °C, respectively.[17–19] PHBs have high molecular mass so that their physical properties are similar to those of synthetic commodity polymers such as PP.[20,21] Therefore, PHB has been extensively studied as an environmentally friendly polymeric material. Nevertheless, PHB shows poor mechanical performance[22] due to high brittleness and very close melting and degradation temperatures, which limit the PHB processing window. As a consequence, the processing parameters must be carefully optimized to minimize residence time in the manufacturing equipment.

To improve PHB properties, blending of PHB with high or low molecular weight components, such as suitable additives, represents a valuable approach to provide both an upgrading of processing and manufacturing performance, and a relative inexpensive strategy to enhance polymer physical properties.[23] It has been demonstrated that natural phenol-based compounds added to polymeric matrices can act as antioxidants, processing aids and plasticizers.[24–26] In particular, the addition of natural phenols to PHB can decreases the polymer melting temperatures, leading to an enlargement of the processing window.[27]

In the present research, a bio-waste of winery industry, the pomace extract (EP), was selected as a natural additive for poly(3-hydroxybutyrate) (PHB), with the aim of tailoring its properties in a totally bio-based system. The effect of EP on the polymer processability was evaluated by rheological measurements. PHB in a powder form was supplied by Biomer, Germany (code T3, $M_w = 840000$ Da). The grape-based additive, supplied by CTAEX (Spain), was obtained from a dried Cabernet pomace (about 4 wt.% residual water content) through hydroalcoholic extraction at room temperature using a 70:30 (v/v) ethanol:water mixture as a solvent. The analysis of dry EP revealed that the content of total carbohydrates was 79.0 ± 4.2 wt.% and the total phenolic content (as quercetin) was found to be 4.3 ± 1.2 wt.%. The remaining fraction most likely contained simple carbohydrates and organic acids derived from tartrates and malates, typically present in grape pomace.

Lyophilized EP was dissolved in methanol, then PHB powder was added and the solvent evaporated. The resulting suspension was kept at 50 °C under stirring to allow solvent evaporation. Blends containing 5 and 15% of EP were prepared (PHB5 and PHB15, respectively).

Rheological properties of the PHB-based samples were measured using a rotational rheometer equipped with parallel-plates (20 mm diameter) in the dynamic flow field at 190 °C. By means of this method, it was possible to study the polymer stability upon time under severe thermal conditions, since the linear viscoelastic properties in dynamic experiments are sensitive to thermal degradation that leads to chain scission phenomena. The experimental procedure was based on a time sweep test, and the viscosity was evaluated as a function of time (Fig. 1).

From Fig. 1, it can be inferred that, due to the low average molecular weight of EP, in the early stage of the experiment, its viscosity values at 120 °C were significantly lower than those of PHB at 190 °C. Longer permanence at 120 °C caused the viscosity

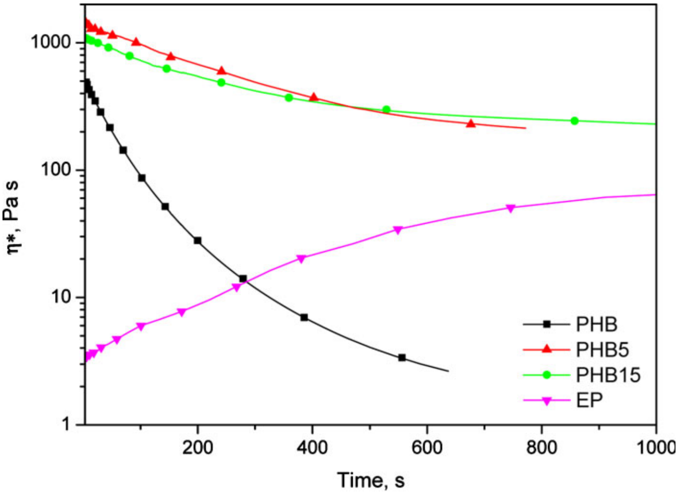


Figure 1.
Complex viscosity versus time at 1 rad s^{-1} for EP (at 120 °C) and PHB-based samples (at 190 °C).

to increase, probably due to the formation of a more tightened structure, maybe ascribed to condensation between hydroxyl groups of molecules present in EP.

The initial viscosity of neat PHB was lower than that of PHB5 and PHB15, probably due to the occurrence of polymer-additive interactions leading to more entangled melts. At longer times, the viscosity of pure PHB dropped down dramatically due to thermal degradation, while EP significantly improved the polymer stability over time. As a matter of fact, the viscosity of PHB and PHB5 measured respectively at 30s and 500s, had the same values.

It can be also noticed that the initial viscosity of PHB15 was slightly lower than that of PHB5, as a consequence of the higher content of EP in the blend. According to the above reported results, it can be claimed that EP has the potential to efficiently stabilize PHB against thermal degradation, thus allowing the polymer to prolong its permanence in processing equipments.

Steady shear viscosities as a function of shear rate for PHB, PHB5, PHB15 at 190 °C were also measured to evaluate the flow behaviour of the blends (Fig. 2).

All samples displayed a shear thinning behaviour attributed to the alignment or arrangement of chain segments of polymers in the direction of applied shear stress due to the gradual loosening of polymer intermolecular forces.[28] High viscosity at a low shear rate provides the integrity of the melt during extrusion, and the low viscosity at a high shear rate enables low injection pressure, and high speed, as well as reduced cycle times. It can be noted that the shear viscosity of PHB5 and PHB 15 was 2 orders of magnitude higher than that of pure PHB over the entire range of explored shear rates, suggesting the achievement of a higher flow consistency.

The weight average molecular weights (M_w) and polydispersity index (PI) of unprocessed PHB as well as of injection molded PHB, PHB5 and PHB15 have been evaluated by GPC. The results are listed in Table 1. According to GPC data, M_w of unprocessed PHB are significantly higher than those of the injection molded one, indicating that during processing the thermal degradation caused the molecular weight reduction. On the other hand, polymer chain scission was efficiently hindered by the pomace extract, being M_w of PHB5 and PHB15 greater than

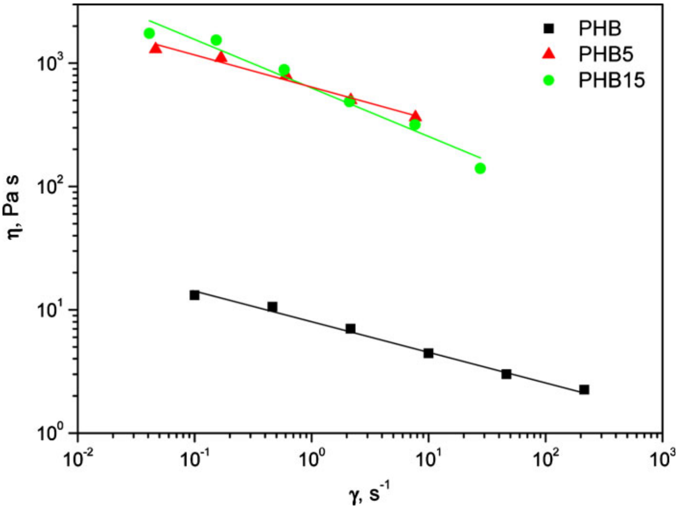


Figure 2.
Steady-state shear viscosities as a function of shear rate for PHB, PHB5, PHB15 at 190 °C.

those of the injection molded PHB. As expected, the extent of this stabilizing effect is related to the amount of additive used, as PHB15 exhibited a slight reduction of molecular weight with respect to the unprocessed virgin sample. These results confirm the outstanding efficiency of EP as thermal stabilizer, already evidenced by the rheological analysis.

Conclusion

The world of biodegradable polymers from renewable resources is still in a sort of infancy, when compared to the world of oil-based non biodegradable plastics. Biodegradation and compostability are for sure fundamental from the environmental perspective, but if they are going to conquer larger market shares and the favour of consumers, the challenge of functional properties and specialization has to be faced and, finally, a good cost/performance balance, not to remain a niche market.

In our research experience, we have been working, among many other biopolymers, on poly(3-hydroxybutyrate) (PHB), a bacterial polyester very promising for its intrinsic properties. The use of a pomace extract (EP) was found to be very effective to improve processability and thermal stability of this biopolymer.

It was observed that EP was able to reduce thermal degradation of PHB, as confirmed by GPC analysis, which demonstrated that the polymer maintained high molecular weight after injection molding. This experimental evidence was corroborated by the significantly slower decrease in viscosity over time observed by rheological tests. These findings entail that the additive provides the PHB with higher processing stability, thus allowing longer residence times in processing equipment. The observed effects were explained in terms of hydrogen bonding interactions occurring between the functional groups of PHB and EP. Overall, the reported results demonstrated the feasibility of the conversion of an agro-food by-product into a bio-resource, aimed at improving the features

Table 1.
M_w and polydispersity index of unprocessed PHB and injection molded PHB, PHB5 and PHB15.

Sample	M_w (Da)	PI
Unprocessed PHB	840 000	2.1
PHB	134 000	1.9
PHB5	540 000	3
PHB15	648 000	2.3

of natural polymers in an environmentally friendly and cost-effective way.

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[1] International Biodegradable Polymers Association & Working Groups: Bioplastics at the Leading Edge of Change. Renewable Raw Materials Make their Entry in the Plastics Industry. Jan 30, **2006**, http://www.ibaw.org.

[2] Biodegradation is a degradation caused by micro organisms (e.g. fungi, bacteria, algae). Final products are, like in natural processes, water, carbon dioxide or methane depending on the oxygen amount during the process.

[3] Compostability is a property of a material to be biodegraded under composting conditions.

[4] The Compost Bin:Natureworks biodegradable packaging. http://www.compost-bin.org. September 10, **2006**.

[5] A. Jaklenec, E. Wan, M. E. Murray, E. Mathiowitz, *Biomaterials* **2008**, *29*, 185.

[6] C. I. Onwulata, S. Isobe, *UJNR Food & Agricultural Panel Proceedings* **2006**, R7742–R71.

[7] P. Bordes, E. Pollet, L. Averous, *Prog. Polym. Sci.* **2009**, *34*, 125.

[8] M. Pluta, A. Caleski, M. Alexandre, M. A. Paul, P. Dubois, *J. Appl. Polym. Sci.* **2002**, 1497.

[9] O. Gain, E. Espuche, E. Pollet, M. Alexandre, P. Dubois, *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 205.

[10] L. E. Nielsen, *J. Macromol. Sci. Chem.* **1967**, *A1*, 929.

[11] *Polymer-Clay Nanocomposites*, T. J., Pinnavaia, G. W. Beall, Eds., Wiley Series in Polymer Science, New York **2000**.

[12] M. Alexandre, P. Dubois, *Mater. Sci. Eng. Rep.* **2000**, *28*, 1.

[13] H. R. Oswald, R. Asper, in: "*Physics and Chemistry of Materials with Layered Structures*", R. M. A. Lieth, Ed., Reidel Publishing Co, Dordrecht **1977**, vol. 1.

[14] D. Kaempfer, R. Thomann, R. Mulhaupt, *Polymer* **2002**, *43*, 2909.

[15] C. S. K. Reddy, R. Ghai Rashmi, V. C. Kalia, *Bioresour. Technol.* **2003**, *87*, 137.

[16] J. Ivica, L. Igor, C. Ivan, *Polym. Degrad. Stabil.* **2002**, *77*, 35.

[17] S. Godbole, S. Gote, M. Latkar, T. Chakrabarti, *Bioresour. Technol.* **2003**, *86*, 33.

[18] E. R. Coats, F. J. Loge, M. P. Wolcott, K. Englund, A. G. McDonald, *Bioresour. Technol.* **2008**, *99*, 2680.

[19] M. Avella, M. E. Errico, *J. Appl. Polym. Sci.* **2000**, *77*, 232.

[20] L. L. Madison, G. W. Huisman, *Microbiol. Mol. Biol. Rev.* **1999**, *63*, 21.

[21] F. Tsuyoshi, S. Harumi, M. Rumi, J. M. Zhang, Y. X. Duan, N. Isao, O. Shukichi, O. Yukihiro, *Macromolecules* **2005**, *38*, 6445.

[22] M. Khanna, S. Srivastava, *Proc. Biochem.* **2005**, *40*, 607.

[23] L. Wang, W. Zhu, X. Wang, X. Chen, G.-Q. Chen, K. Xu, *J. Appl. Polym. Sci.* **2008**, *107*, 166.

[24] P. Iriondo, J. J. Iruin, M. J. Fernandez-Berridi, *Polymer*, **1995**, *36*, 3235.

[25] V. Ambrogi, P. Cerruti, C. Carfagna, M. Malinconico, V. Marturano, M. Perrotti, P. Persico, *Polym. Degrad. Stabil.* **2011**, *96*, 2152.

[26] P. Cerruti, G. Santagata, G. Gomez d'Ayala, V. Ambrogi, C. Carfagna, M. Malinconico, P. Persico, *Polym. Degrad. Stabil.* **2011**, *96*, 839.

[27] J. Li, T. Fukuoka, Y. He, H. Uyama, S. Kobayashi, Y. Inoue, *J. Appl. Polym. Sci.* **2005**, *97*, 2439.

[28] D. H. Chang, in: "*BTR heology and processing of polymeric materials*", Oxford University Press, New York **2007**, p.203.