Bioplastics: A Smart Approach to Waste Reduction

Andreas G. Andreopoulos, Chairman of Hellenic Solid Waste Management Association-HSWMA
24 Kaningos Str. 10682 Athens, GREECE
e-mail: andrea@central.ntua.gr

ABSTRACT

In this work, a review was made on the wide applications of plastic materials and the insights of the related market. It was recorded that due to their unique combination of properties, those materials are in extensive use and, therefore, the plastics industry shows a potential for growth, with appreciable volume of sales and job opportunities. However, the conventional plastics have been criticized for environmental problems both, during their synthesis, as well as during their life cycle and disposal. Bioplastics, a new generation of polymeric materials made of biomass or other alternative resources that guarantee degradability, might be a solution to the above issues arising for the use of plastics, allowing a spectacular and environmental friendly reduction of the waste stream that should, otherwise, be incinerated or disposed to landfills.

INTRODUCTION

Plastic materials

Plastics is a very important class of materials, with numerous market applications, due to their unique combination of properties, such as: ease of processing, light weight, chemical and corrosion resistance, good mechanical properties per weight, recyclability combined with low cost. In addition to the above, plastics are versatile and can easily incorporate reinforcing fillers to produce composites with ultra high strength and stiffness or other impressive properties.

As a result, these materials have become an essential part of our modern lifestyle. LCD flat screen televisions or touch-screen smartphones and tablets are some characteristic examples of today's applications. Plastics allowed us to practice most sports, since a wide range of equipment and outfits are made of plastics, including balls, boots, racquets, helmets, skis, surf boards, swimming or diving suits. In the medical, pharmaceutical and safety area, plastics are enabling major breakthroughs. The latest medical techniques use plastics as artificial implants as well as many pharmaceutical devices, such as controlled release systems are based on polymeric plastics. Their use in aerospace, renewable energy and military applications is also well known, with amazing achievements.

The Market

In 2012, the plastics industry including producers, converters and machinery accounted for an estimated 1.4 million jobs in the European Union’s (EU) 27 Member States and had a combined turnover of above 300 billion €. With more than 62,000 companies in operation in the EU, plastics not only enable modern lifestyles, but the material also contributes to research and innovation, to higher standards of living and to the overall welfare of the European citizens. In the second half of the 20 th century, plastics became one of the most universally-used and multi-purpose materials in the global economy. Today, plastics are utilised in more and more applications and they have become essential to our modern economy. The plastics industry has benefited from some decades of growth with an average yearly expansion of 8.7% from 1950 to 2012.

Although 2009 witnessed a fall in the number of employees as the industry as a whole faced the consequences of the global financial crisis, its labour force is now growing and approximately 30,000 new jobs have been created. These figures are another proof that the European plastics sector is slowly but steadily recovering.

More specifically, in terms of turnover the European plastics industry has not yet reached its pre-crisis levels and in 2012 sales volumes showed a slight decrease for both sectors: plastics producers experienced a turnover of 87 billion € and converters achieved 202 billion € in sales.

The relatively modest growth in 2012 compared to2011 is mainly due to the continuing recession in Southern European countries as well as significant declines in manufacturing production which lead toa 0.3% contraction in terms of GDP in the Europeaneconomy. Moreover, competition in the industry is constantly growing and plastics markets are increasingly shifting towards Asia and specially China.

Plastics provide for a wide variety of markets, as shown below (data published by PlasticsEurope (PEMRG) / Consultic / ECEBD for EU-27+N/CH)

- Packaging applications are the largest sector representing 39.4% of the total plastics demand.
- Building and construction is the second largest sector with 20.3%
- Automotive is the third largest sector with a share of 8.2%,

followed by:

- Electrical and electronic applications with a 5.5%
- Agricultural applications which have a share of 4.2%.
- Other application sectors, such as appliances, household and consumer products, furniture and medical products comprise a total of 22.4%.

Environmental Problems of Plastics

Plastics are not considered as toxic, but they have been accused for the possibility to contain residual monomers, polymerisation chemicals, degradation products or additives with toxic properties. On the other hand, it is believed that hazardous substances and degradation products, may be released during the life cycle of a plastic product. In addition, it is well known that several of the chemicals used to produce plastics are considered hazardous. Typical example of the above category was a wide application commodity plastic, namely poly (vinyl chloride) (PVC). It is well known that the monomer (vinyl chloride-VCM) used for synthesis of the above [polymeric material is a recognized carcinogen and its emission to air must be carefully controlled as well as its concentration into the PVC granules (where it can be trapped as residual monomer) has to be below ppm. In addition, additives used for compounding of PVC contained toxic metals, such as lead or cadmium, or plasticizers based on phthalic acid esters etc. Finally, the incineration of PVC wastes could produce dioxin or other hazardous compounds.

The management of plastic waste and especially disposal in landfills is another major issue of criticism. In fact, moving towards a “zero waste society”, it is unacceptable to dispose plastic materials in landfills, taking into account their increased endurance against corrosive and environmental attack.

The Response of Plastics Industry

The response of the industry in the case of PVC, is a characteristic example of the the attempts to satisfy sustainability specifications and to conform with the safety ang hygiene standards. In fact, VinylPlus, the European PVC industry voluntary commitment to sustainable development, is said to have spent about 7 million € in 2012 for compliance to sustainability specifications. Specific targets of the above are: controlled loop management, organochlorine emissions, sustainable use of additives and sustainable energy and climate stability. Also, an ad hoc Task Force on Sustainability Footprinting was set up in 2012, with initial focus to develop a Product Environmental Footprint (PEF) to be extended into a Sustainable Product Footprint at a second stage. On the other hand, the Renewable Raw Materials Task Force, established in December 2011, is focusing its work on investigating renewable resources, alternative to oil, for the production of PVC. In 2012, the Task Force screened potential alternative renewable resources, including plant-based sugars and Starches. In addition to the above, PVC resin manufacturers have signed 5ndustry charters for the production of PVC by the suspension (VCM & S-PVC Charter) and emulsion (E-PVC Charter) processes, aimed at reducing their environmental impact in the production phase.

A new verification took place at the beginning of 2012. The results showed:

- 96% full compliance,
- 1% partial compliance
- 1% non compliance
- 2% of all applications of standards could not be verified.

Safe Transport, i.e. without VCM leakages etc is also within the scope of this attempt.

Regarding the management of plastic waste and especially their disposal in landfills, it can be seen that a constant improvement is established for the products at the end of their service life and fewer of them are ending up in landfills.

There is a positive trend to be observed in the recovery and recycling of plastics in the EU-27. In 2011, 59.6% of plastics were recovered, while in 2012 this increased to 61.9%. Thus, total recovery increased by 4% and this growth shows a continuously strong trend. At the same time, there was a reduction of 5.5% of landfilled plastics, which also shows a general positive development. Collection for mechanical recycling shows a growth of 4.7%, while feedstock recycling even on a lower level of

86 thousand tonnes increased by 19.4%. Energy recovery also increased by 3.3%.

Since 2009, the total amount of post-consumer plastics waste has been increasing in Europe but since 2011 it has remained at more or less the same level with 25.2 million tonnes generated in 2012. More than three quarters (77%) of this waste was generated in the following seven countries: Germany, UK, France, Italy, Spain, Poland, and the Netherlands while the rest originated from the remaining 22 countries.

Packaging dominates the waste generated from plastics, covering 62.2% of the total. Other applications like building and construction, electrical and electronic products and agriculture count for 5 till 6% each.

The largest share of recycled plastics, at about 82%, are plastics packaging products. The overall recovery rate of plastics packaging waste was 9.2%, meaning an increase of 3.3% from 2011. In total, 34.2% of packaging waste was mechanically recycled in Europe, 0.5% went to feedstock recycling and 34.5% went for energy recovery (5.4 million tonnes) both in incineration plants and as refuse derived fuel (RDF). It is encouraging that nearly all Member States have reached the 22.5% target set by the European Packaging Directive in 2012.

Some EU Member States such as Germany, Austria, Luxembourg, Belgium, Sweden, Denmark and the Netherlands but also Norway and Switzerland have achieved between 90% and 100% plastics waste recovery rates.

This was achieved, among other methods, by imposing a ban on landfilling plastics

recovery waste and should serve as an example of best-practice. By comparison, Malta, Cyprus, Greece Bulgaria, Lithuania and Latvia all show recovery rates below 30% and these EU Member States usually have little or no capacity for energy recovery, which sets them at a disadvantage.

In 2012, about 26% of total post-consumer plastics waste was collected for mechanical recycling, 0.3% went to feedstock recycling, and 35.6% was recovered

for energy. Amongst the European countries, Norway had the highest level of collection for mechanical recycling at 36.9% and Malta the lowest with 12.4%. Energy recovery data includes both plastics waste in municipal waste incineration plants and waste used as refuse derived fuel (RDF) material. In Switzerland, Luxembourg and Austria the overall energy recovery ratio reached more than 70%, which is the highest level in Europe. However, energy recovery is non-existent in Malta, Lithuania and Cyprus, while in Greece, Latvia, the UK and Bulgaria the energy recovery ratio is still below 10%. Another 11 countries have lower energy recovery rates than the average of 36%.

Overall, the trend in the last five years shows a significant decrease in landfilled plastics. However, with the disposal rate at 38.1%, there is room for improvement and further action is needed to reach a zero plastics waste to landfills by 2020 in Europe.

Turning waste into a resource is a goal the European plastics industry is committed to achieve to improve Europe's resource efficiency. This goal is impossible to achieve with 38% of plastics waste still going to landfill.

As such, landfill is a major hurdle that must be eliminated for such an ambitious goal to be reached. Recycling and energy recovery are both complementary and necessary to achieve the zero plastics to landfill by 2020 goal.

Since recycling may not always be the most sustainable option for plastics, energy recovery should remain a viable option to realise the full potential of the diverted waste which to generate electricity and heat. Therefore, the industry is calling for measures to avoid the landfilling of recyclable and high calorific waste.

RESULTS AND DISCUSSION

New Technologies for the Elimination of Waste from Plastic Products

The management of plastic waste is undoubtedly critical for their use, due to the increased consumption capacities and has grown in importance at a fast rate during the last years. In the framework of a strategy based on a) prevention and reduction of waste, b) increase of recycling and reuse and c) safe disposal of unavoidable waste, the research and development activities have focussed on the production of degradable polymers. These materials can decompose after disposal due to the combined action of UV radiation and atmospheric oxygen. In the same category can be classified biodegradable plastics, based on macromolecules with chemical structure that enables degradation by microorganisms or enzymes. Composite materials consisting of a polymeric matrix and a dispersed phase (e.g. starch) are considered as part of this class. Another approach to biodegradability is the growth of micro-organisms specified for degradation of commodity plastics.

In general, polymers susceptible to biodegradation are aliphatic polyesters, polyether sans polyamides. The side groups and substitution on their macromolecular chain may inhibit the action of enzymes. Also, crystallinity and cross-links restrict enzymes as they are suitable for a specific reaction in a given bond of a chemical structure. Finally, the presence of aromatic rings inhibits the attack by micro-organisms.

Synthesis, characterization and property testing of aliphatic polyesters showing biodegradability, has been the focus of many researches so far. Most interestingly, copolymers of lactic acid with various aromatic hydroxyl acids were synthesized by simple polycondensation and their in vitro degradability was studied. Also, homopolymers deriving from the same monomer have been extensively studied. More specifically, due to its biodegradable character, poly(lactic acid) (PLA) became a material of scientific, technical and commercial interest. It works well in many biomedical applications and also has potential use in environmentally friendly packaging. In recent years, due to the increasing demand for this kind of polymers (i.e. biodegradable polyesters with acceptable mechanical properties), much attention has been devoted to the study of their synthesis, morphology, thermal and mechanical behaviour, swelling and degradation mechanisms, both under in vivo and in vitro conditions.

It is well known that two different enantiomeric forms, D- and L-lactic acid can be found, being the starting materials for two different corresponding enantiomeric polymers, as a consequence of the maintenance of the chiral centre. While the D,L polymers are fully amorphous, because of the syndiotacticity and/or atacticity of methyl groups, PLLA can crystallize since it shows an isotactic conformation.

PLA shows good mechanical strength, thermal plasticity, fabricability and can undergo chain scission into the human body to give oligomers and finally monomeric units of lactic acid, which are fully resorbable as a natural intermediate in carbohydrate metabolism. In particular, the L-isomer as a biological metabolite of the human body.

As far as synthesis of PLA is concerned, the following two methods are currently available: direct polycondensation of lactic acid and ring-opening polymerization of lactide, i.e. the cyclic dimmer of lactic acid. Synthesis of PLA through condensation of the lactic acid monomer was reported to give weight average molecular weight (M_w) lower than $1.6x10^4$. However, Ajioka et al. have reported that products with much higher molecular weights can be synthesized by one step condensation, provided that appropriate azeotropic solvents are employed. Akutsu et al. investigated the direct polycondensation of lactic acid using various condensation procedures and found that successful polymerization leading to products of M_n equal to 15400 with yield of 89%, was achieved when the system N,N-dicyclohexylcarbodiimide/4-dimethylaminopyridine in dichloromethane was used at room temperature for 24h. It should be emphasized that the molecular weight of PLA is of critical importance for the type of biomedical application. In fact, construction of screws and plates for use as orthopedic implants needs tough material with high Young's modulus and, therefore, the molecular weight must be in the area of several hundreds of thousand. On the other hand, the preparation of slabs for use in controlled release requires fast biodegradation characteristics, low melting point for ease of the drug incorporation while mechanical strength is not of prime importance. In that latter case, molecular weights in the area of $2\text{-}3x10^3$ appeared most suitable for the application.

The established route for the production of high molecular weight PLA is ring-opening bulk polymerization of lactide. Various metallic, organometallic, inorganic and organic compounds of zinc and tin have been used as catalysts. Tetraphenyl tin, stannous chloride and stannous octoate have found to be the most effective. Among them, a preferred initiator is stannous octoate because of its acceptance by the FDA as a food additive. It is evident that even traces from the above catalysts must be removed if the polymers are to be used for medical applications.

Although only few reports have been published on the polymerization of lactides and lactic acids, it seems that industrial companies have accumulated a large amount of data on this topic. Cargill Dow LLC has developed a patented, low-cost continuous process for the production of lactic acid based polymers followes a solvent free process and a novel distillation technique to produce a range of PLA polymers. The process combines the substantial environmental and economic benefits of synthesizing both lactide and PLA in the melt rather in solution, and for the first time, provides a commercially viable biodegradable commodity polymer made from renewable resources. The process starts with a continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA pre-polymer. Next, the pre-polymer is converted into a mixture of lactide stereoisomers using tin catalysis to enhance the rate and selectivity of the intramolecular cyclization reaction. The molten lactide mixture is then purified by vacuum distillation. Finally, PLA high molecular-weight polymer is produced using tin-catalyzed, ring-opening lactide polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvents.

Furthermore, Mitsui Toatsu company utilizes a solvent based process, in which a variety of polymers with different molecular weight can be produced by direct condensation using azeotropic distillation with suitable solvent to remove continuously the water deriving from the reaction

Enzymatic polymerization emerges as one of the most viable alternatives to avoid toxic catalysts. Enzymatic synthesis is an environmentally bening method that can be carried out under mild conditions and can provide adequate control of the polymerization process. The reaction temperature and water content on the stability of enzyme were studied. Specifically, the recovery of PLA after the reaction, the interaction of lipase with the solvent, and the potential mistakes in measurement of the conversion by titration were explored.

PLA is a sustainable alternative to petrochemical-derived product, since the lactides from which it is ultimately produced can be on a mass scale by the microbial fermentation of agricultural by-products mainly carbohydrate rich substances.

Some agricultural byproducts which are potential substrates for lactic acid production are corn starch, lignocellulose/hemicellulose hydrolyzates, cotton seed hulls, Jerusalem artichokes, corn cob, corn stalks, beet molasses wheat bran, rye flour, sweet sorghum etc.

One of the most positive points of PLA production in comparison with other hydrocarbon-based polymers is the decrease of carbon dioxid (CO_2)emission, being undoubtedly a highly important contributor to global climate change and its warming. Because carbon dioxide is absorbed from air when corn is grown, use of PLA has the potential to emit fewer greenhouse gases compared to competitive hydrocarbon-based polymers. “Net” or “residual” emissions are calculated as total emissions from the cradle to the factory gate minus carbon dioxide uptake that occurs during corn production. This amount is negative from present PLA production. It means the total CO_2 consumption from the cradle to factory is more than its emission to the environment.

CONCLUSIONS

The broader class of bioplastics is expected to show over 40% yearly growth in the five-year period ending 2015. In the years 2000 to 2008, worldwide consumption of biodegradable plastics based on starch, sugar, and cellulose – so far the three most important raw materials – has increased by 600%. Because of the fragmentation in the market and ambiguous definitions it is difficult to describe the total market size for bioplastics, but estimates put their usage in the US at about 572,000 in 2010, and almost 1,460,000 in the EU. It should be noted that global consumption of all flexible packaging is estimated at around 12.3 million tonnes, which means that a huge market has already been created, capable of absorbing the new products as substitutes of the existing.

COPA (Committee of Agricultural Organisation in the European Union) and COGEGA (General Committee for the Agricultural Cooperation in the European Union) have made the following assessment of the potential of bioplastics in different sectors of the European economy:

Catering products: 450,000 tonnes per year
Organic waste bags: 100,000 tonnes per year
Biodegradable mulch foils: 130,000 tonnes per year
Biodegradable foils for diapers 80,000 tonnes per year
Diapers, 100% biodegradable: 240,000 tonnes per year
Foil packaging: 400,000 tonnes per year
Vegetable packaging: 400,000 tonnes per year
Tyre components: 200,000 tonnes per year
Total: 2,000,000 tonnes per year

BCC Research forecasts the global market for biodegradable polymers to grow at a high rate during the next years, since new areas of resources and available techniques are now being explored. These research and development trends, together with the social pressure for cleaner environment, will undoubtedly be a strong levering for the further growth of bioplastics.

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