

# Using milk industry waste in production of biodegradable polymers

Sławomir MAŚLANKA, Maria SIOŁEK, Łukasz HAMRYSZAK, Dawid ŁOPOT – Glokor Sp. z o.o., Gliwice, Poland

Please cite as: CHEMIK 2014, **68**, 7, 600–611

## Introduction

Innovative technologies aiming at reusing onerous waste products are playing more and more pronounced role in modern-day global economy. One of such onerous products is whey, with annual production in Poland reaching 2–3 Mio. m<sup>3</sup>. Whey makes ca. 65–90% of the waste from production of cheese and quark; it is an unstable, rapidly degrading, greenish liquid, with specific, unpleasant and persistent odour [1]. This waste can be reused in the milk fermentation process, thanks to the content of sugar – lactose, which in the presence of *Lactobacillus*, *Lactococcus* and *Leuconostoc* is converted to lactic acid, which in turn is used in production of biodegradable polymers and copolymers. Poly(lactic acid) and its copolymers have a wide range of application, in all fields, such as medicine, production of disposable packages [2]. Poly(lactic acid) (PLA) makes as much as 40% of all biodegradable polymers produced [3]. In addition, waste whey can be used as a substrate in production of resins and casein polymers. Production of modified casein based polymers consists mostly in the reaction of coupling casein with acrylic acid and its derivatives, such as ethyl acrylate. Reaction initiators are organic peroxides, e.g. benzoyl peroxide [4]. Among the most known applications of casein is production of galalith – a plastic mass cross-linked with formalin, used in cloth industry and in production of artificial fibres called Lanital in the process of casein reaction with thinned solution of sodium hydroxide. Casein can also be used as a binder in water based paints, a component of coating materials, as a substance useful in painting of leather or as a component of plaster mortars [5].

## Global production and application of PLA

Presence in the PLA structure of ester bond determines its high flexibility, permitting degradation under varying pH conditions to non-toxic compounds. Thus, PLA and its copolymers, are among the most common environmentally-friendly biodegradable materials. It is foreseen that global production of this polymer in 2020 shall reach 800–900K t/year. As of present, production capacity of industrial facilities is in the excess of 180 K t/year. The largest global producer of PLA is company NatureWork, operating in the USA and Thailand. NatureWork output is as much as 140 K tons of PLA a year, which makes 78% global production capacity of this polymer [6]. The revolution in PLA application began in 1970's, when United States Food and Drug Administration admitted its application for medicinal and alimentary purposes. Ever since that time PLA-based polymers have been broadly adopted, among others in production of surgical threads, clamps, bone plates, artificial skin, and also used as ideal carriers of medicines in controlled release systems. PLA is also used in production of surgical masks, dressings, compresses, clothing of medical personnel, diapers, tissues and cosmetic swabs [7–9]. In recent years, due to continuous development of tissue engineering, PLA and its copolymers are commonly used as scaffolds in tissue cultures [6, 10, 11]. Lactic acid polymers, and their copolymers, are

an alternative for mass-produced packages of synthetic polymers, mostly the product of petroleum processing, featuring high stability and marginal degradation in the environment [12, 13].

## Physical properties of PLA and copolymers

Among many of biodegradable polymer groups, the best known and studied one is PLA, with brittleness and rigidity making it on par with polystyrene. Its resistance to fats and oils is similar to that of PET [3]. Off-the-shelf PLA is in the form of a mixture of enantiomers D and L [14]. A number of important physical properties of PLA is determined by the ratio and the sequence of distribution of enantiomers D and L in its structure. Poly(lactic acid) can contain in its structure a crystalline phase or amorphous (formless) phase, or both in various proportions – depending on stereochemical structure. Amorphous structure of PLA is obtained by polymerization of both enantiomers of lactic acid. Resulting polymer degrades much faster than the one comprising only isomer D- or L- of lactic acid. In addition, amorphous structure ensures better penetration of intermolecular space by water. This property allows PLA application in production of resorbable threads. Linear optical isomer L-PLA degrades much faster with loss in molecular weight, whereas degradation of branching PLA is independent from its molecular weight. It has been proved that the content of enantiomer L in PLA in the excess of 90% allows production of polymer with crystalline properties, whereas the lower content results in amorphous properties. Based on the research it has been observed that decrease in enantiomer L content is accompanied by decrease in flow temperature ( $T_p$ ), glassy temperature ( $T_g$ ) and crystallinity [12]. Knowledge of  $T_g$  values for PLA determines its potential applications on the commercial scale.  $T_g$  value for enantiomers D-PLA and L-PLA is 52–65°C, at average molecular weight exceeding 25.000 Da, whereas  $T_m$  value is in the range 170–180°C [3, 15]. Racemic mixture D,L-PLA demonstrates glassy temperature of 57°C, and its  $T_m$  is higher than in individual isomers D- and L-PLA; in this case mixture D,L-PLA can, at higher temperatures, change its structure into crystalline, reaching the melting temperature  $T_m = 230^\circ\text{C}$ . Solubility tests determined that PLA is soluble in both polar and non-polar solvents, such as benzene, THF, DMSO, acetone, dioxan [16].

## Methods of producing PLA

Poly(lactic acid) is produced in ring opening polymerization (ROP) process, with lactide as an intermediate substrate, and in direct polymerization process, directly from lactic acid, skipping intermediate phases [14]. The product of indirect polymerization process is high-molecular-weight PLA; it is a two-phase method, which consists first in synthesizing the lactide, i.e. dimer of lactic acid. Lactide is a cyclic diester of lactic acid, produced in the result of condensation of two lactic acid molecules. Synthesis of lactide was described for the first time by Pelouze in 1845 [17]. He observed that a cyclic dimer – lactide – is also produced, in addition to lactic acid pre-polymer, during condensation of lactic acid. Presently ROP is the most commonly used industrial production method. The process is complex and requires many stages of lactide

Corresponding author:

purification, which increases the price of PLA as compared with the price of synthetic polymers. Ring Opening Polymerization process can be held in solution, in bulk, in melt, and in suspension. Such polymerization can be based on cationic, anionic, coordinating or radical mechanism [18]. Poly(lactic acid) can be also produced in the process of direct polymerization. This method can be divided into three major phases: a) removing water (concentration of lactic acid), b) pre-polymerization, i.e. receiving the oligomer of lactic acid, c) bulk polycondensation, obtaining high-molecular-weight polymer. The first phase aims mostly at removal of water from the system; small quantities of lactic acid oligomers can be produced as early as in this phase. In the second phase lactic acid is converted to low-molecular-weight PLA or in lactic acid oligomer. Due to low viscosity of reaction mixture the content of water does not affect the phase of producing a pre-polymer; significant effect is that of a catalyst [19]. In the third phase production of polymer is determined mostly by the quantity of water present in the reaction mixture. In order to accelerate the reaction of polycondensation and prevent transesterification remove produced water completely from the reaction system. PLA produced in the polycondensation process has lower molecular weight, worse mechanical properties, and therefore limited range of application. Direct polycondensation from lactic acid allows, in majority of cases, to produce low and medium molecular weights ( $M_w$ ), not exceeding 20.000 Da. Kokugan and associates carried out a reaction of non-catalytic polycondensation in vacuum, at temp. 200°C for 89 hours, and they produced a polymer with molecular weight of 90.000 Da (as related to polystyrene as a standard dissolved in chloroform at temp. 40°C), with PLA efficiency in the order of 52–75% [20]. Other studies presented the effect of variety of catalysts to conditions of direct polycondensation of lactic acid. Lei and Moon teams used in their research a binary system of catalyst-activator to produce L-PLA isomer. The catalyst used was a tin chloride dihydrate and succinic anhydride, or metallic/half-metallic alkoxides, such as aluminium, titanium, yttrium, silicon and germanium or p-toluenesulfonic acid constituting the activator of tin catalyst. Addition of the latter allowed to produce L-PLA with efficiency reaching 80% and  $M_w=40.000-500.000$  Da after 5–15 h of reaction, in vacuum, at temp. 180°C [21–23]. Aji team described in their works a research of catalysts containing tin, used in the reaction in organic solvents, in vacuum, at temp. 130°C, producing PLA with  $M_w = 300.000$  Da (as related to polystyrene standard in chloroform at temp. 40°C) [24]. Yoon and associates carried out a synthesis of medium-molecular-weight L-PLA with  $M_w = 130.000$  Da (polystyrene standard) using titanium butoxide (IV) as the catalyst, reducing reaction time to 7 h; they also carried out bulk polymerization [25]. The novel solution was using lipases as biocatalysts of polymerization in the process of PLA synthesis. The advantage of this process is its low temp. 60°C, and disadvantages include long reaction time, reaching 96 hours, and very low molecular weight of resulting polymer, not exceeding 2000 Da [6, 26, 27]. Indirect polymerization process, however, allows production of polymer with much higher molecular weight (above 50.000 Da) and incomparably better mechanical properties, higher glassy temperature and melting point. The literature presents many chemical compounds used as metal-based initiators of lactide ring opening, that is lean, zinc, iron, aluminium, yttrium, bismuth, copper, calcium, producing complexes, alkoxides, acetates [8, 28 – 31].

### PLA copolymers – physical properties

In order to improve PLA properties – rigidity, permeability, crystallinity and thermal stability – and to expand its range of application, copolymers are produced (graft copolymers, block copolymers) or its molecular architecture is modified (star-shaped polymers, hyper-branched polymers). Functional groups in polymer

molecule can also be modified or blends produced, by mixing with other polymers [12]. Copolymers are produced by combining lactic acid or lactide with, among others, glycolic acid, polyethylene glycol (PEG), (R)- $\beta$ -butyrolactone (BL),  $\delta$ -valerolactone (VL),  $\epsilon$ -caprolactone, styrene derivatives [18]. In the result of lactide combination with polyglycolides (PGA) a copolymer is produced demonstrating lower crystallinity and softening point ( $T_m$ ) than PLA and PGA [5]. Addition of  $\epsilon$ -caprolactone to the blend of copolymers obtained from lactide and glycolic acid results in extension of degradation time to years. The value of glassy temperature ( $T_g$ ) increases with increase in concentration of  $\epsilon$ -caprolactone and glycolic acid in the mixture system [5]. Higher content of  $\epsilon$ -caprolactone also results in increase of flexibility, at the cost of reduced ductility. Depending on copolymerization method values of average molecular weights of PLA-co-GA are in the order of 50.000–160.000 Da, at  $T_g = 55^\circ\text{C}$  [12]. Ajioka and associates studied differences in thermal properties of copolymers produced directly from lactic acid and from lactide. Copolymers with glycolic acid (hydroxyacetic acid), 6-hydroxyhexanoic acid and  $\epsilon$ -caprolactone were produced. Melting temperature of copolymer produced by opening of lactide ring in the reaction with glycolic acid was 145°C, and thus  $T_m$  was higher by 10°C as compared with copolymer produced directly from lactic acid. Glassy temperatures of resulting copolymers were comparable, both in direct copolymerization process and in lactide ring opening process with glycolic acid. The situation was different in case of PLA copolymers with 6-hydroxyhexanoic acid, differential  $T_g$  of which was 10°C for copolymer produced by opening of lactide ring. PLA copolymers with 6-hydroxyhexanoic acid are amorphous [32]. In order to improve hydrophilic properties of lactic-acid based copolymer, it is modified by copolymerization with polyethylene glycol. Resulting combination allows creation of polymer material that is not toxic and demonstrates high biocompatibility [7]. Another method of PLA modification is blending. The example is the material produced using dextrane, featuring much better affinity to cells and hydrophobic properties as compared with pure PLA [33]. Another way of modifying is by grafting functional groups, for example combination of lactic acid functional groups with randomly selected amine groups of chitosan. The resulting product is much less crystalline than pure chitosan, but it is due to disturbances to regularity of its structure, which improves its physical properties in terms of medicinal applications, among others as a medicine carrier [5].

### Own research

Four stages can be identified in hitherto own research under the Operational Programme Innovative Economy 2007–2013, implemented by GLOKOR Sp. z o.o. Stage one was producing lactic acid from lactose contained in sour whey in the process of lactic fermentation. Such sour, unlike sweet whey (which can be used e.g. as a fodder), has a higher content of lactic acid, in order of 0.7%. Stage two of research, during which the goal was to check and optimize the effectiveness of lactic fermentation of lactose in post-process whey, in the presence of *Lactobacillus* bacteria. Such optimization consisted of selecting suitable composition of mediums, temperature and duration of fermentation process. In consequence of the research the content of lactic acid in post-fermentation whey was increased to 4%. Following completion of fermentation process development, the resulting lactic acid was filtered and used in stage three research, namely concentration of lactic acid in pervaporative separation process. The concentration of lactic acid produced in those processes reached tens percent (35–55%). In stage four this acid was used in production of PLA and its copolymers using metallic organic catalysts based on zinc (Zn), tin

(Sn) and zirconium (Zr). Stage four of the research is in the process. The research is oriented on producing the optimum catalytic system and optimum conditions for running of polymerization process.

### Summary

This publication reviewed the literature demonstrating that PLA and its copolymers constitute an ideal biodegradable polymer that might find application in a variety of industry sectors, among others in production of biodegradable bottles and disposable packages, resorbable surgical threads and dental implants. It is estimated that in near future PLA can substitute onerous, non-biodegradable, polyolefines and other polymers from non-renewable materials. This is why PLA production faces an uptrend. Lactic acid polymerization processes, described in the article, are still a novelty that requires further research, aimed at optimization of PLA production processes.

### Acknowledgements

The research is financed with funds from the project "Development of innovative and environmentally-friendly technology of production biodegradable polymers" under Measure I.4 "Support for goal-oriented research" within the Priority Axis I "Research and development of modern technologies" under the Operational Programme Innovative Economy 2007–2013 implemented by GLOKOR Sp. z o.o. Project no. POIG.01.04.00–24–124/11.

Śławomir MAŚLANKA, Ph.D. in chemistry, a graduate of the University of Silesia in Katowice (2001), specialising in chemical technologies and chemistry of large-molecule compounds, didactics in chemistry. In 2008 he was granted a Ph.D. degree in chemical science by defending the Ph.D. thesis titled "Model oligoesters and polyesters for relaxation research on polymers". Following his defence, he was employed by US in Katowice as a specialist. Since 2012 he has been also employed by the company Glokor Sp. z o.o. in Gliwice as the Manager of Project Management Team, working also at KW PSP in Katowice as an advisor on ABC rescue issues. Scientific interests: analytical chemistry, nuclear physics, physicochemical examination of polymers, high technologies and general and diagnostic medicine.

Maria SIOŁEK, M.Sc., a graduate of Silesian University of Technology in Gliwice, Faculty of Chemistry (2010). Since 2011 she is a Ph.D. student at the Institute of Chemistry at Faculty of Mathematics, Physics and Chemistry of the University of Silesia in Katowice. Scientific interests: NMR examination of acrylic polymer microstructure, chemistry and technology of polymer materials.

Łukasz HAMRYSZAK, M.Sc., a graduate of Silesian University of Technology in Gliwice, Faculty of Chemistry (2010). Since October 2012 he has been a researcher at the Polymerization Team in Glokor sp. z o.o. company in Gliwice. Scientific interests: chemistry and technology of polymer materials, organic synthesis, chemical reactions engineering.

Dawid ŁOPOT, a sophomore student of Complementary Master's Course at the Faculty of Mathematics, Physics and Chemistry at the University of Silesia in Katowice, in major of medicinal chemistry. In 2012 he defended a B.Sc. thesis in physical chemistry. Since August 2013 he has been a researcher at the Polymerization Team in Glokor sp. z o.o. company in Gliwice. Scientific interests: physical chemistry, physicochemical examinations of polymers and ionic liquids.