Andrzej K. Błędzki[1,2], Adam Jaszkiewicz[2], Magdalena Urbaniak[3], Dobrosława Stankowska-Walczak[4]

West Pomeranian University of Technology in Szczecin,
[1])Institute of Materials Science and Engineering,
[3])Department of Mechanics and Machine Elements,
Al. Piastow19, 70-310 Szczecin, Poland
E-mail: andrzej.bledzki@gmx.de,
magdalena.urbaniak@zut.edu.pl

[2])Universität Kassel, Institut für Werkstofftechnik,
Möncheberg str. 3, 34125 Kassel, Germany

[4])Pomeranian Medical University in Szczecin, Medicinal Chemistry Department,
Al. Powstanow Wlkp. 72, 70-111 Szczecin, Poland

Biocomposites in the Past and in the Future

Abstract

Due to increasing environmental awareness nowadays, biocomposites are becoming important and prevalent materials, as they were centuries ago. The development of high-performance engineering products made from natural resources is increasing worldwide. Natural fibre composites have become more and more efficient as new compositions and processing methods are being intensively researched, developed and consequently applied. This paper, above all, is intended to provide a brief outline of the development and modification trends which aim to make biocomposites more user-friendly and eco-friendly by means of novel processing methods. These methods produce biopolymers with an improved melt behaviour and use naturally occurring raw materials.

Key words: *biopolymer, polylactide, chain extender, cellulose fibre, biocomposite.*

Introduction

Today, plastic products are an indispensable part of our life, such that recent decades can be described as the plastic age. Therefore, the history of plastics, its present and its prospects for the future are worth presenting to anyone who is interested in developments which have occurred in materials.

***Figure 1.** Medallion frame (Germany - 1800), proteinoplast [1].*

***Figure 2.** Writing set (France - 1880) ebonite [1].*

Throughout the centuries, thanks to readily accessible and easily processable materials like a clay, flint or horn, mankind was able to solve technical problems or to achieve artistic effects. However, we have always been on lookout for better materials. In the late Middle Ages, specially hardened and filled lactoprotein products were used as a substitute for natural horn for inlaid work, small medallions (***Figure 1***) and other artistic wares [1]. The rapidly developing and constantly changing social structures in the 18th and 19th centuries then led to an increase in imitations and surrogate materials allowing ordinary people access to those objects which had been reserved for the wealthy. In this time, a mixture of linseed oil and powdered cork on a cloth base (linoleum) was first used as a floor covering and substitute for a simple wooden floor, and celluloid was used as synthetic ivory. The first technically viable plastic product was vulcanised natural caotchouc, a hard rubber called Ebonite, became a substitute for ebony (***Figure 2***) and replaced natural tortoise shell [1]. This phase of modified natural materials derivatives made of casein, cellulose (***Figures 3*** and ***4***) and natural caotchouc was followed by Bakelite as the first completely synthetic product. It was named after Belgian chemist Leo Hendrik Baekeland who in 1872 discovered this polymer made of phenol and formaldehyde [1, 2]. However, this phenolic resin was not initially put into any practical application. It marked the starting point for the development of various synthetic thermoplastic materials from the 1920s and 1930s (***Figure 5,*** see page 16). The first reports concerning the syntheses of biopolymers dates back to 1925 when French microbiologist Maurice Lemoigne described polyhydroxybutyrate (PHB), which gave rise to bioplastic materials used mostly for medical and later also for packaging applications. However, the last few decades were a time period fully dominated by petrochemical polymers, since the growth of chemistry based on crude oil

***Figure 3.** Post card (Portugal - 1905) celluloid [1].*

***Figure 4.** Table lamp (Germany - 1930) celluloid [1].*

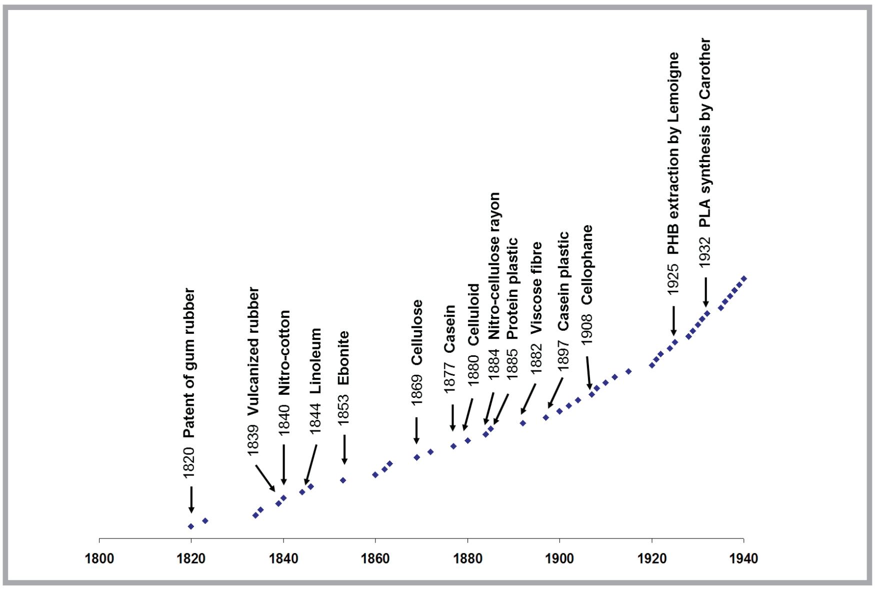


Figure 5. *Historical diagram of plastics [3].*

revolutionised the cost-efficient production of plastics. As a consequence, lower-performance applications have become under the aegis of thermoplastics, whereas thermosets have taken over the field of high-performance composites.

Accordingly, in long-established technical application areas, the major thermoplastic engineering composite is still polypropylene reinforced with glass fibre, as its cost/performance ratio is one of the best of all. Nevertheless, the most important polymer construction materials have become thermosetting composites. They have proven to be useful in all branches of the economy and business areas, mostly in building of boats, yachts and other sport equipment, in the aviation and armaments industries and especially in the automotive industry. At first, they were introduced as agricultural-based polymer materials composed of paper and soybean resin for automotive parts by Henry Ford (1941) (***Figure 6***). However, the technologies employed up to the present for producing thermosets do not comply with the stringent rules and regulations concerning preservation of the environment. This is why, in recent years, many research centres all over the world have been intensively occupied in searching out and scientifically examining new composites based on raw materials from renewable resources. This is reflected in the increasing number of publications on natural fibre composites in recent years. Satyanarayana *et al.* [4] found by entering the words "biodegradable, polymer, fibre" in the ISI database that, after the year 2000, the number of publications and patents on biodegradable lignocellulosic fibre-based composites rose significantly (***Figure 7***).

The main area of increasing usage of these composite materials has become the automotive industry, predominantly in interior applications. Lately, the use of biocomposites has increased by about 50% per annum in this industry [5] due to new legislation forcing car makers to reuse and recycle materials. The increased importance of renewable resources for raw materials and recyclability or biodegradability of the product at the end of its useful life is demanding a shift from petroleum-based synthetics to agro-based biofibres and biopolymer not only in automotive applications [6, 7].

As a result of the increased environmental awareness among customers, there is a growing market for products based on renewable raw materials. This environmentally conscious motivation has resulted in the development of standards which determine the percentage of such materials (% bio-based) in the product. Currently, certification of bio-based products has been established in Belgium (OK biobased certification in 2009) [8], Germany (DIN Certo certification in 2010) [9] and the USA (USDA Certified biobased products in 2011) [10] (***Table 1***). Due to this standardisation, renewable materials are becoming attractive alternatives to glass and other fibre-reinforced petroleum-based polymer composites in the customer market. However, further research is still required to overcome obstacles such as moisture absorption and increased long-term stability for use in exterior components. New, technically advanced, high quality

Figure 6. *One of the most famous photographs (1941) of Henry Ford who is trying to crack a rear deck lid composed of paper and soybean resin with a sledge hammer.*

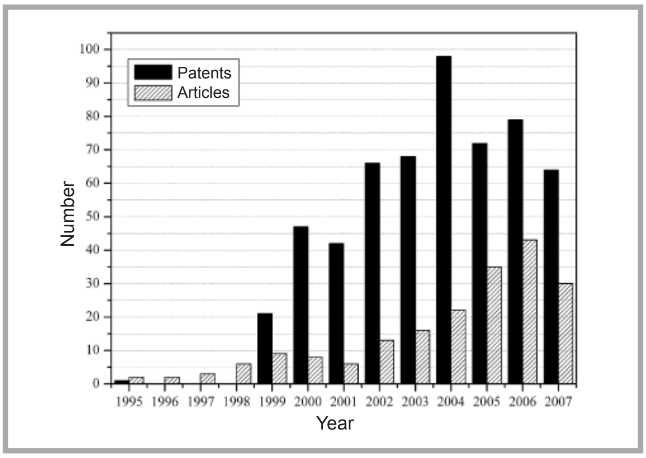


Figure 7. *Number of publications and patents on biodegradable lignocellulosic fibre based composites (1995–2007) (found in the ISI database by entering the words 'biodegradable, polymer, fibre') [4].*

materials from renewable resources, that are stronger, cheaper and eco-friendly, should soon be achieved due to the interaction between chemistry, physics and engineering technology.

Natural fibres

Total worldwide biomass harvested in 2008 reached ca. 13 billion tons and most of this was utilised for animal feed (58%), food (15%), wood energy use (10%) and wood material use (11%). Utilisation of biomass as renewable raw materials for energy and material use amounted to only 2.7 and 3.3%, respectively [11]. The use of biomass for renewable raw materials (as for every other use) throughout the world is based on a mosaic of different types of biomass [11]. These include renewable resources from agriculture and forestry (e.g. timber, plant oils, starches, sugars, specific components) and biogenic residues (e.g. straw and other waste from agriculture, wood off-cuts, organic waste, animal fats and proteins). While the potential use of biomass for energy production is limited (direct burning, biofuels, biogas or biomass gasification), in contrast, material use of biomass (***Figure 8***) can be characterised by a large spectrum of potential applications. The raw materials used to produce biocomposite components are mostly plant oils and natural fibres (***Figure 9***) [11].

Natural fibres surpass the usual reinforcing fibres, for instance glass fibres, with respect to low cost, low density, toughness, acceptable specific strength, enhanced energy recovery, recyclability, biodegradability, etc. [12 - 14]. Moreover, natural fillers are able to minimise environmental pollution, allowing these composites to play an important role among eco-friendly materials [15, 16]. However, natural fibre properties can differ greatly depending on type, grade, harvest quality, processing method, yield, etc. Only natural fibres of high technical quality guarantee sufficient reproducibility of the mechanical characteristics of biocomposites [17]. The overall characteristics of reinforcing fibres used in biocomposites, including source, type, structure, composition, as well as mechanical properties, are widely reviewed in the literature [18].

Since the beginning of our civilisation, natural fibres have been used as a reinforcement in composite materials, such as when grass and straw or animal hair were used to reinforce mud bricks. They were, most likely, the first man-made composites filled with natural fibres in human history. Classification of the natural fibres used nowadays, including excellent raw materials for manufacturing of so called "green products" as well as mineral fibres, is shown in ***Figure 10*** (see page 18) [19]. The properties of selected fibres (flax, hemp, jute, sisal, abaca, cotton, man-made cellulose), i.e. those which may successfully compete with glass fibres, are shown in ***Table 2*** [19, 20]. The chemical and physical structure of natural fibres presented in ***Figure 11*** (see page 18) [21] generally shows an example where its elements are "designed" for strength and stiffness.

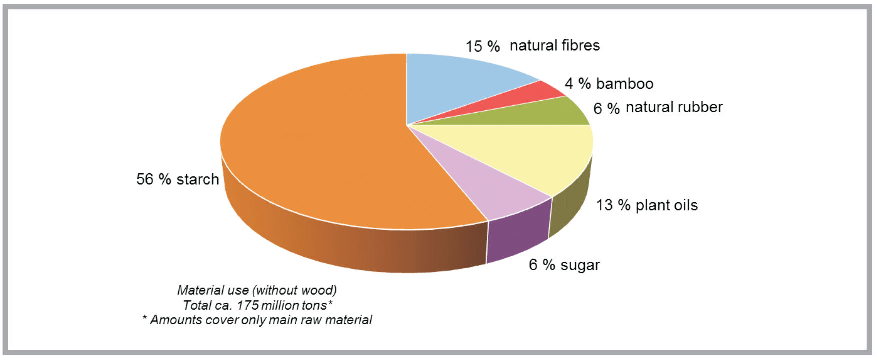


Figure 8. *Worldwide use of renewable resources for materials in 2008 [11].*

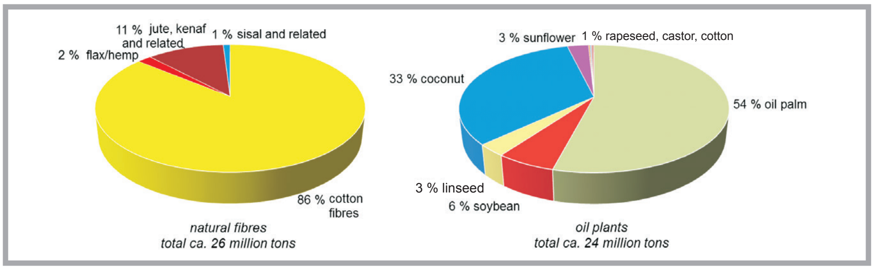


Figure 9. *Worldwide use of natural fibres and vegetable oils for materials in 2008 [11].*

Table 1. *Certification of bio-based products [8 - 10].*

Certification	Bio-content	Denotation of bio-content
Belgium	20 - 40% 40 - 60% 60 - 80% > 80%	designated by number of asterisks on the label
Vinçotte - Certest Products "OK biobased" certification *September 2009*		
Germany	20 - 50% 50 - 85% > 85%	given on upper semicircle of the label
DIN CERTCO certification *April 2010*		
USA	min. 25%	exact % listed on the label
US Dpt. of Agriculture "USDA Certified Biobased Products" *February 2011*		

Table 2. *Engineering properties of natural fibres compared to glass fibre [19, 20].*

Fibre	Density, g/cm^3	Tensile strength, MPa	Young's modulus, GPa	Specific modulus, GPa/g/cm^3	Elongation to break, %	Moisture absorption, %	Diameter of elementary fibre, μm
E-Glass	2.55	2400	73	29	3	-	10 – 20
Flax	1.40	800 – 1500	60 – 80	26 – 46	1.2 – 1.6	7	15 – 22
Hemp	1.48	550 – 900	70	47	1.6	8	17 – 24
Jute	1.46	400 – 800	10 – 30	7 – 21	1.8	12	15 – 35
Sisal	1.33	600 – 700	38	29	2 – 3	11	15 – 30
Abaca	1.50	980	-	-	-	-	10 – 30
Cotton	1.51	400	12	8	3 – 10	8 – 25	15 – 24
Man-made cellulose	1.49	885	27	18	12	8	12

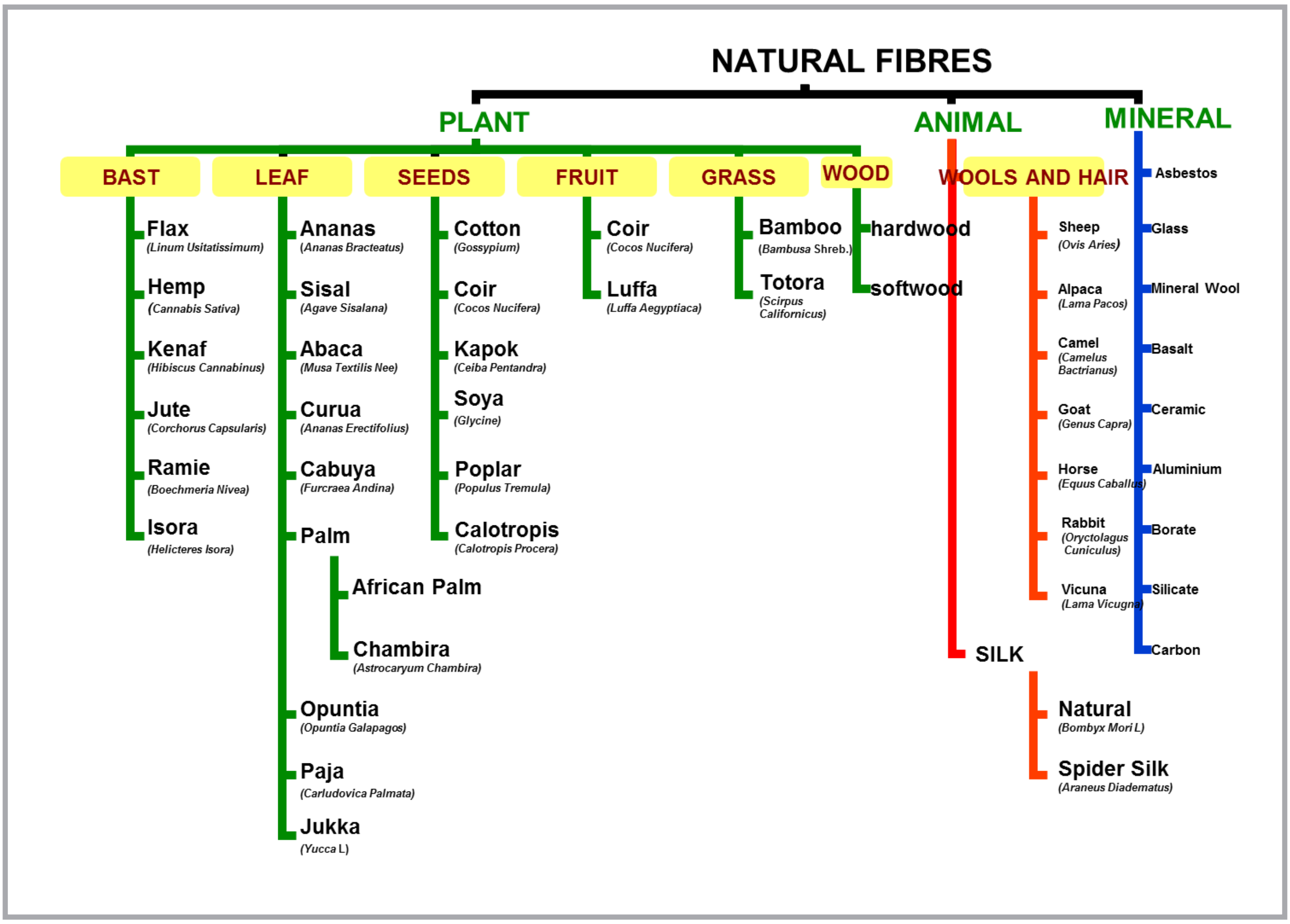
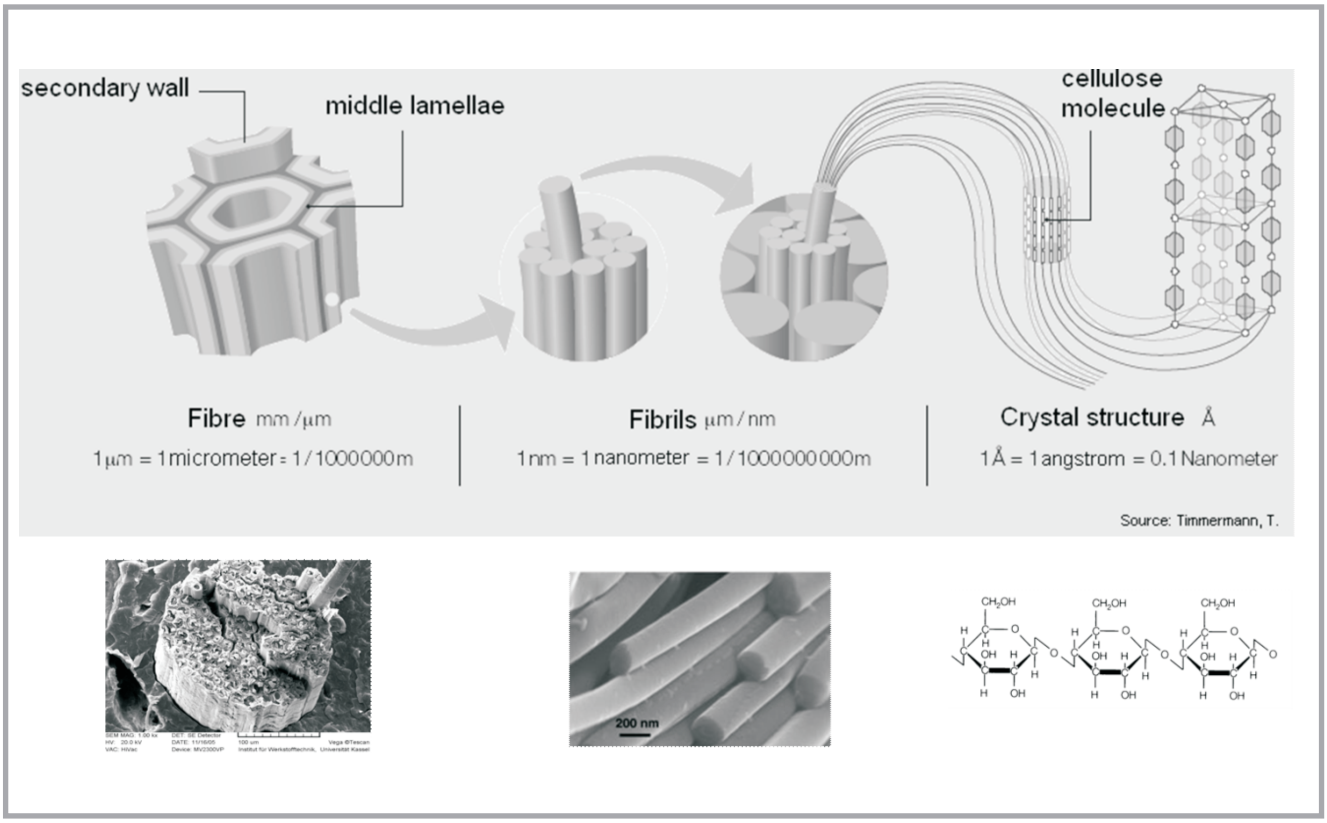


Figure 10. *Classification of natural fibres [19].*



Source: Timmermann, T.

Figure 11. *Structure of natural fibres [21].*

A fibrous structure made of cellulose, a natural polymer with high strength and stiffness per weight with multi-ply construction composed of long fibrils consisting of many microfibrils at different angles to the fibre axis, can be an effective reinforcement for a composite matrix, due to hindered polymer flow caused by the fibre filler [6].

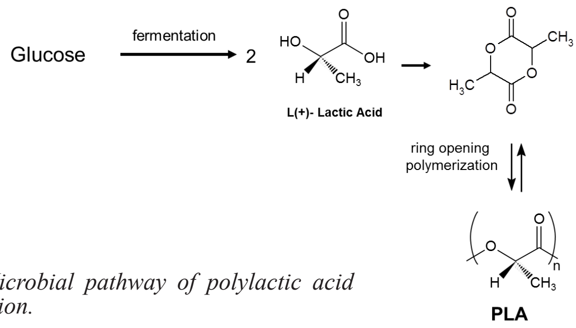


Figure 12. Microbial pathway of polylactic acid (PLA) production.

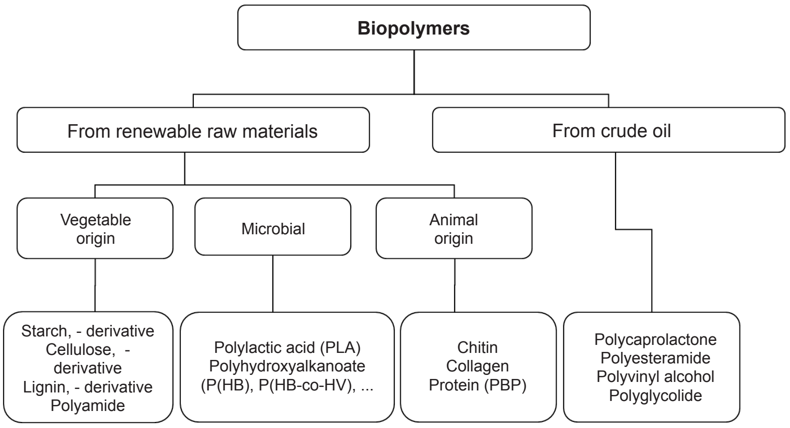


***Figure 13.** Biopolymers classification [22].*

Biopolymers

Public concern about the environment, climate change and limited fossil fuel resources are important driving factors to find alternatives to crude oil. Bio-based plastics may offer important contributions by reducing the dependence on fossil fuels and the related environmental impacts. Biopolymers have experienced a renaissance in recent years. A lot of new polymers have been developed from renewable resources and many others, such as starch, i.e. a naturally occurring polymer, were re-discovered as plastic materials. Other examples are polylactic acid (PLA) that can be produced from fermentable sugars, partly by the microbiological route via lactic acid formation and following ring opening polymerisation (Fig. 11) and polyhydroxyalkanoates (PHAs) obtained from polysaccharides during metabolic processes in bacteria cells. These developments in emerging bio-based plastics are spectacular not only from a technological point of view. The biopolymer market has been experiencing rapid growth. The global average annual growth rate was 38% from 2003 to 2007 and as high as 48% in Europe in the same period. The worldwide capacity of bio-based plastics will likely increase from 0.36 million in 2007 to 2.33 million tonnes in 2013 and to 3.45 million tonnes in 2020. The greatest production volumes are to be reached by microbial biopolymers PLA and PHA, called “starch plastics” [6].

There are a number of other biological materials, quoted in ***Figure 13***, that have been examined and manipulated by biopolymer researches. The design of such materials usually begins with a conceptual application. The renewable and biodegradable polymers that may be employed in packaging receive more attention than those designated for any other application because 41% of plastics are actually used in packaging, mostly for food products [23]. The most important biopolymer applications can be found in the field of medicine. PLA materials developed for medical devices such as resorbable screws, sutures and pins reduce not only the risk of tissue reaction but suffering and recovery times of patients and the costs of the health service as well. Many biopolymer materials are currently incorporated into adhesives, paints, engine lubricants and construction materials, especially in sport equipment and agricultural applications. There are an endless number of areas where biodegradable polymer materials may find use. The industrial sectors of agriculture, automotive, medicine and packaging all require environmentally friendly polymers. Biodegradable plastics containing starch and/or cellulose fibres are most likely to experience continual growth in usage. Because the level of biodegradation may be customised to specific needs, each industry is able to create its own ideal material. The various modes of biodegradation are also a key advantage of such materials because disposal methods may be tailored to industry specifications. Recycling appears to be a viable way to reduce pollution and environmental damage since it was first introduced as a waste reduction technique. However, as time has passed, it is now obvious that the use of plastics based on renewable feedstocks which are biodegradable is a more sensible choice than conventional plastic recycling, as the end products are organic matter, and toxic emissions are avoided. Therefore, the growth of plastics which are compostable or easy degraded must be encouraged and the infrastructure for sorting and composting organic waste must be developed more intensively [23].

Easily degraded biopolymers based on PLA are predestined for conventional processing especially by means of extrusion and injection moulding due to their sufficient melt stability provided that the prescribed processing conditions and procedures are kept. In order to improve the mechanical properties of biopolymers based on PLA, some research has been carried out lately. The matrix used was a polylactide PLA4042D (from NatureWorks LLC, USA). The PLA was blended with PBAT [poly(butylene adipate-co-butylene terephthalate)] (trade name Ecoflex® from BASF SE, Germany) at a weight ratio of 70/30 (PLA/PBAT). An epoxidised styrene-acrylic copolymer as the chain extender was delivered from Clariant Masterbatches, Germany in the form of a masterbatch (CESA-extend®).

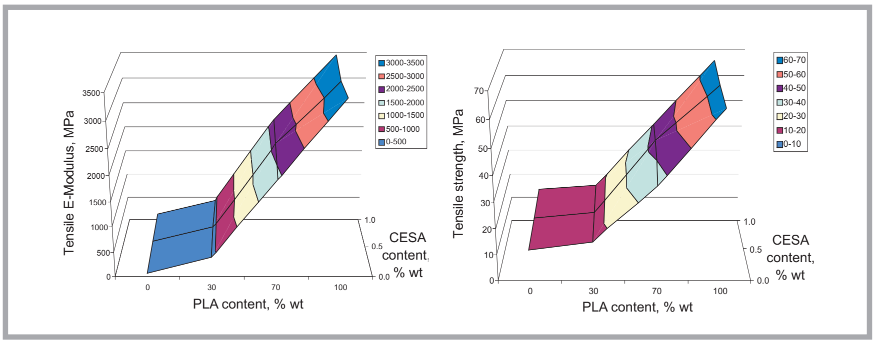
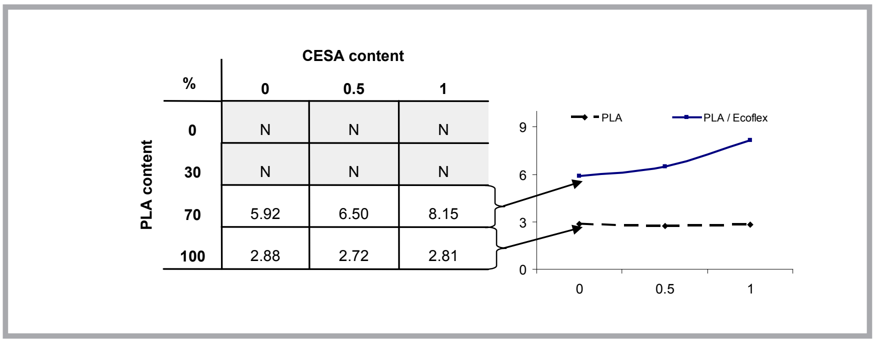


Figure 14. *Results of the tensile test on PLA/Ecoflex blends [24].*



PLA content, %	CESA content 0	0.5	1
0	N	N	N
30	N	N	N
70	5.92	6.50	8.15
100	2.88	2.72	2.81

Figure 15. *Results of Charpy A-notch impact strength of PLA/Ecoflex; T=+23°C [24].*

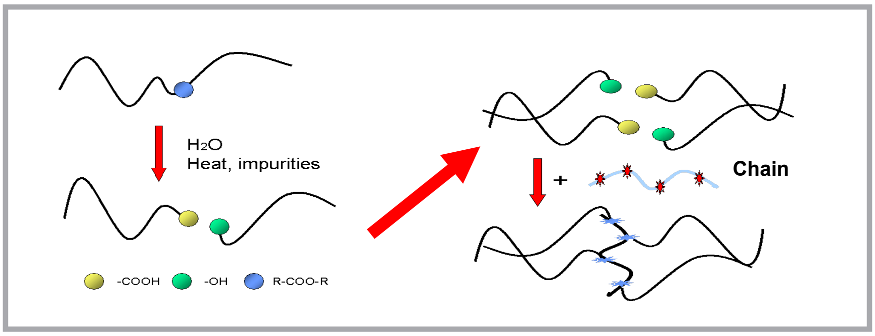


Figure 16. *Mechanisms of chain extension [25].*

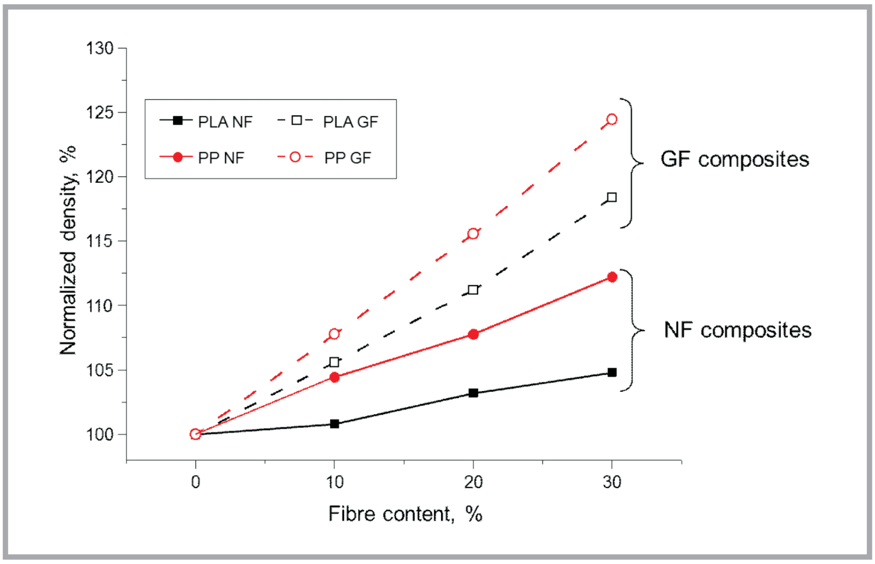


Figure 17. *Density of PLA and PP composites with various content of natural or glass fibres [24].*

The matrix was compounded together with the chain extender via a coating nozzle and cooled to ambient temperature. The pellets were dried and compounded on a single-screw extruder. All components were dried in a convection oven with a fan before further processing**.**

Figure 14 shows the results of the tensile test on unreinforced PLA/PBAT blends modified with a chain extender. It is obvious that with an increasing PBAT content, both the E-modulus and the tensile strength decreased significantly. This is due to the ductile character of Ecoflex compared to rigid PLA. Furthermore, the addition of the chain extender had only a negligible influence on these parameters [24].

By adding CESA, enhanced compatibility between two polymer phases (PLA as matrix and Ecoflex as modifier) was observed and, consequently, significantly improved impact strength was achieved (***Figure 15***) [24]. The chemical interaction of the epoxy reaction groups of CESA is depicted in ***Figure 16*** [25], where a crosslinking reaction of multiple functional side groups (epoxy or anhydride, respectively) with the end groups of the polylactide chain (e.g. –COOH or –OH) leads to non-linear chain extension of the PLA chains. Primarily, the addition of PBAT improves the Charpy A-notch impact strength by a factor of 2. Furthermore, increasing the chain extender content increased the impact resistance up to 8.15 kJ/m², which corresponds to 2.8-fold improvement compared to native PLA [24].

The molecular architecture of the biopolymer modified using such multifunctional additives affects not only on its mechanical properties but determines the melt behaviour during compounding as well. Due to this innovative modification with the use of chain extenders, thermomechanical stability of the biopolymer can be achieved.

Biocomposites

There is a wide variety of biocomposite processing techniques, as well as factors (fibre type and content, additives and others) affecting these processes [18]. Biocomposites with natural fibres can be processed using a special coating technique where dried fibres are introduced into a coating nozzle and covered with the melted polymer using a screw ex-

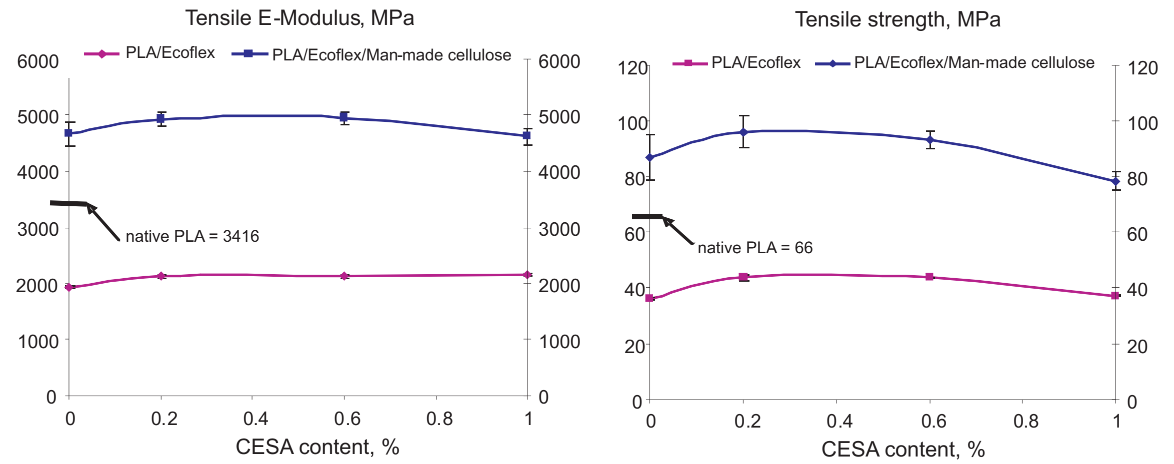


Figure 18. *Tensile test results of PLA/PBAT composites with man-made cellulose fibres [24].*

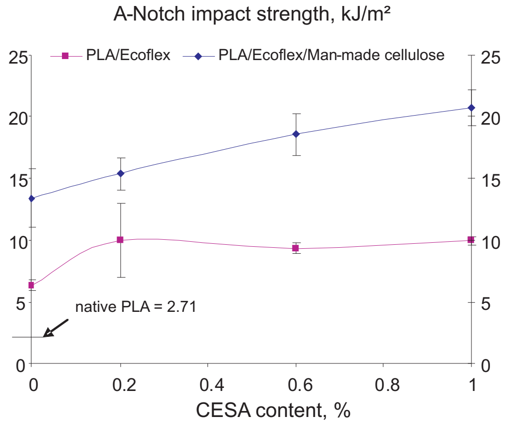


Figure 19. *Charpy A-notch impact strength of PLA/PBAT composites, T=+23 °C [24].*

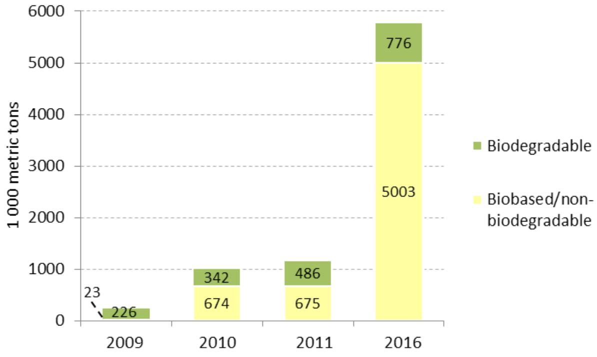


Figure 20. *Global production capacity of bioplastics [28].*

truder. Biocomposites are up to 20-30% lighter than their glass fibre counterparts (***Figure 17***), whereas other mechanical parameters can be comparable or even enhanced [26]. In order to improve the mechanical properties of cellulose-fibre reinforced polymers, the combination of optimised processing conditions and customised additives is a matter of greatest importance. Another essential aspect is the detailed analysis of the material's micromechanical behaviour comprising an analysis of the microstructure, load-displacement curves, and finally determining the influence on the macroproperties of the biocomposites. Since impact strength is one of the most important properties for biocomposite technical applications, all reinforcing effects of cellulose fibre on brittle polylactide composites must be utilised in every possible manner. One of them is the utilisation of reactive processing via special chain extenders by which chain extension is done by the reactive end groups of polycondensates with a bi- or multifunctional reactive component.

Research focused on improving the mechanical properties of reinforced PLA/PBAT blends with man-made cellulose fibres (30% by weight) from the Cordenka company (Germany) delivered as industrial yarn (Cordenka® 700 Super 3; linear density /nominal/dtex=2440, number of filaments 1350, breaking force 128.6 N, single fibre diameter 12 µm) shows that a meaningful enhancement in mechanical behaviour of the biocomposite can be achieved (***Figure 18***). Analogous to unreinforced blends, CESA slightly influences the mechanical parameters. At lower chain extender contents, a little improvement can be seen; however, by increasing the CESA concentration, another tendency can be observed, i.e. a greater amount of branching occurs, which leads to gelling. As a result, the composite becomes more ductile and stiff but its strength decreases [24].

By adding CESA to the PLA/PBAT composites, obviously not only increased compatibility occurs between PLA and PBAT, but also a kind of chemical interaction at the matrix/fibre interphase. It is possible that the epoxy groups of the chain extender react chemically with the hydroxyl groups of cellulose, increasing bonding between the fibre and the matrix (***Figure 19***) [24].

Future of biocomposites

The demand for supplies of biocomposites is growing in the world from year to year. This growth in Europe is actually estimated at 32% per annum, from 0.3 million tons in 2011 to 1.2 million tons in 2016. Similar growth can be observed in North and South America. The United States alone modestly estimates annual growth of 0.25 million tons in the same period. Higher growth is expected in Asia, i.e. 41% per annum, reaching production capacity ca. 1.1 million tons in 2016 [27]. By far, the bio-based, non-biodegradable groups, especially the bio-based version of bulk plastics like PE and PET, show the strongest growth in global production capacity. Leading the field is partially bio-based PET, which has accounted for about 40% of global bioplastics production in 2011 and will continue to extend its lead to more than 4.6 million tons by 2016 (80% of the total). Also, biodegradable plastics, especially PLA and PHA, have demonstrated impressive growth rates which will increase by 2/3 by 2016, reaching an estimated 298,000 and 142,000 tons, respectively (***Figure 20***) [28].

There is a growing trend to use biofibres as fillers and/or reinforcement in plastic composites. Their flexibility during processing, high specific stiffness and low cost (on a volumetric basis) make such biocomposites attractive to manufacturers. These composites are predestined to find more and more applications in the near future, especially in Europe where pressure in terms of environmental protection from both legislation and the public is rising. The renewable nature (biodegradable and recyclable properties) as well as significant processing advantages and the high specific strength of such composites pave the way for them to markets that are currently unexplored. However, new markets will develop when natural fibre composite products become more durable, dimensionally stable, moisture-proof, and fire-resistant [29]. The effort to overcome these obstacles is ongoing worldwide.

Conclusions

The weak points of natural fibres, i.e. inconsistent fibre geometries and distributions which are reflected in the properties of the composites, can be smoothened out with appropriate processing. Extrusion, injection and compression moulding processes are the preferred methods of biocomposite production. However, one ought to be aware that, at any time, new processes or materials can be developed. The production costs consisting of the process, tools, materials and labour costs are the most crucial criteria.

At first, any problem should be strictly defined, then we can approach it and find a solution. We can be convinced that:

- From an engineering point of view: ***always*** correlate processing and the resulting performance.
- Processability is only a matter of ***know-how***, process optimisation and additives.
- The weaknesses of biopolymers can be absolutely ***compensated for*** via additives or fibres.
- Polymer price is still strongly dependent on raw ***material cost and capacity***.

References

1. Dynamic Plastics - Vom Bakelite zum High Plast, Katalog zur *Ausstellung im Landesmuseum Volk und Wirtschaft,* Düsseldorf 2.11.-8.12.1989, Herausgegeben vom Kunststoff-Museums-Verein e.V., Redaktion: Günther Erdmann, Verlag: Dr. Neufang KG, Gelsenkirchen.
2. Daenens L, Bucquoye M, Verpoest I. *From Bakelite to Composite: Design in New Materials*, StichtingKunstboekBvba, 2002.
3. Jaszkiewicz A.: Werkstoffliche Verwendung von Nachwachsenden Rohstoffen für Technische AnwendungenTTN-Jahrestagung, Workshop 2: *Biomaterialien*, Universität Kassel, 07. September 2009, Kassel.
4. Satyanarayana KG, Arizaga GGC, Wypych F. *Prog. Polym. Sci.* 2009; 34, 9: 982–1021.
5. Suddell BC, Evans WJ. Natural fiber composites in automotive applications, 2005, Chapter 7 in *Natural Fibers, Biopolymers and Biocomposites*, eds.A.K. Mohanty, M. Misra, L.T. Drzal, USA.
6. Bledzki AK, Faruk O, Jaszkiewicz A. *Composites* 2010; 10, 3: 282-288.
7. Maya J, Sabu T. *Carbohydrate Polymers* 2008; 71: 343-364.
8. “OK biobased” certification: http://www.okcompost.be/
9. “DIN CERTCO” certification: http://www.dincertco.de/
10. “USDA-Certified Biobased Products”: http://www.biopreferred.gov/Biobased_Products.aspx/
11. Raschka A, Carus M. Industrial material use of biomass basic data for Germany, Europe and the world, NOVA-Institut, 2012.
12. Gassan J, Bledzki AK. *Composites Part A* 1997; 28, 12: 1001-1005.
13. Bledzki AK, Gassan J. *Prog Polym Sc* 1999; 24, 2: 221- 274.
14. Chakraborty A, Sain M, Kortschot M. *ASC Symp Series* 2006; 938: 169-186.
15. Hornsby PR, Hinrichsen E, Tarverdi K. J Mater Sci 1997; 32*:* 1009–1015.
16. Thakur VK, Singha AS. Bull Mater Sci 2010; 33, 3: 257-264.
17. Bledzki AK, Jaszkiewicz A, Scherzer D. *Bioplastics Magazine* 2008; 3, 2: 12-15.
18. Faruk O, Bledzki AK, Fink HP, Sain M. *Prog Polym Sci* 2012; 37, 11: 1552-1596.
19. Kozłowski R, Władyka-Przybylak A, Kicińska-Jakubowska A. *7th Global WPC and Natural Fibre Composites Congress and Exhibition*, A14, June 18-19, 2008 in Kassel, Germany.
20. Brouwer WD. Natural Fibre Composites in Structural Components: Alternative Applications for Sisal? In: *Proceedings of a seminar held by the UN(FAO) and CFC,* Rome 2000.
21. Raven PH, Evert RF, Eichhorn SE. Biologie der Pflanzen. *Walter de Gruyter,* Berlin, 2000.
22. Jaszkiewicz A, Bledzki AK. *Polymers from Renewable Raw Materials – Today and Tomorrow*, Humboldt College, Collegium Polonicum Frankfurt (Oder)/Slubice 13-15 November 2008.
23. Kolybaba M, Tabil LG, Panigrahi S, Crerara WJ, Powell T, Wang B. *ASAE Meeting*, RRV03-0007, (2003), 1-15.
24. Jaszkiewicz A. *Gegenüberstellung von biobasierten Polylactid- und Polypropylen-Compositen- Funktionsadditive, Cellulose- und Glasfasern, Prozessführung*. Dissertation, Universität Kassel, 2011, ISBN 978-83-7815-404-4.
25. Awojulu A, Edison M, Frenz V, Scherzer D, Van der Meer R, Villalobos M. Multifunctional Polymers as Chain Extenders and Compatiblizers for Polycondensates and Biopolymers, *In:* Proc. *Society of Plastics Engineers Annual Technical Conference,* ANTEC-0993-2008.R1, Milwaukee, Wisconsin, USA, 22-24.06.2008.
26. Bledzki AK, Jaszkiewicz A, Feldmann M. Biopolymere zu Biokunstoffen und Biocompositen verarbeiten – eine Herausforderung moderner Kunststofftechnik, *Biopolymer Kolloquium*, Germany, Berlin, 25 January 2011.
27. Worldwide market of bio-composites 2009–2016: http://www.bccresearch.com/.
28. Global production capacity of bioplastics 2009–2016: http://en.european-bioplastics.org/.
29. Faruk O, Bledzki AK, Fink H-P, Sain M. Biobased Materials - 9th Global WPC, Natural Fibreand other innovative Composites Congress, PL3, June 19-20, 2012 in Stuttgart, Germany.

Received 16.10.2012 Reviewed 30.11.2012