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Biodegradable Synthetic Polymers in Textiles – What Lies Beyond PLA and Medical Applications? A Review.

Biorazgradljivi sintetični polimeri v tekstilstvu – kaj sledi PLA in medicinskim načinom uporabe? Pregled.

Original scientific article/Izvirni znanstveni članek

Received/Prispelo 9-2020 • Accepted/Sprejeto 10-2020

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Abstract

Biodegradable polymers are currently discussed for applications in different fields and are becoming of increasing interest in textile research. While a plethora of work has been done for PLA in medical textiles, other biodegradable polymers and their textile application fields are studied less often, presumably due to higher costs and fewer market opportunities. However, some are emerging from research to pilot scale, and are already utilized commercially in packaging and other sectors but not, unfortunately, in textiles. The commercialisation of such polymers is fuelled by improved biotechnological production processes, showing that textile applications are increasingly conceivable for the future. Additionally, commonly accepted definitions for biodegradability are probably misleading, if they are used to estimate the environmental burden of waste management or recycling of such materials. In this review, the current state of research in the field of biodegradable polymers for the application in textile materials is presented to identify emerging developments for new textile applications. It was clearly seen that PLA is most dominant in that field, while others facilitate new options in the future. The production costs of raw materials and the current patent situation are also evaluated. A special focus is placed on fibre raw materials, coatings, and additives for clothing and technical textiles. Fibre-reinforced composites are excluded, since polymers applied for the matrix component require very different properties compared to the textile materials. This represents a topic to be discussed separately. As a result, these new biodegradable polymers might serve as interesting coating materials for textiles that seem to sneak on to the textile market, as the patent search for such coating formulations suggests. Moreover, new biodegradable fibrous materials for clothing applications can be suggested, but some material properties must be addressed to render them processable on common textile machines.

Keywords: biodegradable polymers, recycling, biodegradability, PLA, textile coatings

Izvleček

Danes so biorazgradljivi polimeri predmet razprav za rabo na različnih področjih in postajajo čedalje bolj priljubljeni v raziskavah na področju tekstilstva. Medtem ko je raziskava rabe PLA za medicinske tekstilije veliko, pa se drugi biološko razgradljivi polimeri in njihova raba v tekstilstvu verjetno zaradi večjih stroškov in manjših tržnih možnosti proučujejo manj pogosto. Nekateri od njih so že na stopnji pilotskih raziskav in jih že tržijo za embalažo in v drugih sektorjih, na področju tekstilij pa žal še ne. Trženje takšnih polimerov spodbujajo izboljšani biotehnoški proizvodni procesi, kar kaže, da bo v prihodnosti njihova raba za tekstilije bolj razširjena. Poleg

tega splošno sprejete opredelitve biorazgradljivosti verjetno vodijo do zavajajočih sklepov, če se upoštevajo le ocene obremenitve okolja z ravnanjem z odpadki ali recikliranjem takšnih materialov. V tem pregledu je podano trenutno stanje raziskav na področju biološko razgradljivih polimerov za rabo na področju tekstilij z namenom, da bi identificirali nastajajoči razvoj novih tekstilnih aplikacij. Ugotovljeno je bilo, da na področju tekstilne rabe prevladuje PLA, medtem ko drugi polimeri odpirajo nove možnosti v prihodnosti. Ocenjeni so tudi proizvodni stroški surovin in trenutno stanje patentov. Poseben poudarek je na tekstilnih surovinah, premazih in aditivih za tekstilije za oblačila in tehnične namene. Kompoziti, ojačeni z vlakni, niso zajeti, ker so zahtevane lastnosti za polimerne matrice drugačne kot za tekstilije in bi to področje moralo biti obravnavano posebej. Novi biološko razgradljivi polimeri bi se lahko uporabljali kot funkcionalni premazi na tekstilijah, saj jih, kot je mogoče razbrati iz poizvedb za tovrstne patentirane formulacije premazov, že tržijo tudi za področje tekstilij. Predlagati je mogoče tudi nova biološko razgradljiva vlakna za oblačila, vendar je treba nekatere njihove lastnosti prilagoditi, da jih bo mogoče predelovati na standardnih tekstilnih strojih.

Ključne besede: biorazgradljivi polimeri, recikliranje, biorazgradljivost, PLA, tekstilni premazi

1 Introduction

Current legislation and increasing public awareness about polymer waste call for new options in the recycling of such materials. While everyday products such as bags, nettings or packaging materials are already manufactured from biodegradable plastics to some extent, the development of textile products appears to be more challenging. In this overview, only synthetic polymers are discussed, since natural polymers like cellulose or proteins are already well-known and utilized in the textile sector. Therefore, this report will focus on manmade polymers for textile purposes. In this narrowed field, primarily three applications can be considered: fibre-reinforced composites, fibrous substrates and coatings/finishings. The first field has been already widely addressed and thus will not be discussed here. However, interesting options emerge in the latter two sectors of fibrous substrates and textile coating materials. The majority of publications for biodegradable fibrous substrates address the medical sector and, to a lesser extent, technical textiles. Thus, a systematic literature review was conducted to identify previously evaluated materials and developments, as well as new opportunities in these fields. Biodegradable textile coatings are even less prominent in the literature, so a patent search was also conducted.

Moreover, commonly accepted definitions for the term “Biodegradability” do not address environmental requirements sufficiently, since degradation products are either defined too strictly or are left completely vague. An extended definition may serve to characterize possible future products more meaningfully instead.

2 Definitions

The term *biodegradability* needs to be defined first, since every material will degrade in the environment over a sufficient amount of time and/or under appropriate environmental conditions. To narrow down the temporal and environmental conditions, consideration of the field of application looks promising. For the medical sector, the timeframe should be in the range of the targeted duration of therapy, which may be in the order of several weeks or less, while environmental conditions are physiological (nearly neutral pH, 37 °C, water-based surrounding, etc.). For technical textiles, the definition will obviously be different, since degradation is meant to be fulfilled by microorganisms. In this context, the OECD (Organisation for Economic Co-operation and Development) gives four classifications of biodegradability [1]:

- primary biodegradation

It is understood as the loss of certain properties of a material; consequently no complete decomposition has to occur.

- ultimate biodegradation

Here the material has to be decomposed completely into carbon dioxide, water, minerals, and potential biomass (of the microorganism involved in the degradation).

- readily biodegradable

Materials screened by strict tests on ultimate biodegradability that assume a rapid and complete biodegradation in aquatic environments.

- inherently biodegradable

Materials in this class exhibit unambiguous biodegradation behaviour in any tests.

These definitions and the associated test methods all address degradation in natural environments

and assess material degradation by direct or indirect measures of organic carbon, usually after 28 days. However, the transformation products of the degradation process and possible non-degradable residues are not taken into account by these definitions and tests, but must be assessed for a complete picture. If those residues exist and are bio-accumulative, the continuous emission of small amounts may lead to future issues, as seen in fluorinated compounds today. For this reason, such tests only deliver useful results if the material is completely degraded into carbon dioxide, biomass and water.

In a practical example, the biodegradability of mineral oils was investigated and found to be up to 70% in some cases by using a test method where the time-frame was 20 weeks (CEC-L-33 A-93). Testing was done by extracting the oil soluble phase and subsequent infrared spectroscopy using the 2950 cm^{-1} band of CH-vibrations. It remained unclear what kind of residues are present in the extract and also which metabolites remained in the aqueous phase [2]. Although some sources consider this method as outdated, [3] other actual sources such as OECD 301 and the above-mentioned OECD definitions also do not evaluate residues.

For the context of this report, the OECD definitions above, except *primary biodegradability*, and an extended degradation time of up to one year, will serve valid criteria for review.

While this definition addresses only natural environmental conditions, industrial composting is also considered a form of biodegradation in the context of this report. Several standards do exist to characterize the industrial compostability of materials, usually demanding a 90 % decomposition in 180 days, [4] where the EN 13432 is probably the most common standard. An additional classification to *biodegradable* must be introduced for this review, which will be named *bionneutral degradation* (see Figure 1 for a summary of its definition). While *biodegradability* requires the complete breakdown into water, carbon dioxide and biomass, *bionneutral degradability* will include every substance that will break down into naturally occurring substances in the respective eco system. For practical application, it can be assumed that these reaction products will blend into the natural substance cycles, without significant environmental impacts. This is obviously a question of quantity as for the definition of biodegradability as well. It can be assumed that such residues will be degraded into carbon dioxide and water after some time.

Bionneutral degradability:

Material is degradable

- ◆ in the neutral environment, under physiological
- ◆ conditions or in an industrial process
- ◆ completely into naturally occurring substances
- ◆ which blend *neutrally* into naturally existing material cycles.

Figure 1: Concept of bionneutral degradability

Therefore, literature for this overview qualifies if it is about a manmade polymer and meets at least one of the three following criteria:

- biodegradable under physiological conditions;
- biodegradable or bionneutral degradable in natural environments with respect to [1], or materials assumed to fit in that category; and
- biodegradable in industrial composting similar to EN 13432, or materials assumed to fit in that category.

Materials that are not tested explicitly but can be assumed to fit in these categories are not excluded to ensure the widest overview on current substances.

3 Materials

Most synthetic biodegradable polymers can be categorized either as plant-based, microorganism-based or animal-based. The latter consists mainly of chitin and its derivatives and gelatine, which is rarely used to produce fibrous materials. However, chitosan is often utilized in antibacterial textile finishing. Polymer materials produced by microorganisms can be alginate-based materials, but also polymeric esters, proteins and other biological macro molecules, since such organisms can be easily genetically modified to produce a wide variety of materials. Plant-based polymers are mostly based on carbohydrates and can be obtained from starchy or cellulosic biomass. Polymers of greater interest in the field of biodegradable polymers are polylactic acid (PLA), and polyhydroxy alkanates (polyhydroxy fatty acids). PLA is a very common thermoplastic for many applications including melt spinning into fibres, mainly for medical applications. It is also used for the 3D-printing of structures on textile materials [5].

In general terms, most biodegradable polymers are esters, since hydrolytic cleavage of esters by enzymes is a common reaction in nature (see Figure 2). It is further assumed that aliphatic esters are of better degradability than aromatic ones, since the former may fit better in enzymatic active sites [6].

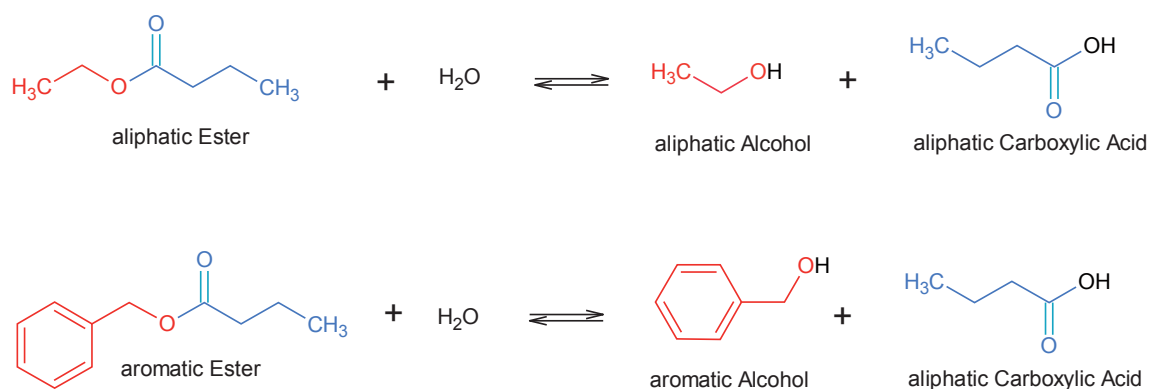


Figure 2: Hydrolytic cleavage of aliphatic and aromatic esters; hydrolysis is greatly accelerated by catalysts such as strong acids and bases, but also enzymes. Aromatic esters contain at least one aromatic carbon ring system, either in the alcohol or in the acid part.

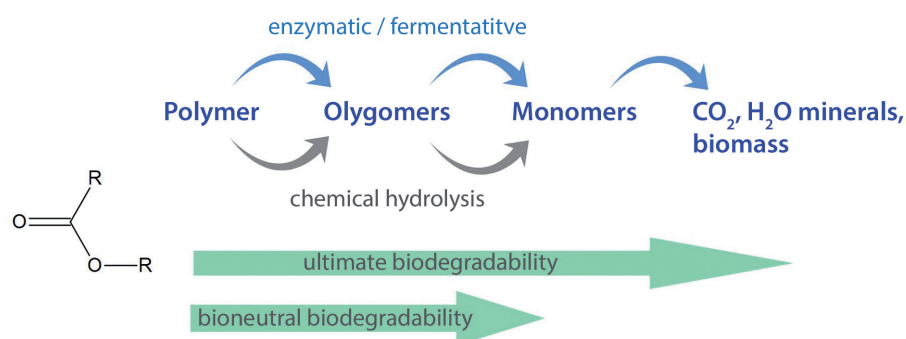


Figure 3: Stages of hydrolysis for polymeric esters, according to new and old definitions

Polyhydroxy alkanooates (PHA) are a class of polymers formally consisting of a fatty acid chain, with an additional hydroxyl group that can be used to form ester linkages between monomers, which places them in the class of bio-polyesters. The degradation of polymeric esters by hydrolysis can reach different endpoints as shown in Figure 3, while ultimate degradation will lead to carbon dioxide and water.

PHAs can be synthesized by different bacteria, which lead to the different types of esters [7]. Bacteria use these structures for energy storage and internally depolymerize these molecules for energy production. Since most PHA polymers also depolymerize under human physiological conditions, they also are used in the medical field in non-textile areas like implants, etc. [8]. The decomposition products will be hydroxyl alkanooates, i.e. fatty acids, which will be easily degradable by most natural organisms.

Beside the inherent bioneutral degradation capability of such polymers, it is interesting to note that homopolymers as well as copolymers can be synthesized by using different substrates for the bacteria. Furthermore, changing the substrates over time also

allows for the production of block-copolymers [9]. Variations of chemically modified substrates can also be used to produce modified polymers [10]. In such cases, however, the environmental impact and corresponding biodegradability must be assessed individually.

The main drawback of these polymer types is the high cost. Although new developments led to a high yield of polymer output in bio reactors, production costs are governed by the raw materials, namely fatty acids. Production efficiency can possibly be increased through the bioengineering of the corresponding microorganisms, while the optimization of the fermentation process may lead to lower production costs [11]. Moreover, PHA polymers may be suitable for specialized applications, where low costs are not the main requirement.

Another natural carboxylic acid is hexanoic acid, or capronic acid. The cyclic form ϵ -capro lactone can be polymerized into poly- ϵ -caprolactone (PCL). The material can thus be understood as related to PHA. Monomeric raw material is usually produced industrially through the oxidation of cyclohexanone that

was derived from benzene in the first place. Most of the PCL available on the market is therefore of fossil origin, although biodegradable. Recent developments show processes for synthesizing capronic acid from corn stover and also discuss market opportunities for this approach [12], potentially rendering the polymer bio-based and biodegradable.

Poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) are also polymers built from natural monomers, so that their decomposition products will be lactic acid, succinic acid and a diol component. Because these building blocks are available on large industrial scales, a significant cost advantage can be achieved compared to PHA.

PLA can be manufactured in three different ways: the direct condensation of lactic acid, azeotropic condensation, and ring opening polymerization after prior lactide formation (cyclic lactic acid dimers), where the last two methods are the most common ones [13]. The raw material for all processes is lactic acid, which can be produced either by chemical synthesis or the fermentation of carbohydrates. The last process is widely investigated and optimized, so that most of the lactic acid for technical applications is produced in that manner [14]. Current processes utilize starchy biomass for fermentation, but recent developments applying metabolic engineering methods open opportunities to metabolize lignocellulosic substrates, which leads to a further reduction in costs [15]. For chemical synthesis, a multi-step approach involving the addition of HCN to acetaldehyde forming lactonitrile is followed. While the chemical synthesis delivers racemic products, stereo-chemically pure substances can be obtained through fermentation [16]. Thus, homo- and copolymers of L- and D- forms can be obtained exhibiting different thermal and mechanical properties.

To obtain PBS, succinic acid is used as a commodity that is produced mainly through fermentation [17]. Substrates can vary along different types of carbohydrates, depending on the chosen microorganism. As a rule, succinic acid is only one single product among others in the metabolic cycle of a bacterium. Accordingly, metabolic engineering is used here too, to delete pathways for the production of unwanted by-products [18]. Succinic acid is then directly polymerized with butane diol to form PBS.

The above-mentioned materials can be classified, at a minimum, as bionutral degradable, since decomposition will lead to monomeric building blocks that all have natural origins.

Other polymers, copolymerized from the building blocks of non-biodegradable and biodegradable polymers, sometimes show a significant biodegradability. However, this property is highly dependent on the ratio of the different monomer types involved. If decomposition products occur that are made of the initial building blocks or even of more complex nature, the sweeping claim of a bionutral degradability cannot be made as in the aforementioned cases. In fact, it must be determined whether an ultimate degradation eventually takes place or an assessment of the residues on the environment is necessary.

In particular, numerous studies have been conducted with the aim of determining whether microorganisms and/or enzymes are capable of decomposing such copolymers [19–21], sometimes evaluating decomposition by the weight loss of the polymer [22] or solubility [23]. Although remarkable efforts considering the amount of polymer types covered were made, these works give no insight into biodegradability or bionutral degradability as long as xenobiotic monomer building blocks were involved.

Thus, copolymers involving, for example, terephthalic acid or 1,4-butanediol may be decomposable by microorganisms, but the residues must be assessed. Since both substances are xenobiotics, the bionutral degradability of such polymers cannot be generally assumed.

Although not biodegradable by any means, it is interesting to look at the relatively new substance poly(ethylene furanoate) (PEF), which is discussed as a potential alternative to poly(ethylene terephthalate) (PET). It is partially manufactured from biomass and, although its production appears to be quite ambitious, it finds itself at the brink of becoming commercially relevant, which demonstrates that such processes can possibly be implemented successfully. It is obtained through the polycondensation of poly(ethylene 2,5-furandicarboxylate) (FDCA) and ethylene glycol. Publications discussing technical production from lignocellulose [24] and investigating material properties in depth [25] date back only five years. The chemical synthesis of furan derivatives as a precursor is reported by using starch [26] and cellulose [27]. An interesting approach for synthesizing 2,5-furandicarboxylate using supported noble metal catalysts was reported recently [28]. Industrial pilot plants started up in 2011 to produce 40 t/a of 2,5-furandicarboxylate. In the years that followed, different major chemical companies developed new processes, and partially joined forces to increase the

production of FDCA [29]. In 2016, AVA Biochem announced its objective to achieve a production capacity of 30,000 tonnes/year, increasing to 120,000 tonnes/year [30]. Textile applications have not yet been reported in patent or scientific literature. The material thus seems to be new and interesting as a replacement for PET-based polyesters. This may serve as a promising model for some of the above-mentioned processes, which are not yet commercialized.

3.1 Thermal properties

For technical applications, the thermal properties of the materials are of crucial interest. In Table 1, glass transition temperatures and melting ranges are shown for different homopolymers. Specific requirements will evolve from targeted applications, and polymers can be adapted through either copolymerization or blending. As long as bionutral degradable components are utilized, degradability should not expect to be altered. However, secondary reactions are possible and should be assessed before larger commercialisation efforts.

Table 1: Thermal properties of selected biodegradable polymers and PA, PP for comparison [31–34]

Biodegradable polymer	T _g (°C)	T _m (°C)
PLA	45–60	150–162
PLLA (L isomer of PLA)	55–65	170–200
PCL	–60––65	58–65
PHB	5–15	168–182
PH-octanoate	–32.6	162
PBS	–28.5	116.4
PA	50	265
PP	–15	176

A wide window of technical opportunities can be utilized by copolymerization, blending and the addition of plasticizers. Such additives need to be biodegradable too, so a wide range of materials can be considered, which is not covered here, but maybe in a future overview.

4 Degradation pathways

The molecular biodegradation of organic substances is usually conducted using microorganisms, such

as bacteria or fungi. For degradation in natural environments, the biodiversity of such organisms is crucial for ultimate biodegradability. Testing should therefore be done using organisms of ubiquitous occurrence in the targeted eco system and under respective test conditions. For industrial composting, the conditions can be adjusted, so a wider range of polymers may be utilized, if such a recycling method is targeted. Actually, commonly accepted test methods do not focus on that issue, which addresses a regulatory gap, should these substances gain wider market relevance.

Bionutral degradation can hypothetically occur chemically, since most of the mentioned polymers will eventually be hydrolysed. However, the rapid environmental ability to hydrolyse and lifetime durability frame a solid conflict of interest, which may be solved best only for single-use products or materials for indoor applications.

Degradation by microorganisms can take place intra or extra cellular. In the latter case, enzymes are secreted in the substrate which catalyse the degradation reactions. In every case, the physical properties of the polymer also contribute to the degradation properties. Besides the molecular weight, the crystallinity of the polymer also influences the degradation rate, since amorphous phases are generally more prone to the enzymatic attack [35, 36]. Also, higher melting temperatures are usually linked to the reduced ability to achieve enzymatic hydrolysis [37].

5 Costs

Many promising chemical efforts have been made to develop polymers with their respective production process to potentially produce biodegradable products. The issue of costs nevertheless remains a drawback. In 2000, the costs of PLA were estimated to be approx. five times that of PP, and PHA noted even more. A comparison with other commodity plastics do not show other major differences [38]. Ten years later, prices were reported to USD 3.5 to 4.5/kg for PHB and GBP 1.5 to 2.5/kg for PLA, while a prognosis for PHA cited that price could reach as low as EUR 1 to 2/kg [39]. In late 2017, prices for commodity polymers (US export) are as follows: USD 2.7/kg for PET, USD 8.4/kg for LDPE (low density polyethylene), USD 9.2/kg for PA and USD 1.9/kg for PLA [40] However, a wide range of prices was found depending on the exporting country. This shows that at least PLA prices are similar to those of commodity

polymers. Since lactic acid for the production of PLA is mostly synthesized through fermentation and PLA is gaining market share, the reduction in price may be a scaling effect. From this, it can be estimated that prices of other polymers such as PHA/B and PBS will also be competitive, if scaling markets will allow for that. Available data for the commodity pricing of PHB is rare, but Mudliar et al. published an evaluation of production costs for a hypothetical production plant, and determined a value of USD 5.38/kg for the best investigated case [41].

6 Textile applications

Synthetic polymers in textiles can be considered in three fields: the fibrous material itself, coatings and finishings, and fibre-reinforced composites. The latter has already been widely investigated for example using natural fibres and bio-based or biodegradable polymer matrices. Since matrix development is a broad field and is also closely linked to the used fibres, this topic is not further discussed here. However, interesting opportunities are given in the field of coating and finishing, and in the field of fibrous raw materials.

Research method

To assess the current situation regarding the use of biodegradable polymers in these fields, a systematic literature and patent review was conducted. For this, the academic search engines *Google Scholar*, *Microsoft Academic*, *Crossref*, and *Clarivate's Web of Science* were consulted, while the patent research was conducted using a search engine provided by the German patent office.

The first three databases were queried using the keywords “*biodegradable polymers*” and a search period of the last 30 years if applicable. This delivered approx. 2,000 results. The results were exported to the open source literature database *JabRef* [42] and filtered by the regular expression `title="fibre"` or `title="fabric"` or `title="textile"`, resulting in 83 hits.

Clarivate's Web of science was queried using the regular expression `ts=(biodegradable polymer$) AND (Ti=textile$ or ti=fibre$ or ti=fabric$)` to search within the category of *biodegradable polymer(s)* for publications with *textile(s)*, *fibre(s)* or *fabric(s)* in their titles. The results were then refined using the Web of Science category *Materials science*, subcategory *textiles*, delivering 81 results.

Since the initial manual overview showed a high number of papers dealing with electrospun PLA nanofibres mostly for medical applications, both results were filtered in *JabRef* using `abstract!=PLA` and `title!=PLA` and `abstract!=nanofib` and `title!=nanofib` and `abstract!=electrospun` and `title!=electrospun` and `title!=lacti`, which excludes publications with the respective substrings in the title leaving 95 results that were manually evaluated by title and abstract, delivering 47 results.

A similar approach was applied for PLA and electrospun nanofibres, delivering 45 and 15 results, respectively, regarding these topics alone.

For the topic of biodegradable coatings, *Clarivate's Web of Science* was queried using `ts=(biodegradable coating$) AND (ts=textile$ or ts=fibre$ or ts=fabric$) AND ti=biodegradable`.

A patent search was conducted exclusively for the coating topic using `ti=biodegradable UND PUB>1.1.2000 UND AB=coating UND (AB=textile? ODER AB=fibre? ODER AB=fibre? ODER AB=fabric?) NICHT ti=wound NICHT ti=medical`, delivering 132 results which were manually revised, leaving 25 hits for further evaluation. *Ti* searches in the title, *PUB* defines the publication time, *AB* searches within the abstract and the question mark acts as wildcard for one or more characters. Since the search engine is German, the operator *UND* stands for *and*, *ODER* for *or*, and *NICHT* for *not*. However, international patents from the world patent office (WPO) were also delivered by these queries.

Results for PLA and electrospun fibres for medical applications

As expected, PLA and its derivatives are the most common biodegradable polymers for fibre fabrication. A wide field of application is given in medical contexts. For example, stents made from PLA and coated by a layer-by-layer technique with chitosan have been investigated [43]. Scaffolds for tissue engineering are another field where physiological biodegradation is useful. The degradation of PLA in vivo may lead to local decrease of pH due to the produced lactic acid, while medium molecular weight oligomer degradation products can also potentially initiate immune responses in some patients. It is therefore crucial to understand the influences or fabrication parameters on the degradation rate, since extrusion speed and twist of the spun PLA fibres is reported to have an impact on those, besides the chemical composition of the polymer

[44]. Further research in that direction was done by studying the influence of plasma treatment on the moisture wicking behaviour of PLA fabrics [45]. Shape memory textiles are interesting materials in the medical field, for example for self-adjusting implants, scaffolds or anchor systems for grafts. Nonwoven materials fabricated using melt blown PLA-PHB blends have shown shape memory properties while being biodegradable [46]. Biodegradable ligament replacements can be considered to be made of PLA-PCL copolymers, so their creep and stress-relaxation properties have been investigated [47]. The rheological properties of PLLA and PLDA (L and D isomers of PLA) have been studied to produce physiological degradable fibres having a potential drug delivering property [48]. Hollow PLA fibres obtained by melt spinning can serve as platforms for the delivery of drugs in the medical field, but also for the retarded release of pesticides in agricultural settings. Melt spun PLA 9 fibres have been investigated for that purpose based on different physical properties [49]. Sutures are another field where PLA is a useful polymer. The stiffness of pure PLLA was reported to be reduced by blending with PLA-co-caprolactone copolymer [50].

In addition, potentially implantable sensors made from PLA components have been reported, with the advantage of not requiring explantation after therapy [51]. A special composite made from PLA and CNTs was produced using a melt blown process to produce sensory fibres [52].

The antibacterial properties of PLA fibres coated with titanium oxide have been investigated. However, the use of such material in medical applications requires a thorough assessment of possible side effects and cytotoxicity [53].

It can often be seen that lots of effort is put into developing new medical materials or devices, but regulatory issues are not addressed in the early stages of such research. This can lead to obstacles in the subsequent development to commercialized medical products [54]. Commercially available melt spun PLA fibres often contain finishings from secondary spinning, which may hinder medical uses. Jozwicka et al. studied different PLA fibre types and found glycerol as a suitable finish for medical appliances [55].

Electrospinning is a process capable of delivering nanofibre fabrics exhibiting a high surface area and small pore sizes, but can only be utilized in small scales. This issue renders the process suitable for only specialized applications. However, the possibility of

incorporating additional substances, such as pharmaceuticals, make these materials interesting candidates for drug delivery [56, 57]. A material spun from polyethylene oxide and poly vinyl alcohol was investigated for the use as a scaffold for potential tissue engineering [58]. In addition, blends of PLA and PCL with added hydroxyl apatite were investigated as electrospun nanofibre mats [59]. Additional insights on electrospun biodegradable scaffolds are given by Sun et al. [60]. A further detailed review on biodegradable polymers for tissue engineering is also given by Xing et al. [61].

Summary of medical applications of PLA

A wide range of ambitious applications can be seen for the utilization of PLA fibres in the medical sector. Electrospun nano fibres made from physiologically degradable polymers are promising substrates for tissue engineering and drug delivery.

It is therefore obvious that lots of effort is currently directed to that area. It is furthermore known that commercial feasibility is crucial for the widely accepted clinical use of medical products. One pathway is keeping the investment burden low by addressing regulatory issues in the early stages of research. This is especially necessary for the development of new textile products in that field, since they mostly address market fields with modest profit opportunities.

Results beyond PLA and medical applications

Research in biodegradable polymers in the textile context, excluding PLA and medical textiles, has been reported in fewer publications.

A drawback of PHBV (poly hydroxy butyrate valerate) lies in its low crystallization rate, which challenges melt spinning. Hufenus et al. investigated a core shell structure with PLA in different configurations, together with a special spinneret, to overcome this issue [62]. As early as 2000, Schmack et al. investigated the melt spinning of PHB and the dependency of drawing speed on the resulting crystal structures using wide-angle X-ray scattering [63] for use in textile applications. PHB and PHBV have limitations in the melt processing, since at higher temperatures (above 160 °C as reported), cis-elimination leads to random chain breaks. Moreover, bacterially produced PHB is strongly isotactic; together with its glass transition temperature of 5–15 °C, the material shows significant brittleness. The underlying cause of high crystallinity lowers its degradation rate under physiological conditions [64]. The authors also summarized different

works dealing with spinning conditions to control the crystallisation behaviour of the spun fibres, including the use of cyclodextrins as nucleation agents.

Bicomponent fibres were also studied based on the poly butylene terephthalate/poly butylene succinate lactate system. The drawing speed influenced the core shell ratio, while the range between 65% and 35% delivered the maximum fibre strength [65]. Also, here the ultimate biodegradability can be questioned due to the terephthalic acid monomer. Although less toxic, the substance can be considered a xenobiotic.

Twarowska-Schmidt evaluated two commercially available PBS derived polyesters (poly butylene succinate adipate (PBSA) and poly butylene adipate terephthalate) in terms of their fibre forming capability in a melt spin process, as well as their degradability. For the latter, only the weight loss of the fibres was recorded, so it is highly likely that at least terephthalic acid or potentially oligomers will be found in the substrate. As expected, the aromatic ester was degraded to a higher extent, but this only remains true for higher degradation temperatures. Thus, the general rule for the aliphatic esters is only partially valid here. Although the low glass transition temperatures of the materials (-33 °C and -44 °C) can be an issue for apparel, technical applications such as those in the medical or agricultural sector are considered to be feasible [66].

The cost issue of PHA is addressed by a recent publication regarding the production of PHB in cyanobacteria [67]. However, commodity prices for PHAs, PBS or similar polymers are not available, since the materials are not yet commercialized.

Summary beyond PLA and medical applications

The remaining field, after excluding medical applications, composites and PLA materials, spans mostly across PBS and different types of PHA. The production of fibrous materials out of these polymers remains challenging, when mechanical requirements set higher stakes. While the degradation over time is the key feature in drug delivery systems, technical applications require specific tensile stiffness, elongation behaviour, brittleness, etc. together with textile haptics in the final fibrous product. Furthermore, the processing properties of the polymer must be met, e.g. processing temperatures, viscosities and crystallization rate, to successfully melt spin them into these fibres. Subsequently, the produced fibres must be spun secondarily to yarns and woven, knitted or fabricated otherwise into textiles.

Results of biodegradable textile coatings

During the review of literature, it became evident that almost no scientific publications exist that address the coating of textiles using biodegradable polymers, with some exceptions in the medical field utilizing chitosan. Consequently, an additional literature search was conducted, together with a patent search on that topic.

Some authors have reported the development of a super hydrophobic coating made from soya bean oil, stearic acid and ZnO [68]. This approach will probably lack an ultimate biodegradability because of the ZnO particles. A similar approach was established using poly dopamine [69]. Yarn sizing using nano cellulose and soy protein has been investigated [70]. Antibacterial coatings achieved by silicone containing cations have also been reported [71], but the ultimate biodegradability can be questioned, at least because the ultimate degradation of silicones is not defined. As a result, the most meaningful definition may state silicon oxide as end product.

The patent search delivered even fewer results, excluding medical applications. Glycerol together with gelatine for coating of natural fibres is described in KR000100647872B1 (2006). A coating for a biodegradable textile is described in FR000002879224A1 (2004) using natural rubber latex, and proteins. The coating of sheet substrates and fabrics is considered in US020050031882A1 (2005) by PHA copolymers. An aqueous dispersion of PHB is described in EP000001566409A1 and in JP002004099883A (2003) for PVA, which can potentially be applied as a coating. JP002003221786A (2002) utilizes PVA together with sulfonic acid polymers for polyester fibre finishings. However, the sulfonic acid polymer may not be ultimately biodegraded. The Canadian application CA000002410457C (2010) deals with different PHA copolymers for the coating of fabrics, threads or yarns. In JP002002121288A (2002), the use of more or less degradable plasticizers for formulating an aqueous dispersion of a biodegradable resin is claimed.

Summary of biodegradable textile coatings

Scientific literature only discusses textile, biodegradable coatings for non-medical applications to a lesser extent. However, patent literature shows some evidence for commercial attention in that area, although this is also limited. The patents found likely address textile coatings more as an additional option. But aqueous coating dispersions are also discussed there, which is valuable, since the discussed polymers in

this study are thermoplastics and one would consider extrusion coating in the first place. However, a water-based coating is a common textile technique, and the associated patents allow for conceiving such an application onto textiles too.

PVC (polyvinyl chloride) is a cheap and widely utilized coating substrate for textiles, but acrylates and polyurethanes are also applied. Thus, it is somehow surprising, that nearly no biodegradable alternatives are discussed in recent literature.

7 Future opportunities

Younes classified different biopolymers regarding their commercialization in a review in 2017. Classes ranged from *research, pilot plant, commercial, large scale, to mature* [72] Maturity was assigned only to cellulosic materials, which is not surprising. PLA was noted as the only one in the *large scale* group. PHA/B was classified between pilot plant and commercial, and PBS in the research state. It can be assumed that cost effects play a major role here, since petrol-based and non-biodegradable polymers are usually more cost efficient. Congruent with his findings is that PLA is narrowing its price gap to petrol-based commodity polymers. In the medical sector, physiological biodegradability represents an additional function that justifies higher costs. However, public pressure and/or regulatory issues may shift parts of the textile economy to biodegradable materials.

In the sub field of geo textiles, biodegradability can be conceived as an additional function, making it an interesting application sector. The need for development is given by the tailoring of the degradation rate, depending on operational conditions. It would also be a great advantage if such geo textiles could be fabricated with a defined lifetime and if the degradation rate over time could be engineered. But as discussed previously, manufacturing requirements must also be met by such new materials. Meeting both challenges may lead to new products, which could result in higher market prices. It should be noted that different semi-finished products can be found on the path from polymer, over fibres, yarns, possibly textile surfaces or nets to the finally confectioned product. Thus, many production steps must be covered.

Other fields in technical or apparel textiles will most probably not make use of the biodegradation function directly. That function may, however, be beneficial in the recycling of these products.

The direct utilization of fibrous materials in apparel can be considered. For this, however, different issues must be addressed: Again, the material properties must be designed so that production on conventional machinery for all intermediate semi-finished products is realizable. Secondly, the degradation rate must be tailored so that it will not take place at significant rates during the normal product life. Thus, hydrolyzability issues might need to be addressed. PHAs, in particular, may release fatty acids during hydrolyzation, which can lead to olfactory discomfort, even in lower amounts that do not affect the substrate's mechanical stability. Furthermore, such new products should exhibit comfortable textile haptics. However, synthetic materials offer numerous opportunities to fine tune these kinds of properties.

The literature and patent search resulted in a significant gap in the field of textile coatings. A few research bodies are already aware of this gap [73]. It is therefore a highly interesting field for research and new developments. It is also interesting for recycling purposes to develop materials composed of similar chemical substances, since no material separation is necessary. The variety of synthetic biodegradable polymers due to the abundance of raw materials, and the ability to form blends, copolymers and introduce additives can pave a way to coated textiles, where the fibrous substrate and the coating are made at least of similar biodegradable chemistry. Biodegradable fibres, either natural or manmade, are gaining market share in the technical textiles sector, while biodegradable coatings seem to lie inevitably on the way.

Coatings can be applied on textiles through the extrusion of thermoplastics or by applying aqueous dispersions of polymers, e.g. by knife coating or other means. One research target is therefore the manufacturing of such stable and applicable dispersions with the new polymers, which includes issues such as viscosity tailoring, degradation and storage stability, and drying properties of the applied wet film.

In addition, crosslinking offers the opportunity to develop possibly biodegradable duromers, which may also help to enhance the mechanical stability of such coatings. It is thus additionally of fundamental research interest to study the degradation pathway and decomposition products of such crosslinked polymers.

Further general fields of research are the development of biodegradable plasticizers, flame retardants, crosslinkers, and other additives.

8 Potential textile products

Many textile products can be conceived assuming the successful outcome of the above-described research and development efforts. To start with, blended fabrics, currently made of wool and polyester for suit fabrics, offer a high-priced market segment. The replacement of petrol-based polyester by a natural, ultimately biodegradable polyester could lead to a fully biodegradable product. Even buttons could be easily made of such polymers. While zippers out of plastics may not appear very reliable, buttons can be a replacing design element here. The additional feature of ultimate biodegradability may result in a premium on the price, considering current consumer sentiments. In the area of textile coatings application fields in protective clothing, textile membranes or laminates, carpets, tents, artificial leather and others can be considered, as they offer a wide range of addressable research topics. An interesting point here is the control of the degradation rate. It could be beneficial to switch the degradation behaviour of such coatings through environmental parameters, for example temperature together with humidity, or the presence of certain auxiliary substances (e.g. pH). The materials could be rendered resilient to the influence factors of the desired application, but could be compostable on an industrial scale. However, those materials may not degrade easily in natural environments. Thus, issues of littering or abrasion of micro particles cannot be avoided by chemical means alone.

9 Conclusion

For the assessment of manmade biodegradable polymers, first some definitions must be commonly accepted. Some already exist, but the handling of possible degradation products may not be regulated very well, although they are of great importance from an environmental point of view.

Only a few manmade biodegradable polymers in the narrow definition of this report are already commercialized. This is especially true for the textile sector beyond medical textiles, and fibre-reinforced composites. However, the most dominant polymer of that kind is PLA. Other polymers are in the research or development state, but offer interesting opportunities for textile fabrics and coatings due to the diversity of the substance classes. Coatings, in particular, are only rarely covered in recent literature, which makes

it a promising field of further development, given that textile base substrates will be replaced by more eco-friendly substances in the future.

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