Polymer Degradation and Stability 95 (2010) 2147–2161

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Environmental and resource aspects of sustainable biocomposites

Francisco Vilaplana [a,b], Emma Strömberg [a], Sigbritt Karlsson [a,*]

[a] School of Chemical Science and Engineering, Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, SE-10044 Stockholm, Sweden
[b] Centre for Nutrition and Food Sciences (CNAFS) and School of Land, Crop and Food Sciences (LCAFS), University of Queensland, Hartley Teakle Building, Brisbane, Qld 4072, Australia

ARTICLE INFO

Article history:
Received 12 March 2010
Received in revised form
16 July 2010
Accepted 26 July 2010
Available online 4 August 2010

Keywords:
Biocomposite
Degradation
Nanoparticle release
Renewable resources
Life cycle analysis

ABSTRACT

This review critically discusses the environmental and resource implications for the design of sustainable biocomposites. Sustainable biocomposites should satisfy several requirements: (i) renewable and/or recycled resources should be utilized for their manufacture; (ii) the synthetic, modification, and processing operations should be benign and energy effective; (iii) no hazardous environmental or toxicological effects should arise during any stage of their life cycle; and (iv) their waste management options should be implemented. The future integration of biorefineries and green chemistry will guarantee the availability of a wide range of raw materials for their preparation. The emission of volatile organic compounds and the release of nanoparticles should be evaluated from a toxicological and environmental point of view. Finally, the susceptibility of sustainable biocomposites towards degradation, including abiotic effects (water absorption, thermo- and photo-oxidation) and biofilm formation and biodegradation, must be considered, to guarantee their structural and functional stability during service life, and to ensure their biodegradability and assimilation during composting.

1. Introduction: sustainability concepts for biocomposite materials

Mankind faces global challenges during these first years of the new century, in the attempt to maintain the economic growth and social welfare achieved during the last decades. The industrial revolution brought unimaginable benefits to humanity in terms of optimised material and energetic products and processes, together with increased living standards for most societies, but has also compromised the fragile environmental equilibrium of the last 10,000 years in the so-called Holocene geological epoch. Indeed, some researchers argue that the environmental stress caused by the uncontrolled industrial development may have pushed our planet into a new geological era, the Anthropocene, in which human activities are the main driving force for environmental changes [1]. A recent study driven by the Stockholm Resilience Centre introduced the concept of planetary boundaries, a number of measurable environmental parameters (e.g. climate change, biodiversity loss, nitrogen and phosphorous cycles, ozone depletion, ocean acidification, global freshwater use, land use, atmospheric aerosol loading, and chemical pollution) that should not be surpassed to avoid unacceptable environmental changes and to preserve the environmental equilibrium and stability of the Holocene epoch [2]. Although three of these boundaries may have already been surpassed, there is a high level of uncertainty about how long it takes for these excesses to cause irreversible effects [3]. There is therefore a pressing need for a paradigm shift in our material and energetic production and consumption patterns, by truly becoming sustainable societies, taking into account these planetary boundaries and thus preserving environmental stability.

It is interesting for the purposes of the present review to perform an “etymological” study and dig into the origin of the concept of ‘sustainable development’. The term ‘sustainable development’ or ‘sustainability’ was first coined by the Brundtland Commission (formally the World Commission on Environment and Development of the United Nations in 1983), and was defined as the “*social and economic advance to assure human beings a healthy and productive life, but one that did not compromise the ability of future generations to meet their own needs*”. [4] The significance of this definition is that, for the first time, environmental and social effects were placed at the same level of importance as economical benefits. Recent policy guidelines from the United Nations encourage sustainable industrial development through cleaner and more resource-efficient industrial production (addressing industrial waste streams, minimizing the use of hazardous substances, and implementing suitable health and safety procedures) and promoting corporate environmental and social responsibility [5]. Similarly, the European Commission set the grounds for a long-term European Union Sustainable Development Strategy (EU SDS), revised in 2006, through 7 key priority challenges [6,7]: (i) Climate

---

[*] Corresponding author. Tel.: +46 8 790 8581; fax: +46 8 100775.
E-mail address: sigbritt@kth.se (S. Karlsson).

0141-3910/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2010.07.016

change and clean energy; (ii) Sustainable transport; (iii) Sustainable consumption and production; (iv) Conservation and management of natural resources; (v) Public Health; Social inclusion, (vi) demography and migration; and (vii) Global poverty and sustainable development challenges. The implementation of the EU SDS is continuously evolving through new policy actions and being monitored, especially in the current situation of economic and financial crisis, to turn the disadvantageous circumstances into an opportunity of creating a true "*low-carbon*, *resource-efficient*, *knowledge-based*, *socially-inclusive society*" [8].

During the last 25 years a new metadiscipline of 'sustainable science and technology' has emerged, which aims to integrate basic research, education, and technological transfer to meet this view [9]. A main hindrance to the effective implementation of sustainable solutions in industry and society is the vagueness of the concept of sustainable development. It is necessary to translate the implications of sustainability into each scientific, technological, and industrial field, by creating operational definitions and introducing metrics for evaluating sustainability in each specific case [10]. The introduction of Life Cycle Assessment (LCA) studies in product and material processes has definitely been extremely helpful in assessing environmental impacts across all stages of production, use, and waste management. In the case of science and technology of polymeric materials, the implications of sustainability need to be addressed and identified, including the choice of raw materials, the synthetic routes for material design, material processing into desired products, exploitation during service life, and final waste management. It is the vision and the aim of the present review to discuss and illustrate these factors.

Natural polymers and biocomposites have been known and utilized by mankind since ancient times. However, the use of these nature-based polymers was completely outpaced in the twentieth century by the explosion of the use of synthetic polymers. Conversely, during the last two decades, interest in biopolymer and biocomposite research has grown as a result of environmental concerns and the depletion of fossil resources, as it can be demonstrated by the exponentially rising number of patents and publications about biocomposite materials [11]. Several recent review articles have been published since year 2000 in different material and polymer science journals, devoted to the preparation, processing, and properties of biocomposites for a wide range of applications, and even social and economic issues [11–31]. These reviews offer an excellent perspective on the state-of-the-art of polymeric-based biocomposite materials science and technology research, including the different families of polymeric bio-based matrixes and natural lignocellulosic reinforcements, their preparation and modification routes, their properties and their tailored applications in biomedical, packaging or structural applications. The objective of this review differs, however, in that it aims to cover the environmental implications of the design and use of biocomposites from a sustainable perspective. Biopolymers and biocomposites have been described as sustainable materials in contraposition to traditional synthetic polymers and composites reinforced with inorganic synthetic fibres, in terms of the usage of existing renewable resources as raw materials, their low eco-toxicity, and their biodegradability. This review will discuss the sometimes confusing definitions for biomaterials, biopolymers, natural polymers, and biocomposites, and will offer a proposal for defining sustainable biocomposites. The review will address as well the resource implications for the design of sustainable biocomposites, the different routes for chemical modifications of both matrixes and reinforcements from a green chemistry perspective, the environmental implications of the use of biocomposites in terms of emissions of low molecular weight compounds and toxicological effects of emitted nanoparticles, and their (bio)degradability issues.

2. Definitions: biomaterial, biopolymer, natural polymer, biodegradable polymer, biocomposite, bio-based composite, green composite and sustainable biocomposite

It is important to clarify the definitions of the new sustainable materials emerging in research and on the market, to avoid confusion in the use of the related terminology. Terms such as biopolymer and biomaterial are often used interchangeably, though a biomaterial should strictly be referred to as a biomedical material and does not necessarily need to be a polymer. In this review we propose a classification of the definitions and the discussion is based on the terminology suggested in an upcoming CEN-standard [32].

The proposed definition for biopolymers involves materials consisting of units that are entirely or in part derived from biomass (e.g. materials with biological origin) [32]. Accordingly, a wide range of materials can be considered as biopolymers; for example, poly(lactic acid) (PLA), in which the monomer/repeating unit is derived from natural resources by fermentation of starch, is included in the definition even though the polymer itself is a product of a chemical or enzymatic synthesis. It is therefore necessary to distinguish natural polymers amongst biopolymers; natural polymers are defined as polymeric materials synthesised as such in nature, e.g. cellulose, starch, proteins. In this case, all natural polymers can be considered as biopolymers, but not all biopolymers are natural polymers.

Several definitions for biocomposites have been suggested during the past years. Mohanty et al. [33] defines biocomposites as composite materials in which at least one of the constituents is derived from natural resources. This definition corresponds well to the definition of biocomposites stated in the CEN standard. This offers endless possibilities for the design of the composite matrixes, ranging from biopolymers to petroleum-based virgin or recycled polymers. The possibility of using recycled polymers in the design of biocomposites, improving the material properties of the recyclates by the incorporation of renewable reinforcements, can result in products with lower environmental impact. Within the definition, the reinforcement materials can originate from renewable resources or be inorganic fillers (in the case of a biomass-based matrix). Biodegradable biocomposites, in which the polymeric matrix can originate from biomass or be petroleum-based, can be referred to as green composites. It is fundamental to differentiate biopolymers from biodegradable materials since the origin of the raw material can vary. For example, poly(ε-caprolactone) (PCL) is a petroleum-based polymer but is completely biodegradable and therefore can be classified as a green matrix. These composites can be degraded by anaerobic or aerobic biological processes, leading to the formation of carbon dioxide, water, methane, biomass, and mineral salts. Reinforcement of the biodegradable materials with natural fibres give improved material properties, desired in various applications, without compromising biodegradability. If both the matrix and the reinforcement are derived from biomass the resulting material can be referred to as a bio-based biocomposite.

When designing a new product, the time-dependency of the resource renewability should be considered. There is a substantial difference when comparing rapidly renewable materials, with an agricultural or bacterial base, to raw materials that take several years to restore, for example wood, or to oil with a nearly infinite formation time.

The concept of sustainable materials is problematic to define. True sustainability is obtained by considering the whole life cycle of the product, from the origin of the raw material to the waste management. Here we propose a new definition for sustainable biocomposite: A composite material in which at least one of the constituents is derived from natural resources and the impact of the material throughout its entire life cycle can be considered positive without interfering with the surrounding environment. The source and production of the raw materials, the material processing, the service-life of the product and waste management should be evaluated in terms of energy and chemical consumption, emissions, and toxicology upon use and disposal for a biocomposite to be considered sustainable. Sustainable biocomposites should thus satisfy several requirements: (i) renewable and/or recycled resources should be utilized for their manufacture; (ii) the extraction, synthetic, modification, and processing operations should be benign and energy- and cost-effective; (iii) no hazardous environmental or toxicological effects should arise during any stage of their life cycle by emissions of degradation compounds, additives or fillers; and (iv) their waste management options (recycling, composting, and incineration) should be effectively considered and implemented to guarantee the return of the material and energetic value of the biocomposite back to the cycles.

3. Resource and environmental considerations for the design of sustainable composites

The design of sustainable composites should consider all the stages involved in their life cycle, including extraction of the raw materials, synthetic and modification processes, processing and manufacture into final products, service life, and subsequent waste management of the residues (Fig. 1). This section critically analyses each of these interrelated steps, discussing future trends in terms of resources for biocomposites (biorefineries), benign procedures for their synthesis and modification (green chemistry) and evaluation of their environmental performance throughout the life cycle.

3.1. Resources and synthetic routes for sustainable composites: trends, future biorefineries and green chemistry

Considering the definition of sustainable composite, a wide range of raw materials can be used for their design, always taking into account the energy consumption and harshness of the chemical processes involved for their synthesis and modification, the environmental impact during service life, and the waste management processes for the effective return of the material and energetic value of the product to the environment. Considering the polymeric matrix, different families could be utilized:

(i) natural polymers extracted from renewable resources, such as starch, cellulose, proteins, or chitin.
(ii) polymers produced by microbes, such as poly(hydroxyalkanoates).
(iii) polymers synthesized via chemical or enzymatic processes, whose monomers are obtained from renewable resources, such as poly(lactides) or renewable epoxy resins synthesised from vegetal oils.
(iv) recycled synthetic polymers that can be upgraded for new applications by the addition of natural reinforcements.

Taking into account sustainable concepts, the choice of biodegradable polymers that are synthesized from fossil resources, mainly synthetic polyesters such as poly(ε-caprolactone), should be

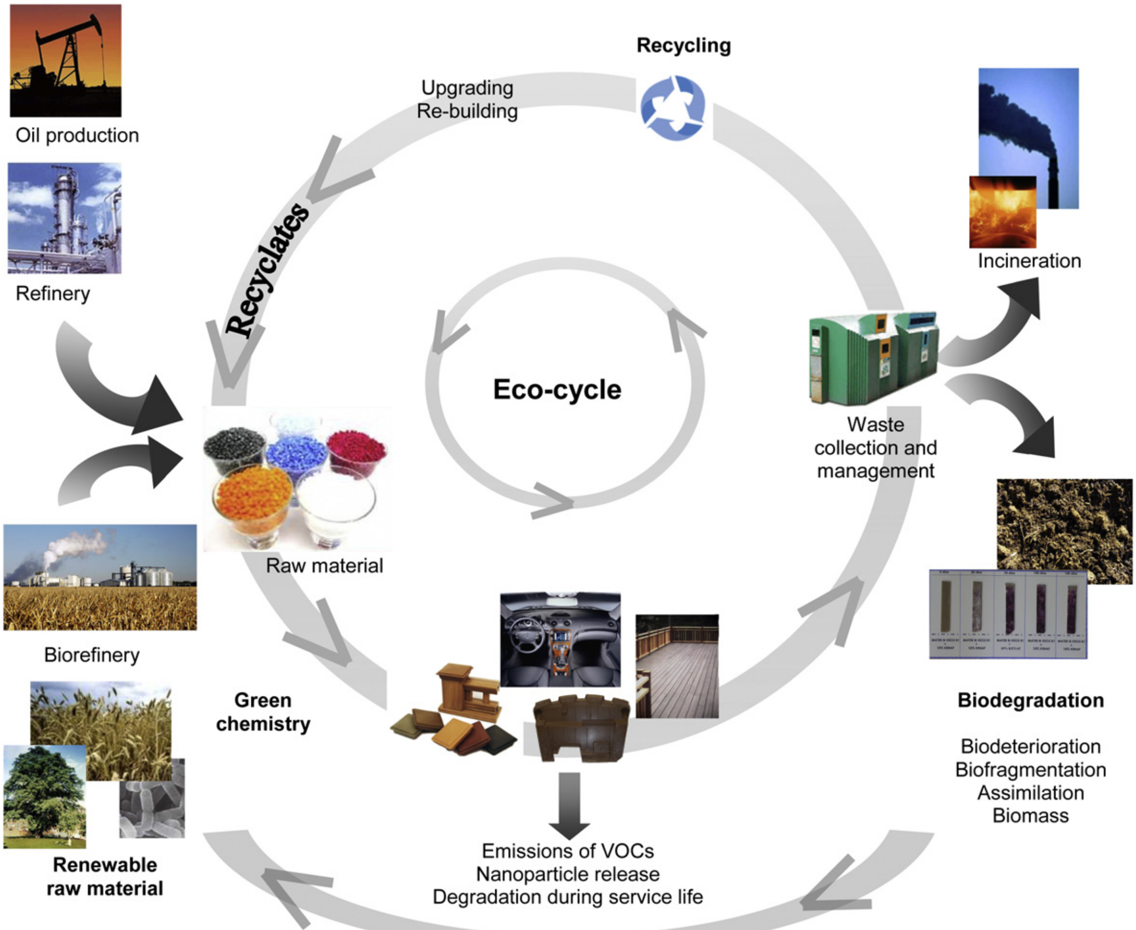

Fig. 1. Life cycle of sustainable composites.

taken with precaution. In these cases, independent life cycle analyses should be performed to evaluate their sustainability.

In terms of the reinforcements, a wide range of materials from various origins can be used in the manufacture of sustainable biocomposites, and can be grouped as follows:

(i) Lignocellulosic materials, including wood flour, natural fibres, and nanofillers (cellulose whiskers and starch nanocrystals)
(ii) Inorganic (nano)reinforcements that may contribute to the enhanced biodegradability of the resulting (nano)biocomposites
(iii) Different synthetic waste materials that can be recycled and incorporated into new products as reinforcements, such as rubber tyres

A preference order for the choice of original raw materials should be defined in terms of sustainability to design new products based on biocomposites. Ideally, the manufacture of green biocomposites should imply that both the matrix and the reinforcements arise from renewable resources; the use of natural polymers as matrixes and reinforcements should be especially encouraged when possible. The use of microbial polymers, e.g. the family of poly(hydroxyalkanoates) (PHAs) and the synthesis of new biopolymers using monomers from renewable resources appears to be a very promising route for designing polymeric matrixes with tailored properties; the eco-efficiency of their synthesis and manufacturing routes should also be assessed in terms of sustainability. Finally, the utilization of recycled synthetic thermoplastic and thermosets as polymeric matrixes in biocomposites should be considered as a favourable step in the sustainability of material technology. The beneficial effect is twofold; on one hand the waste stream volumes of discarded synthetic non-degradable polymers are minimized, and the energetic and material value of once synthesized and processed polymers are maintained by their new use in second-life applications.

However, these resources need to be processed to some extent to be able to be used as raw materials for the preparation of biocomposites; even natural polymers such as cellulose, chitin, and starch need first to be extracted from their natural origin and modified accordingly to the desired properties. These processes will ideally be performed in the near future in an integrated facility, a so-called biorefinery. Similar to the advent of petrochemical plants in the 20th century, the 21st century will see a paradigm shift for energy and chemical production based on biomass in biorefineries [34]. Biorefineries are integrated operating plants capable of accepting different streams of biomass feedstock for energy generation and conversion into valuable chemicals and materials through different physical, chemical, thermal, and enzymatic processes [34–36]. Biorefineries for energy and material production must not compromise at any point the food chain supplies; the choice of biomass feedstock should therefore involve a wide range of renewable resources including low value plants, energy crops and by-products from food crops, sawmills, palm oil production, marine wastes and food wastes [35]. The operations that may be performed in a biorefinery facility will involve (i) the extraction of valuable chemicals from biomass; (ii) the isolation of natural biopolymers and their further modification; (iii) the hydrolysis of biomass and further fermentation into so-called bio-platform molecules (bPM) that will be used as building blocks for value-added chemicals; and (iv) the use of chemical co-products from fuel biorefineries, thermochemical conversions of biomass by pyrolysis, or gasification [37].

In general, biorefineries will produce fuels and different fractions of chemical products, both high-volume low-value and low-volume high-value substances, which could be used for the synthesis of new polymers and composites in a similar fashion to petrochemical plants (Fig. 2). A recent perspective article by Gandini [38] identified the target families of polymers from renewable resources that may play the most important role in mid-term macromolecular science. These materials include polysaccharides and their derivatives, lignin, suberin, natural macromonomers (vegetable oils and tannins), natural monomers (terpenes, furans and lactic acid), bacterial polymers (bacterial cellulose and PHAs), and glycerol and alcohol-based monomers. This list of prospective macromolecular materials from renewable resources agrees well with the expected outcome from future biorefinery integrated plants. Natural polymers such as cellulose, chitin, starch, hemicelluloses, lignin, other non-starch polysaccharides (arabinoxylans,

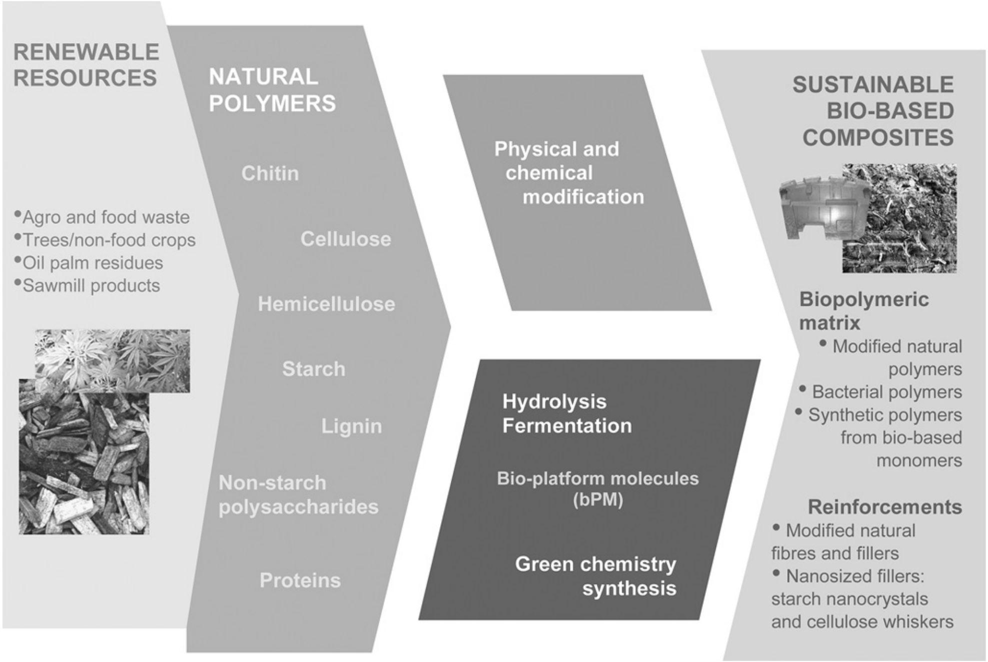

Fig. 2. Future integration of biocomposite manufacture using renewable raw materials from biorefinery processes. Redrawn using information from [35].

glucans), and proteins should be extracted from their natural form in biorefineries using green processes and further modified according to their intended applications. On the other hand, bioplatform molecules (bPMs) can be obtained from hydrolysis of biomass and further fermentation of the hydrolysed mono- and oligosaccharides; these bPMs can be used as building blocks for value-added chemicals and polymers, analogous to petro-platform molecules (ethylene, benzene) [37,39]. A recent report from the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) for the US Department of Energy [40] identified the most important building blocks that can be derived from biomass for further modification into high-value chemicals and polymers. These chemicals include polyalcohols (glycerol, xylitol, sorbitol), organic acids (lactic acid, citric acid, 3-hydroxypropionic acid, fumaric acid, malic acid, succinic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid), and ketones (3-hydroxy butyrolactone). High-performance natural reinforcements for biocomposite materials, such as nanofibrils and nanocrystals, can also be obtained from biomass feedstock by physicochemical operations [24,26]; these processes may as well be integrated in biorefinery facilities in the near future.

Sustainability in material science and specifically in polymers and composites is defined not only by the choice of renewable or environmentally-friendly resources for their manufacture, but also by the development of mild chemical processes that avoid the utilization and production of hazardous substances and thus minimize their environmental impact. This approach, well-known as green chemistry, should be therefore implemented in each step of the manufacturing process for biopolymer and biocomposite materials, including their synthesis and modification. Green chemistry philosophy involves the utilization of benign solvents (aqueous and ionic media or supercritical fluids) in chemical reactions, the minimization and/or use of alternative energy sources in chemical transformations, and the use of non-hazardous catalytic systems [41]. In polymer chemistry, these concepts have been introduced and applied in the recent years to the synthesis of tailored (bio)polymers, by using renewable materials, by employing enzymes and bacteria for polymer synthesis, by recycling and/or removal of metal catalysts, and by performing synthetic reactions in aqueous or ionic media [42–44]. For biocomposite design, modification of the reinforcements and/or the matrixes constitutes an important step in improving the interfacial adhesion between the components, thus enhancing macroscopic properties such as mechanical properties, barrier properties, and resistance towards moisture absorption. In particular, surface fibre modifications are usually performed by chemical means, such as dewaxing, alkali treatment, graft copolymerization, silane treatment, etherification, acetylation, peroxide treatment, or grafting with coupling agents (isocyanates, anhydrides) [28,45]. Some of the compounds employed in such modifications are hazardous, which compromises the sustainability of the manufacturing processes; further work should therefore be devoted to exploring green chemistry processes for the surface modification of the reinforcements in biocomposites. An interesting approach to improving the matrix/fibre interfacial adhesion in PLLA/natural fibre biocomposites was developed by treating the matrix with polydopamine, a new compatibilizer inspired by the adhesive capacity of mussels [46]. Photo-crosslinking with UV radiation of starch dispersions with cellulose microcrystals using glycerol as plasticizer was found to enhance the mechanical properties and water resistance of the resulting biocomposites [47].

Finally, there are important social and economic considerations that will play a role in the selection of resources and processes for the manufacture of sustainable composites. There has been controversy about the sustainability of energy production from biomass origin (biofuels) in every stage of the chain manufacturing process, including large-scale biomass production by agronomic means and the associated biorefinery processes [48–51]. It is important to select carefully the land used for biomass production, in terms of its impact on the availability of natural resources (soil, organic matter, nutrients, and water), the fate of associated chemical elements through environmental cycles, the impact on climate, and most importantly, the effect on living species, including humans [51]. In addition to this, the biomass feedstock that is destined to such processes must be suitable selected so that the food supply availability and food costs are not interfered by the massive biomass production. By-products and waste materials from food and bioenergy industries should therefore be prioritized in the synthesis of new chemicals and materials, by using only low environmental impact chemistry [35]. The importance of biomass feedstock selection for biorefineries has been pointed out in recent life cycle assessments (LCA); such assessment results are mainly affected by raw material selection, the effects of changes in land use, and the effective use of energy throughout the biorefinery processes [52]. The integration of green chemistry practices into the future biorefineries is fundamental for the sustainability of such operations and processes [35,37,53]. This symbiosis will guarantee not only that renewable resources are employed in the manufacture of new chemicals and materials, but also that the chemical processes are environmentally friendly and will not affect future generations.

The design and manufacture of biocomposites should be performed using local natural resources, which will contribute to a sustainable regional development and a reduction in the transport costs and associated environmental impacts. Our group has been involved in a capacity building project with Tanzania, with the aim to develop biocomposite panels from by-products readily available in these regions e.g. rice husks, coir fibres and sisal fibres [54]. Such research examples may contribute to the economical and social development of rural regions and it is expected that they will have an impact on improving the life quality of such communities. However, Bismarck et al. have pointed out, taking as an example the sisal and henequen industries in Mexico for natural fibre production, that these benefits for rural agricultural communities by the increased demand for biocomposites from renewable resources will only be effective with government support, planning and public intervention (public policies) [31].

3.2. Design for service life and subsequent waste processing: incorporating life cycle analysis in biocomposite manufacture

The design of materials for the 21st century should not only consider the choice of renewable resources as raw materials for their preparation, but also should be completely sustainable throughout their life cycle, including synthesis, usage, and waste management [53]. In the case of sustainable composites, the main challenge lies in the design of products that are structurally and functionally stable during their application, using benign synthesis and modification processes, together with appropriate waste management procedures (recycling, incineration, or composting) that complete the return of the material and/or energetic value to the environment. Recyclability of sustainable composites can be difficult due to the sensitivity of the bio-based polymeric matrix and/or reinforcements to thermal processing; a more detailed discussion about this is given in Section 5.1. Composting appears to be the preferable waste management route for sustainable composites, if the matrix is biodegradable; the composting process must, however, be performed at an industrial level, since control of environmental factors such as temperature, pH, and moisture is essential. Incineration should be considered as a final approach to partially recover the energetic value of the biocomposites. The introduction of life cycle assessments throughout the design of sustainable composites will ultimately guarantee their sustainability as suitable alternatives to traditional composites.

A feature article presented in year 1999 casts a doubt on the sustainability of the production of biodegradable polymers from agricultural feedstock (focusing on the production of PHAs from corn starch after hydrolysis and bacteria fermentation), in terms of the higher fossil-origin energy consumption required in comparison to synthetic polymers (polystyrene) [55]; the study did not consider, however, the whole life cycle of the materials, omitting waste management routes and other environmental markers such as greenhouse gas emissions and global warming. Posterior life cycle assessments performed on PLAs have demonstrated the sustainability of such materials versus synthetic counterparts, in terms of energy consumption and greenhouse gas emissions [56,57]. The waste management route (landfilling, composting or incineration) for these materials is crucial in terms of energy recovery and the possible emission or sequestration of carbon compounds. A recent review [58] confirms the better environmental performance of polysaccharide-based materials in each stage of the life cycle compared with their conventional counterparts, in terms of non-renewable energy use and greenhouse gas emissions for diverse applications such as textiles, engineering materials and packaging.

The substitution of inorganic fibres with natural fibres in biocomposite materials offers, in general, positive results in terms of sustainability from several comparative life cycle assessments [59–63]. A review by Joshi et al. [59] summarizes four key points that evidence the higher sustainable performance of natural fibres, including (i) the lower environmental impact of natural fibre production; (ii) the higher content of natural fibres for equivalent performance; (iii) the lower density of natural fibre composites; and (iv) the improved waste management routes for natural fibres. The utilization of pesticides and other types of chemical products may contribute to negative impacts on the environment [59]. However, these disadvantages are outgained by the clear environmental advantages during the service life and the disposal phase of such composites. Indeed, due to the lower weight of natural fibres, benefits are obtained in automotive applications by reducing the fuel consumption and the emissions of greenhouse gases; the longer the product life of natural-fibre-based composites, the more significant the environmental benefits will be. Additional energy can be recovered from waste management processes such as incineration. These results have been verified for different natural fibres utilized for the manufacture of biocomposites for automotive parts, such as wood fibres [60], china-reed fibres [61], jute fibres [62], and curauá fibres [63]. Finally, natural fibres show better environmental performance than nanoscaled organomodified montmorillonites as reinforcements for poly(hydroxyl butyrate) (PHB) composites in applications such as electronic appliances and automotive parts [64].

4. Biocomposites and their interactions with the environment

Once manufactured, products made from sustainable biocomposites must satisfy the requirement that no hazardous effects to the environment or to human health will be derived throughout their service life in the intended application. Two possible cases are discussed here particularly relevant for the design of biocomposites; these are the possible emission of odours and other low molecular weight compounds and the release of nanosized fillers from biocomposites.

4.1. Emission of volatiles and low molecular weight compounds from biocomposites

Polymeric-based materials may retain in their bulk a wide variety of volatile and other low molecular weight compounds from different origins, including polymerisation residues that may have been retained from synthesis, additives incorporated to enhance performance during application, contaminations that may have penetrated in the bulk during service life, and degradation products formed at any stage of the polymer's life cycle. Emissions of these low molecular weight compounds may constitute a potential environmental and toxicological hazard during manufacture, service life, and posterior waste management [65]. Their uncontrolled release may prevent their use in certain applications, such limitations being particularly significant in biomedical and packaging materials.

Reinforced biocomposites possess, in general, limited thermal stability at the required temperatures for thermo-mechanical processing, which may contribute to the formation of low molecular weight compounds as a result of the degradation of either the polymeric matrix or the lignocellulosic fibres used as reinforcements. This may lead to the release of undesirable odours during processing and service life, which may hinder the applicability of biocomposites in indoor applications, such as in construction elements or automotive components. The processing temperatures of natural polymers and natural-fibre-reinforced composites are normally restricted to 200 °C, but even at lower temperatures degradation may occur, leading to volatile compounds formation. The common procedures for the thermo-mechanical processing of biocomposites are similar to those used for synthetic polymers and composites; these include extrusion (including reactive extrusion, foaming, sheet and film forming), compression moulding, and injection moulding [16]. Other procedures such as film casting could be explored to avoid thermal degradation of biocomposites, especially for biomedical or packaging applications. Detailed knowledge about the thermal stability and the thermal decomposition mechanisms under temperature and shear conditions is therefore fundamental for material and product development, to avoid undesired effects such as odour emission or the release of degradation products into the surrounding media.

The thermal degradation and pyrolysis of (bio)polymers and natural fibres has been widely reported in the literature, mostly from the perspective of residue incineration and biomass pyrolysis [66,67]. Thermogravimetric analysis (TGA) has become the routine technique to assess the thermal stability of (bio)polymeric matrix, natural fibres, and their composites and to investigate decomposition kinetics. Coupling of TGA with chemical-sensitive techniques such as Fourier-transform infrared spectroscopy (FTIR) or mass spectrometry (MS) should provide interesting information about the evolved volatiles formed during the process. It is important to point out that the thermal degradation of the components in a mixture may behave differently than the pure components alone, due to strong interactions in the solid or in the gaseous state among the components, especially for natural fibres and biocomposites [68]. The interactions among the different constituents in biocomposites and how they affect thermal stability and the formation of degradation products during processing and thermal degradation are not fully understood. In some cases, the presence of natural fibres enhances the thermal stability of the biocomposites, due to strong interactions between the constituents, and thus prevents the formation of degradation products; in other cases, the reverse phenomena is observed, where the thermal susceptibility of any component of the biocomposite may promote earlier degradation of the overall material. Jimenez et al. reported this dual behaviour when preparing mixtures based on polyesters with different natural fillers. A mutual stabilizing effect of both co-components in mixtures based on microcrystalline cellulose (MC) and PCL was found, due to solid-solid interactions [69,70]; however, the early formation of acidic products from cellulose and hemicellulose decomposition promoted the random scission of ester linkages in a PCL and PHB matrix reinforced with sisal fibres [69–71]. Similarly, a correlation between the amount of volatile products formed during processing and the molecular weight reduction of PHB was observed in their composites with cellulose fibres, which was attributed to in situ formation of acid during melt processing of PHB and hydrolysis of cellulose fibres by such an acid during compounding [72]. It is thus very important to assess the thermal stability while processing the prepared biocomposites, to minimise the production of degradation products that could be emitted as volatile and odorous compounds during the service life of the products contributing to poor indoor air quality.

Oxidized compounds such as alcohols, aldehydes, ketones, and carboxylic acids together with a wide variety of phenolic compounds have been reported to be produced and emitted from sustainable biocomposites based on a recycled polypropylene (PP) matrix reinforced with natural fibres [73]. Fig. 3 shows two different chromatograms of emitted volatile compounds from recycled PP/biofibre composite materials before and after 240 h ageing at 70 °C, using solid-phase microextraction gas chromatography – mass spectrometry (SPME-GC-MS). Among the identified compounds, phenolic degradation products from the antioxidants incorporated in the thermoplastic matrix could be identified in the non-aged material. Other compounds, such as carboxylic acids, alcohols, and esters, which are believed to derive from the degradation of the lignocellulosic fibres, seem to increase their relative abundance after ageing; these compounds may be responsible for the characteristic odour emitted by lignocellulosic composites. Some authors have proposed the introduction of porous absorbents in the composition of biocomposites, to decrease the amount of emitted odorous molecules without major reductions in the material's mechanical properties [74]. Other environmental implications may arise, however, from the application of inorganic fillers in biocomposites.

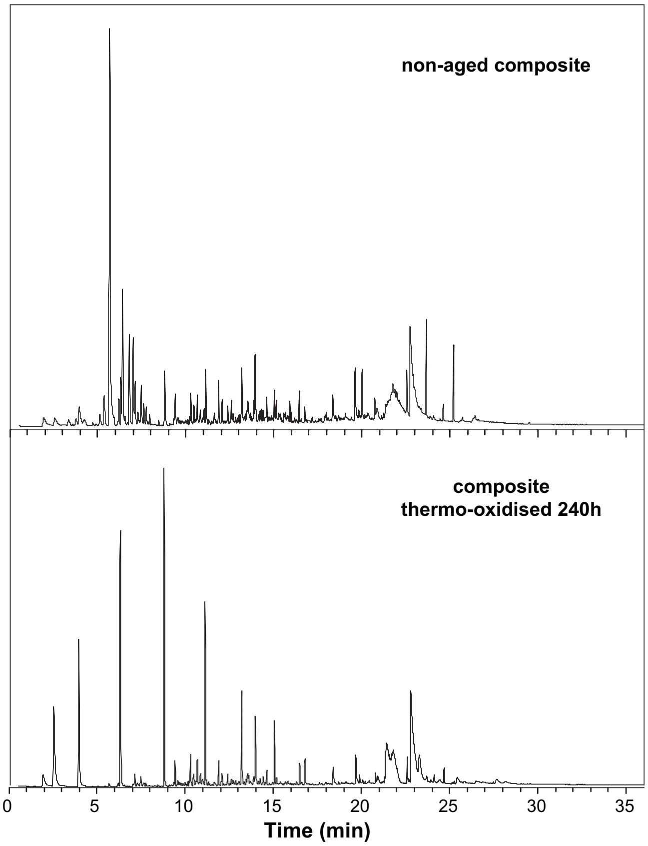

Fig. 3. GC-MS chromatogram showing the volatile organic compounds extracted by SPME from PP/cellulose fibre composites before and after thermo-oxidation during 240 h. Redrawn from Espert et al. [73]. Printed with permission, copyright Elsevier (2005).

4.2. Environmental and toxicological effects of emitted nanoparticles

Nanotechnology and production of engineered nanomaterials constitutes an exciting new research field with endless possibilities for product applications. The possibility of designing materials at the nanoscale level by controlling the structure, properties, and fabrication processes atom-by-atom and molecule-by-molecule represents perhaps the main technological shift of this century. Considering the field of polymer science and technology, the preparation of polymer nanocomposites has attained special attention, due to the remarkable improvement in material properties provided by the incorporation of low concentrations of nanosized fillers into polymeric matrixes. In particular, the addition of nanofillers into biopolymers – designing the so-called nano-biocomposites – constitutes a very interesting new family of polymeric-based materials with enhanced material properties and preserved biodegradation. Several reviews [13,18,19,24,29] explore the recent developments in the design, preparation, and properties of novel nano-biocomposites, focusing on polyesters and polysaccharides as biopolymeric matrixes and either inorganic nanofillers (nanoclays) or cellulose-based nano-reinforcements. However, the environmental and toxicological implications of such nano-sized fillers and the derived nanocomposites are not fully understood yet. Assessing the environmental impacts of these nanomaterials in these early stages of development will therefore contribute to safer manufacturing processes and products and help minimise risks of long-term hazardous effects.

Important research efforts have been devoted to understand the environmental effects and the impact on human health of nanoparticles and nanomaterials; indeed, a large number of review articles have been published in the last five years covering this new scientific field termed "nanotoxicology" [75–83]. Summarizing these studies, knowledge is limited about the environmental and toxicological effects of these newly produced nanomaterials; it is expected, though, that these implications will be completely specific to the type of base material, and its size and shape. Environmental and toxicological studies have focused mainly on carbon-based nanomaterials (fullerenes, carbon nanotubes) and other inorganic nanomaterials (clay and silica nanomaterials, quantum dots, and metallic and metal-oxide-based nanoparticles). Although natural nanoparticles exist in the environment, it is expected that nanomaterials will enter the environment through intentional or non-intentional release during manufacturing, transport, and use [75,82]. The fate of these nanomaterials in the environment is not understood, although issues such as particle deposition and aggregation, the possibility of redox transformation, mobility, modification, and degradation are the focus of new research and understanding [82–84]. In any case, source reduction during manufacture (by internal recycling or in-factory hazard reduction systems, such as washing machines with silver particles) seems to be the most effective way for minimizing possible future hazards. The modification of surface properties and the control of the particle size after material degradation, wear and corrosion are also possibilities to restrict possible hazards during service life [85]. Nanomaterials have demonstrated powerful antibacterial effects (which may have positive applications), but they have the potential to cause oxidative stress in animal tissues, intracellular toxic effects (cytotoxicity), accumulation in organs, and pulmonary inflammatory effects [78,82,83]. The unusual physical shape and high surface area associated with nanomaterials are believed to be responsible for their remarkable biological potential; and their extremely small size enhances the possibilities of increased uptake, faster distribution through the body, and toxic interaction in the target cells [78]. In summary, there are still huge gaps in the understanding of the interactions of nanomaterials in environmental systems and the possible causes for their toxicity in biota and humans, although research in these areas is fortunately increasing. The development of suitable analytical protocols constitutes a key factor for the effectiveness of the risk assesments [79,86].

Regarding the possible release of nanoparticles from polymeric (bio)nanocomposites during their preparation and use, little information is available on the mechanisms, causes, and possible rates of emitted nano-sized compounds to the environment. Preliminary results from our group suggest that the release is dependent on the degree of exfoliation of the nanoparticles in the polymeric matrix, with release prevention in the intercalated state [87]. Further research should focus on minimizing the possible release of such nanoparticles during manufacture and service life, by improving the fixation of the nanoparticles in nanocomposites, reducing the degradative damage to polymer by nanoparticles, and changing the nanoparticle surface, structure or composition [88]. Indeed, since new nanomaterials with biodegradable matrices are emerging, an interesting aspect for investigation is the nanoparticle behaviour during degradation of the materials, e.g. ending up and accumulating in the environment.

The safety concerns of using nanofillers in polymeric films for food packaging applications have been raised, but there is limited data regarding their migration from the packaging material into food and their possible chronic toxicological effects [18]. This should be a subject of attention in the future, because polymer ageing and degradation will certainly influence nanoparticle emissions into surrounding environments. Improvements in polymer nanocomposite formulations, in terms of better nanofiller dispersion or enhanced coupling between matrix and nanoreinforcements will not only benefit material properties, but also affect environmental and human health implications. It is therefore worth emphasizing our responsibility, as scientists in this field, when designing new polymeric (bio)nanocomposite materials, in terms of assessing the possible interactions of these products with the environment, minimising the possible migration of the nanofillers during manufacture and use, and investigating the possible routes for their waste management.

5. Degradation of sustainable biocomposites

A truly sustainable design of biocomposite materials should achieve suitable structural and functional stability during processing and use, together with suitable waste management procedures when discarded, thus ensuring the return of their material and energetic value to the environment. The analysis of degradation processes in biocomposites is even more crucial than in traditional composites due to the environmental susceptibility of their components; degradability studies should therefore be performed to guarantee that the materials are structurally stable during their use, and to verify that they are biodegradable and bioassimilable without ecotoxicological effects when composting is the selected waste management route. Polymer degradation can be defined as any externally induced irreversible alteration in the physical properties of the polymer caused by chemical reactions in the main or side chains of the macromolecules; for the special case of biopolymers, degradation also implies not only chemical changes but also the rupture of highly ordered structures, such as protein denaturation. Polymer degradation can be caused by a wide range of external factors; degradation processes can be classified accordingly into chemical degradation (caused by chemical agents such as oxygen, water, acids or bases – namely, oxidation and hydrolysis), thermal degradation (caused by temperature), mechanical degradation (caused by external stress), biological degradation (caused by biological entities), and degradation by radiation (including UV light and electromagnetic exposure). Normally, degradation processes do not occur by the actions of independent mechanisms, but rather by a combination of several external factors; the most common processes include thermo-oxidation (effect of temperature and oxygen exposure), photo-oxidation (combined effect of light and oxygen exposure, especially interesting in outdoor applications), thermo-mechanical degradation (combination of temperature and shear forces, especially relevant during material processing), and biodegradation (combination of chemical and biological effects). Polymer degradation studies should be carried out in controlled environmental chambers, where different external factors can be adjusted and recorded for monitoring the degradation processes and their effects. Commercial equipment and standard tests are readily available for the study of these different processes. Fig. 4 shows, however, a self-designed environmental chamber for degradation studies, in which humidity, light exposure, chemical environment, and presence of microorganisms can be controlled [89]. The following section comprises a review of the available studies on the degradability of sustainable composites, taking into account both abiotic and biotic degradation processes.

5.1. *Abiotic degradation: water absorption, hydrothermal degradation, recyclability, thermo-oxidation, and photo-oxidation in biocomposites*

The sensitivity to moisture uptake and hydrothermal degradation is a well-known weakness that hinders the performance of biocomposite materials, due to the hydrophilic nature of the (bio)polymeric matrix and/or the natural reinforcement; the analysis of the water absorption phenomenon, its degradative effects, and the different ways to minimize them during service life, constitutes one of the main focus areas of research in the preparation of biocomposite materials. Exposure to high humidity during material storage and composite manufacture can be much more damaging to the interfacial strength of the final composites than post-fabrication moisture exposure [90]. Water absorption largely depends on the hygroscopic components present in the biocomposite material; if the polymeric matrix is hydrophobic, it may act as a semipermeable membrane [91]. Moisture penetration into composite materials is conducted by three different mechanisms: (i) diffusion of water molecules inside the microgaps between polymer chains and natural fillers; (ii) capillary transport into the gaps and flaws at the interfaces between fibres and polymer because of incomplete wettability and impregnation; and (iii) transport through microcracks in the matrix, formed during the compounding process [92]. Accordingly, water absorption in biocomposite materials can be influenced by several factors, including fibre loading (higher fibre content should contribute to

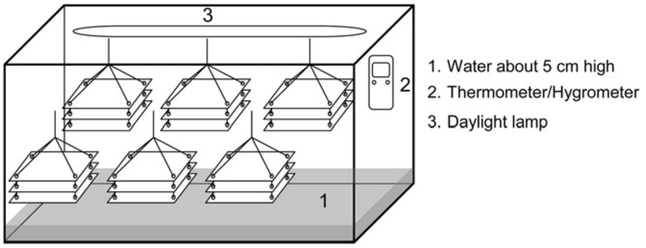

Fig. 4. Microenvironmental chamber for controlled degradation studies of sustainable polymers and composites (suitable for hydrolysis, thermo-oxidation, photo-oxidation, and biodegradation). Redrawn from Strömberg et al. [123]. Printed with permission, Copyright Elsevier (2009).

higher moisture absorption), the chemical nature of lignocellulosic fillers (fillers containing higher lignin content should present lower values of water uptake, because lignin is a hydrophobic compound that acts against hydrothermal degradation), fibre geometry, and, especially, compatibilization between matrix and fillers (improved interfacial adhesion would result in fewer and smaller microgaps where water uptake may occur) [93,94]. The introduction of lignocellulosic fillers in biocomposites with a hydrophobic polymer as matrix increases water absorption dramatically, as expected; however, in bio-based biocomposites with hydrophilic biopolymeric matrixes reinforced with natural fillers, higher water resistance may be observed due to fibre–matrix interactions that are absent in the unfilled matrix, as observed in starch-based composites reinforced with sisal fibres [95,96]. Moreover, different chemical modification processes of the fillers and/or matrix to enhance compatibilization also result in an improved resistance to water absorption [45,97,98]. The mechanism of water absorption in biocomposites has been reported to follow Fickian-behaviour at moderate temperatures [94], whereas uptake behaviour is radically altered at elevated temperatures due to significant hydrothermal degradation [99] or the presence of microcracks [91]. Fig. 5 compares the experimental water absorption results for recycled PP composites reinforced with different concentrations of recycled cellulose fibres, with the theoretical mathematical expression of the Fick's law for a film geometry; the experimental data fit the Fickian diffusion model reasonably well, especially for composites with low fibre content at the initial stage of water uptake [94].

Water absorption and its resulting hydrothermal degradation irreversibly affect the morphology and properties of the polymer matrix and the lignocellulosic fillers, and seriously damage the filler–matrix interface, leading to poor stress transfer efficiencies from matrix to reinforcement [100]. The proposed mechanism for biocomposite hydrothermal degradation initiates with water uptake by the hydrophilic components of the composite (fillers and/or matrix). The presence of water leads to swelling of the reinforcements, which may develop stress at the interface and cause matrix micro-cracking around the swollen fillers; other effects may also occur in the matrix structure, such as chain reorientation and shrinkage. Water absorption and the resulting effects contribute moreover to the loss of compatibilization between fibres and matrix; indeed, hydrogen bonds between water molecules and the hydrophilic components of the biocomposite fibres are formed, resulting in debonding and weakening of the interface adhesion [94,99]. Hydrothermal ageing may also lead to the degradation of natural fibres by a hydrolysis mechanism. The weakening of the matrix/filler interface seems to be the main damaging mechanism induced by water absorption [101]. Small water uptakes may cause a plasticizer effect in the biocomposite structure, leading to a slight improvement in the elongation properties [94,102]; however, the deterioration of the mechanical properties by major water absorption and severe hydrothermal ageing has been thoroughly reported in the literature. The effects of water absorption and hydrothermal ageing on the structure of sustainable biocomposites based on recycled PP reinforced with sisal fibres are shown in Fig. 6; the microfibrils in the structure of the natural fibres appear seriously damaged and the loss of adhesion between fibres and matrix can be clearly observed by the apparition of microvoids in the structure.

The addition of inorganic nanofillers to polymeric biocomposites has a varying effect on the water absorption and the hydrolytic degradative behaviour. Some authors have reported that the inclusion of impermeable inorganic nanofillers may have the potential of reducing the moisture sensitivity of polymeric composites [103,104], attributable to the enhanced barrier properties of the resulting

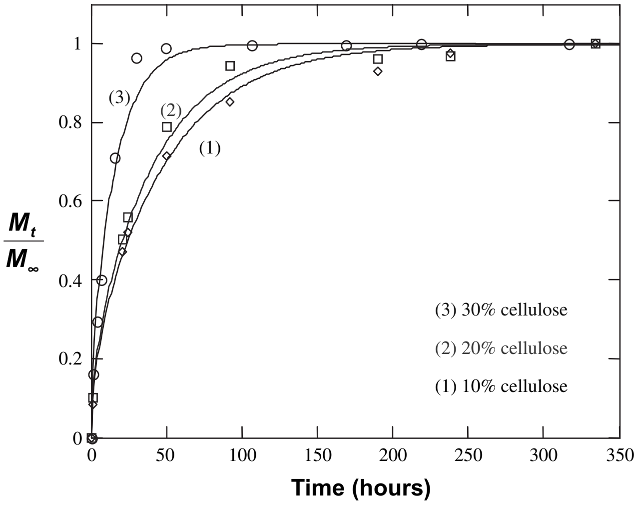

Fig. 5. Comparison between the experimental data and the theoretical Fickian water absorption curves for recycled PPEVA/cellulose composites with different fibre content at 50 °C. The points represent the experimental data and the lines are the theoretical curves. Redrawn from Espert et al. [94]. Printed with permission, copyright Elsevier (2004).

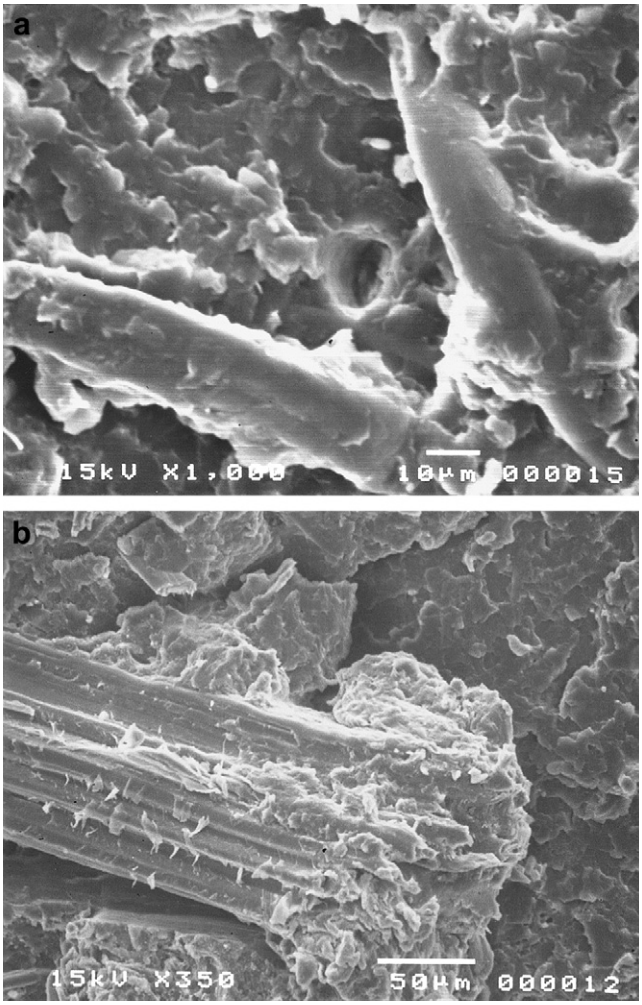

Fig. 6. Scanning electron micrographs for biocomposites based on recycled PP reinforced with 20% sisal: (a) before hydrothermal ageing; (b) after hydrothermal ageing at 50 °C. Redrawn from Espert et al. [94]. Printed with permission, copyright Elsevier (2004).

nanocomposites. Other authors, on the other hand, have observed an increase in the hydrolytic degradation rates when nanoclays were incorporated in the polymeric matrix, especially in polyester-based reinforced nanocomposites [105–107]. Different factors seem to play their own role in controlling the rate of water absorption and, thus, the hydrolytic degradation of such materials; these factors include the nature of the nanofillers, the dispersion of the fillers in the matrix, and the final crystallinity of the nanocomposite. Clay nanofillers have, in principle, a hydrophilic nature, which contributes to increased moisture sensitivity; however, their treatment with organomodifiers and the resulting effective pH has a remarkable effect on water uptake [107]. A higher dispersion rate of the nanofillers influences the diffusion path of the water molecules during water absorption [106] but also increases the contact points between matrix and filler [105]. A similar effect can be expected from the effective crystallinity of the nanocomposite; the presence of crystalline domains will hinder water permeation and absorption, due to an increased tortuosity, a reduction in the mobility of polymer chains, and lower free volumes. In contrast to the hydrolytic degradation of pure polyester matrixes, hydrolytic degradation seems to initiate at the polymer/nanofiller interface, where absorbed water molecules accumulate after moisture uptake and proceed to affect the bulk properties of the nanocomposites.

The long-term effects of thermo- and photo-oxidation on the properties of biocomposites have not been as widely studied as those of traditional composite counterparts, perhaps due to the fact that other degradative mechanisms are more specifically damaging to these materials than long-term oxidative exposure in a dry environment. Some authors [108] have reported the loss of strength of natural fibres during prolonged exposure to elevated ageing temperatures (100 °C), caused by the decomposition of volatile extractables present on the fibre surface. Although cellulose components are supposed to remain stable up to 160 °C, thermo-oxidative reactions may occur alongside prolonged exposure, leading to deterioration of the fibre structure, development of voids in the interface and overall loss of fibre-matrix interfacial adhesion. The incorporation of bonding agents or the performance of fibre chemical treatments used to enhance the compatibility in the interface is expected to preserve the mechanical properties during thermo-oxidation [109].

The recyclability of natural-filler-reinforced biocomposites, based on either a synthetic or a biopolymeric thermoplastic matrix, is a matter of particular interest for the waste management of these novel materials. Some studies [110–113] have been devoted to the multiple reprocessing and recycling behaviour of synthetic polyolefins (mainly PP) reinforced with lignocellulosic fillers. In general, the recyclability of these composites with preserved mechanical properties is guaranteed up to several reprocessing cycles. Multiple processing may enhance the interfacial adhesion between fillers and matrix, contributing to a reported thermal stability in the reprocessed biocomposites. Different degradative effects are caused, however, by repeated recycling on the composite structure, such as fibre length reduction and chain scission in the synthetic thermoplastic matrix, leading to a decrease in its molecular weight and an increase in crystallinity. In principle, biopolymer-reinforced composites are expected to be less recyclable than their synthetic thermoplastic matrix counterparts, due to the composites' sensitivity to thermo-mechanical degradation. This does not offer a disadvantage for their sustainability, since composting and not mechanical recycling is supposed to be the main waste management route for such materials; these implications should, nevertheless, be analysed from a life-cycle analysis perspective. The recyclability of biocompostable flax/poly(L-lactide) composites has been studied [114]; there are indications that their mechanical properties are in fact maintained up to 3 cycles. However, marked changes were observed for extended cycles, including a decrease in the molecular weight distribution, a decrease in the glass transition temperature, a reduction of fibre length, and the separation of fibre bundles.

High-energy radiation (gamma irradiation) has been reported to offer beneficial effects on the interfacial adhesion between fibre and matrix in short-sisal-fibre reinforced natural rubber [109] and in jute-fibre reinforced PCL [115] biocomposites, enhancing the mechanical properties and contributing to slow the degradation rates when subjected to water exposure, weathering and soil burial testing. This treatment may be applied to tailor the properties and degradative rates of selected products for special applications, because gamma radiation is expected to increase the production cost.

The introduction of natural fibres in synthetic thermoplastic-reinforced biocomposites may offer a protective effect against photo-oxidation, similar to that reported for thermo-oxidation. Photo-oxidation promoted by ultraviolet radiation is responsible for chain scission in the thermoplastic matrix and the apparition of surface cracks in the composites [98,116]; the propagation of such cracks and defects can be hindered by increasing fibre load [98] and by enhancing adhesion between fibres and matrix [117] (either by fibre treatment or by the addition of compatibilizers).

On the basis of current literature, it is still difficult to understand the mechanisms of thermo- and photo-oxidative degradation of nanocomposites [118]. It is well known that inorganic fillers often experimentally show a negative effect on the oxidative stability of the polymer, independent of its structure. The complex interactions between the stabilizing system, the filler, and the polymeric matrix seem to play a major role in this behaviour. Factors such as the filler surface area, pore volumes, surface functionality, hydrophilicity, thermal and photosensitisation properties of the filler, and transition metal ion content (manganese, iron, titanium) will influence the oxidative degradation of polymer nanocomposites [119]. Photo-oxidation appears to be even more severe, due to the catalytic effect of species present in the nanoclays (e.g., alkyl ammonium modifiers or iron impurities) [119,120]. However, ongoing research in suitable stabilizing systems, improved dispersion, and interfacial adhesion between nanofillers and polymeric matrix will contribute to minimizing the oxidative sensitivity of such materials.

5.2. *Biofilm formation and biodegradation*

The analysis of the biodegradation process in (nano)biocomposites constitutes an important part of the entire design of these new materials. Complete deterioration and bioassimilation should be achieved, to guarantee the complete closed life cycle of the materials and the return to nature of the products' material value. An excellent overview on the mechanisms and evaluation procedures for polymer biodegradation has been recently presented by Lucas et al. [121]. Biodegradation has been classically defined as the decomposition of substances in nature or in a human body caused by the action of micro- or macroorganisms, enzymes, and/or hydrolysis, leading to the complete recovery of the carbon cycle, mineralization into carbon dioxide, water, and salts, and the creation of new biomass. However, this definition has been expanded due to the complexity of phenomena involved in biodegradation, including the abiotic effects that synergistically complement the biological activity during biodegradation. Altogether, biodegradation embraces the (bio)deterioration processes at the surface of the materials (abiotic degradation and biofilm formation) that lead to an overall change in the structural, physical, and chemical properties of the material, the biofragmentation of the polymeric chains into smaller fragments by different chemical and enzymatic mechanisms, and the final assimilation of the polymeric fragments into microbial cells. Abiotic degradation (water absorption and hydrolysis, photo- and thermo-oxidation) usually precedes the biological attack and causes an increase in the sensitivity of the material for further degradation, but may also be a factor in every step of the biodegradation process. Biodeterioration, or the superficial degradation processes caused by the adhesion and growth of microorganisms into polymeric materials, can occur by physical effects (penetration of hyphae into the material), chemical processes (chemical compounds that may be formed by microorganisms that cause further degradation), or enzymatic phenomena [121]. Biofilm formation has been reported to be a multistep process involving surface fouling, degradation of leaching components from the polymeric matrix, corrosion of the interface, and further hydration and penetration of microorganism components into the polymer structure [122]. After initial biodeterioration, microorganisms have an easier way to initiate the biofragmentation of the polymeric macromolecules into a mixture of oligomers and monomers that may be assimilable by living organisms; biofragmentation is usually performed by selected enzymes, although abiotic processes may be involved as well. Finally, the polymeric fragments are assimilated by the microorganisms (by either anaerobic or aerobic respiration, or by fermentation) closing the material and energetic cycle of the polymer.

The mechanisms and effects of biodeterioration caused by selected fungi and algae species on different biocomposites (recycled polyolefins and polylactide reinforced with lignocellulosic fillers) have been recently reported by our group [123]. Biofilm formation occured on all the studied materials, even if the polymer itself is inert to biodegradation; Fig. 7 shows the microbial growth on the surface of the polymeric matrixes and their biocomposites after 84 days of biodegradation. The incorporation of lignocellulosic fibres in the polymeric matrixes results in enhanced colonization of the surfaces by the microorganisms, which was attributed to an improved environment for biofilm adhesion caused by water uptake by the fibres. Differences in the biodeterioration mechanisms have been reported among the different polymeric matrixes. PP biocomposites are affected by biodegradation mostly on the surface, whereas in PLA composites the effects are also observed in the bulk; this fact may be due to the increased sensitivity to hydrolysis exhibited by PLA. In the long-term, biodegradation of the natural fibres results in a porous PP matrix structure, whereas in PLA composites both matrix and fillers degrade in parallel.

The effects of the addition of natural fibres and other lignocellulosic fillers on the biodegradation process of biocomposite materials is an active topic of research [95,96,118,124–131]. In general, the presence of lignocellulosic reinforcements enhances the microbial attack and the biodegradation rates, although in certain cases, the addition of biofibres and the resulting fibre–fibre interactions caused an initial lag period due to reduced initial water uptake and limited accessibility of microorganisms [96]. The presence of biofibres promotes biofouling and the adhesion of microorganisms to the surface; the surface roughness seems to play an important role in this initial phenomenon [124]. The kinetics of the biodegradation process depends on the susceptibility of the different components of the biocomposite materials, usually with different synergistic behaviour affecting the overall rates; starch is normally the main site for biodegradative attack in starch-containing biocomposites [125–127]. The interfacial adhesion plays a very effective role in controlling the biodegradation rates, by selecting the type of natural filler that exhibits higher fibre–fibre and fibre–matrix interactions (e.g. bacterial cellulose in starch biocomposites [128]), and incorporating suitable compatibilizing agents between the fillers and the matrix if interfacial adhesion needs to be improved [125–127,129]. The hydrophilic nature of the polymeric matrix and the degree of crystallinity are other structural and chemical parameters that control the biodegradation rates, by affecting the accessibility of water and enzymes to the substrates [131]. In this case, PCL biocomposites may exhibit slower hydrolysis and biodegradation rates than other biopolymer-based composites, due to their tailored semicrystalline structure and relative hydrophobicity.

The preparation of biodegradable nanocomposites based on thermoplastic polyester matrixes and nanoclays as fillers constitutes one of the major breakthroughs in polymer materials science in the last decade. The incorporation of nanoclays in polymeric matrixes has been widely reported in the literature to improve the biodegradation of the resulting nanocomposites [29,30,132–137], although the exact mechanisms are not well known yet. Other authors [138,139] have observed a decrease in biodegradability in their biopolymer/nanoclay compositions, which has been attributed to the impaired water uptake caused by the dispersed silicate layers and their effective compatibilization with the polymeric matrix, the crystallinity of the polymeric matrix, and the antimicrobial properties of certain organo-modified nanoclays [139]. The higher degradation rate in the presence of nanoclays has been attributed to the presence of hydroxyl groups in the nanoclays,

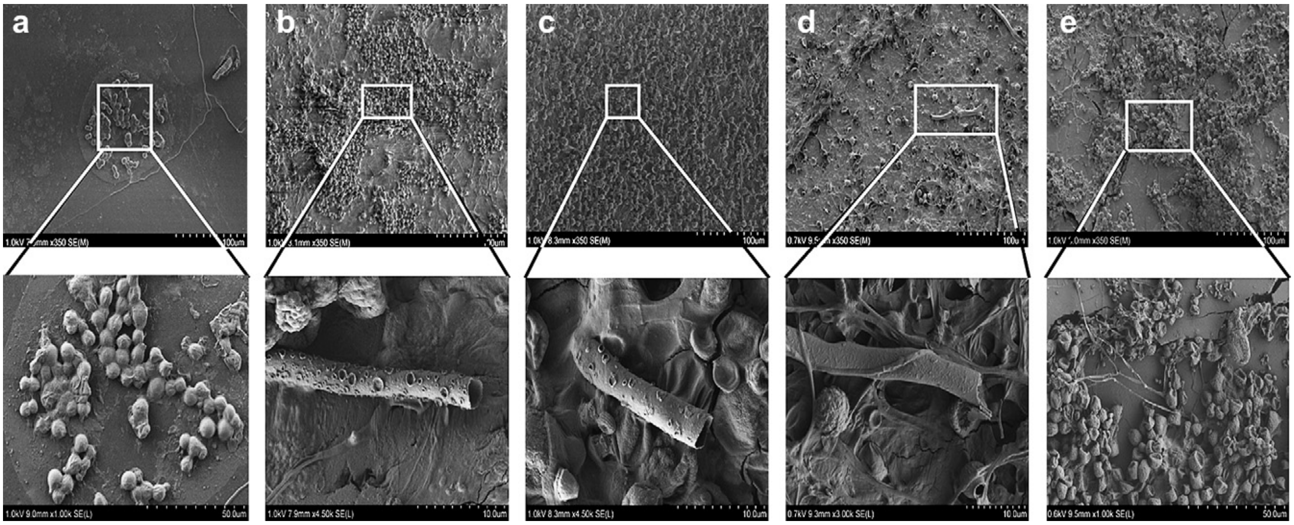

Fig. 7. Biofilm formation on the surface of polymeric matrixes and their biocomposites reinforced with lignocellulosic fibres as revealed by scanning electron microscopy: (a) PP; (b) PP with 50% wood flour; (c) recycled PP (containing 2% EVA) reinforced with 10% Kraft pulp and hemp fibres; (d) Polylactide; (e) Polylactide with 25% wood flour. Redrawn from Strömberg et al. [123]. Printed with permission, copyright Elsevier (2009).

which can promote initial water uptake and hydrolytic degradation of the matrix polymer [136]. Moreover, the different pHs that arise in the proximities of the nanoclays after water absorption may catalyse the enzymatic activity of depolymerase and contribute to a remarkable enhancement of the biodegradation rate in nanocomposites, as has been demonstrated in biodegradation studies using enzymes, compost, and fungi media [137]. The crystallinity of the polymeric matrix also affects the biodegradation process. In semicrystalline polymers, biodegradation starts in the amorphous region; degradation rates are expected, thus, to be affected by the degree of crystallinity, as it has been shown for PHB and PCL composites with nanoclays [136,137]. In general, the factors that may affect the biodegradability of polymer nanocomposites will be similar to those reported for the water uptake. Indeed, the rate of biodegradation may be finely tuned by the choice of the appropriate nanofiller according to its hydrophilic/hydrophobic nature and its characteristic pH values in aqueous solutions, the dispersion of the filler in the matrix, and the control of the final crystallinity of the nanocomposite during either processing or post-treatment annealing (when semicrystalline polymeric matrixes are being used).

Biodegradation studies of newly designed (nano)biocomposites should contain an assessment of the ecotoxicity of the degradation products after fragmentation, to ensure the effective assimilation by microorganisms without any hazardous effects on them and the environment. The available ecotoxicity tests for biodegradable polymeric materials in compost are usually performed on plants, soil fauna (earthworms), aquatic fauna (Daphnia), algae (green algae), and microbes (luminescent bacteria) [140]. Preliminary ecotoxicological tests on starch blends [141] and modified starch reinforced with various cellulose fibres [142] indicate that the biodegradation products of these materials are ecologically safe. An interesting result was however reported by Tuominen et al. [143] in the study of the ecotoxicity of lactic-acid-based polymers under controlled composting conditions. According to these biotests, poly(ester-urethane), poly(ester-amide) and poly(lactide) with 1,4-butane diisocyanate as a chain connector do not exhibit any ecotoxicological effect; contrarily, the use of 1,6-hexamethylene diisocyanate as a connecting agent should be avoided in biodegradable polymers because of the environmental risk. This example illustrates the importance of collecting detailed information on the ecotoxicological effects of the different families of nanobiocomposites before they reach their end of life, especially while new formulations are being explored for the design of new materials with different modified fillers, compatibilizing agents, and additives.

6. Conclusions

This review has discussed the new trends for the design of polymeric-based sustainable, taking into account their resource and environmental implications. The use of renewable materials for their manufacture does not guarantee the sustainability of the resulting composites; benign chemical and physical synthetic and modification procedures should be employed, together with evidence of no hazardous or toxicological effect during service life and guaranteed waste management procedures to return their material and energetic value and close their cycle. Future integrated biorefineries based on green chemistry operations will serve as the basis for providing sustainable raw materials for biocomposite production. Independent life cycle assessment studies should be performed in any new product based on biocomposites, to guarantee their improved environmental performance as alternatives to traditional materials. The susceptibility of biocomposites to environmental degradation still constitutes one major disadvantage for their use in structural applications; further research is therefore needed to design materials with enhanced functionality and stability during processing and service life, and preserved biodegradability if composting is the selected route for waste management.

The present and future look promising for the introduction of sustainable biocomposites as a replacement for traditional fossil-based materials in diverse applications. A wide range of raw materials from recycled and renewable resources will be readily available for choice, together with controlled synthetic and modification routes to tailor the desired properties of the designed biocomposites. However, it is our responsibility from a research perspective, to carefully consider the sustainability of the biocomposites in each stage of the life cycle and not only target at determined macroscopic properties as the goal of material design. Only by the conscious integration of sustainable crop growth, raw material extraction, synthetic and modification steps, material processing and product manufacture, safe service life in the intended application, and suitable waste management will we be able to achieve the true goal of sustainable development in material and product design.

Acknowledgements

F.V. appreciates the support of a postdoctoral fellowship from the Knut and Alice Wallenberg Foundation (Sweden). Steven Muir and Dr. Eustina Oh are acknowledged for constructive discussions and comments.

References

[1] Crutzen PJ. Geology of mankind. Nature 2002;415(6867):23.
[2] Rockström J, Steffen W, Noone K, Persson Å, Chapin FSI, Lambin E, et al. Planetary boundaries: exploring the safe operating space for humanity. Ecology and Society 2009;14(2):32.
[3] Rockstrom J, Steffen W, Noone K, Persson A, Chapin FS, Lambin EF, et al. A safe operating space for humanity. Nature 2009;461(7263):472–5.
[4] Our common future. Oxford, U.K: Oxford University; 1987.
[5] Policy options and possible actions to expedite implementation: energy for sustainable development. Report of the Secretary-General. E/CN.17/2007/2, United Nations. Economic and Social Council; 2007.
[6] Communication from the Commission to the Council and the European Parliament on the review of the Sustainable Development Strategy – a platform for action. COM/2005/0658 final, European Commission; 2005.
[7] Review of the EU Sustainable Development Strategy (EU SDS) – Renewed Strategy. 10917/06, European Council; 2006.
[8] Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – mainstreaming sustainable development into EU policies: 2009 Review of the European Union Strategy for Sustainable Development. COM/2009/0400 final, European Commission; 2009.
[9] Mihelcic JR, Crittenden JC, Small MJ, Shonnard DR, Hokanson DR, Zhang Q, et al. Sustainability science and engineering: the emergence of a new metadiscipline. Environmental Science & Technology 2003;37(23):5314–24.
[10] Satterfield MB, Kolb CE, Peoples R, Adams GL, Schuster DS, Ramsey HC, et al. Overcoming nontechnical barriers to the implementation of sustainable solutions in industry. Environmental Science & Technology 2009;43(12):4221–6.
[11] Satyanarayana KG, Arizaga GGC, Wypych F. Biodegradable composites based on lignocellulosic fibers—an overview. Progress in Polymer Science 2009;34(9):982–1021.
[12] Fowler PA, Hughes JM, Elias RM. Biocomposites: technology, environmental credentials and market forces. Journal of the Science of Food and Agriculture 2006;86(12):1781–9.
[13] Bordes P, Pollet E, Avérous L. Nano-biocomposites: biodegradable polyester/nanoclay systems. Progress in Polymer Science 2009;34(2):125–55.
[14] Mohanty AK, Misra M, Hinrichsen G. Biofibres, biodegradable polymers and biocomposites: an overview. Macromolecular Materials and Engineering 2000;276–277(1):1–24.
[15] John MJ, Thomas S. Biofibres and biocomposites. Carbohydrate Polymers 2008;71(3):343–64.
[16] Liu H, Xie F, Yu L, Chen L, Li L. Thermal processing of starch-based polymers. Progress in Polymer Science 2009;34(12):1348–68.
[17] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Progress in Polymer Science 2006;31(6):576–602.
[18] de Azeredo HMC. Nanocomposites for food packaging applications. Food Research International 2009;42(9):1240–53.

[19] Chivrac F, Pollet E, Avérous L. Progress in nano-biocomposites based on polysaccharides and nanoclays. Materials Science and Engineering: R: Reports 2009;67(1):1–17.

[20] Teeri TT, Brumer Iii H, Daniel G, Gatenholm P. Biomimetic engineering of cellulose-based materials. Trends in Biotechnology 2007;25(7):299–306.

[21] Meyers MA, Chen P-Y, Lin AY-M, Seki Y. Biological materials: structure and mechanical properties. Progress in Materials Science 2008;53(1):1–206.

[22] Mano JF, Sousa RA, Boesel LF, Neves NM, Reis RL. Bioinert, biodegradable and injectable polymeric matrix composites for hard tissue replacement: state of the art and recent developments. Composites Science and Technology 2004;64(6):789–817.

[23] Avérous L, Halley PJ. Biocomposites based on plasticized starch. Biofuels, Bioproducts and Biorefining 2009;3(3):329–43.

[24] Dufresne A. Polysaccharide nano crystal reinforced nanocomposites. Canadian Journal of Chemistry 2008;86(6):484–94.

[25] Ndazi B, Tesha J, Bisanda E. Some opportunities and challenges of producing bio-composites from non-wood residues. Journal of Materials Science 2006;41(21):6984–90.

[26] Azizi Samir MAS, Alloin F, Dufresne A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules 2005;6(2):612–26.

[27] Mishra S, Mohanty AK, Drzal LT, Misra M, Hinrichsen G. A review on pineapple leaf fibers, sisal fibers and their biocomposites. Macromolecular Materials and Engineering 2004;289(11):955–74.

[28] Mohanty AK, Misra M, Drzal LT. Surface modifications of natural fibers and performance of the resulting biocomposites: an overview. Composite Interfaces 2001;8:313–43.

[29] Sinha Ray S, Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Progress in Materials Science 2005;50(8):962–1079.

[30] Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Progress in Polymer Science 2003;28 (11):1539–641.

[31] Bismarck A, Baltazar-Y-Jimenez A, Sarikakis K. Green composites as Panacea? Socio-economic aspects of green materials. Environment, Development and Sustainability 2006;8(3):445–63.

[32] CEN/TR 15932:2010 Plastics – recommendation for terminology and characterisation of biopolymers and bioplastics. Foreseen date of availability March 2010.

[33] Mohanty AK, Misra M, Drzal LT, Selke SE, Harte BR, Hinrichsen G. In: Mohanty AK, Misra M, Drzal LT, editors. Nat. fibers, biopolym., biocompos. USA: Taylor & Francis Group; 2005. p. 1–36.

[34] Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, et al. The path forward for biofuels and biomaterials. Science 2006;311 (5760):484–9.

[35] Clark JH, Budarin V, Deswarte FEI, Hardy JJE, Kerton FM, Hunt AJ, et al. Green chemistry and the biorefinery: a partnership for a sustainable future. Green Chemistry 2006;8(10):853–60.

[36] Fernando S, Adhikari S, Chandrapal C, Murali N. Biorefineries: current status, challenges, and future direction. Energy & Fuels 2006;20(4):1727–37.

[37] Clark JH, Deswarte FEI, Farmer TJ. The integration of green chemistry into future biorefineries. Biofuels, Bioproducts and Biorefining 2009;3(1):72–90.

[38] Gandini A. Polymers from renewable resources: a challenge for the future of macromolecular materials. Macromolecules 2008;41(24):9491–504.

[39] Corma A, Iborra S, Velty A. Chemical routes for the transformation of biomass into chemicals. Chemical Reviews 2007;107(6):2411–502.

[40] Werpy T, Petersen G. Top value added chemicals from biomass. Volume I: results of screening for potential candidates from sugars and synthesis gas. Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL); 2004.

[41] Horvath IT, Anastas PT. Innovations and green chemistry. Chemical Reviews 2007;107(6):2169–73.

[42] Tsarevsky NV, Matyjaszewski K. Environmentally benign atom transfer radical polymerization: towards "green" processes and materials. Journal of Polymer Science Part A: Polymer Chemistry 2006;44(17):5098–112.

[43] Tsarevsky NV, Matyjaszewski K. "Green" atom transfer radical polymerization: from process design to preparation of well-defined environmentally friendly polymeric materials. Chemical Reviews 2007;107(6):2270–99.

[44] Kobayashi S, Makino A. enzymatic polymer synthesis: an opportunity for green polymer chemistry. Chemical Reviews 2009;109(11):5288–353.

[45] Li X, Tabil L, Panigrahi S. Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review. Journal of Polymers and the Environment 2007;15(1):25–33.

[46] Bourmaud A, Riviere J, Le Duigou A, Raj G, Baley C. Investigations of the use of a mussel-inspired compatibilizer to improve the matrix-fiber adhesion of a biocomposite. Polymer Testing 2009;28(6):668–72.

[47] Kumar AP, Singh RP. Biocomposites of cellulose reinforced starch: improvement of properties by photo-induced crosslinking. Bioresource Technology 2008;99(18):8803–9.

[48] Williams PRD, Inman D, Aden A, Heath GA. Environmental and sustainability factors associated with next-generation biofuels in the U.S.: what do we really know? Environmental Science & Technology 2009;43(13):4763–75.

[49] Gopalakrishnan G, Negri MC, Wang M, Wu M, Snyder SW, LaFreniere L. Biofuels, land, and water: a systems approach to sustainability. Environmental Science & Technology 2009;43(15):6094–100.

[50] Petrou EC, Pappis CP. Biofuels: a survey on pros and cons. Energy & Fuels 2009;23(2):1055–66.

[51] Reijnders L. Conditions for the sustainability of biomass based fuel use. Energy Policy 2006;34(7):863–76.

[52] Cherubini F, Jungmeier G. LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. The International Journal of Life Cycle Assessment 2009;15(1):53–66.

[53] Clark JH. Green chemistry for the second generation biorefinery – sustainable chemical manufacturing based on biomass. Journal of Chemical Technology & Biotechnology 2007;82(7):603–9.

[54] Ndazi BS, Karlsson S, Tesha JV, Nyahumwa CW. Chemical and physical modifications of rice husks for use as composite panels. Composites Part A: Applied Science and Manufacturing 2007;38(3):925–35.

[55] Gerngross TU. Can biotechnology move us toward a sustainable society? Nat Biotech 1999;17(6):541–4.

[56] Bohlmann GM. Biodegradable packaging life-cycle assessment. Environmental Progress 2004;23(4):342–6.

[57] Vink ETH, Rábago KR, Glassner DA, Gruber PR. Applications of life cycle assessment to NatureWorks(TM) polylactide (PLA) production. Polymer Degradation and Stability 2003;80(3):403–19.

[58] Shen L, Patel M. Life cycle assessment of polysaccharide materials: a review. Journal of Polymers and the Environment 2008;16(2):154–67.

[59] Joshi SV, Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? Composites Part A: Applied Science and Manufacturing 2004;35(3):371–6.

[60] Xu X, Jayaraman K, Morin C, Pecqueux N. Life cycle assessment of wood-fibre-reinforced polypropylene composites. Journal of Materials Processing Technology 2008;198(1–3):168–77.

[61] Corbière-Nicollier T, Gfeller Laban B, Lundquist L, Leterrier Y, Månson JAE, Jolliet O. Life cycle assessment of biofibres replacing glass fibres as reinforcement in plastics. Resources, Conservation and Recycling 2001;33(4): 267–87.

[62] Alves C, Ferrão PMC, Silva AJ, Reis LG, Freitas M, Rodrigues LB, et al. Ecodesign of automotive components making use of natural jute fiber composites. Journal of Cleaner Production 2010;18(4):313–27.

[63] Zah R, Hischier R, Leão AL, Braun I. Curauá fibers in the automobile industry - a sustainability assessment. Journal of Cleaner Production 2007;15(11–12): 1032–40.

[64] Pietrini M, Roes L, Patel MK, Chiellini E. Comparative life cycle studies on poly(3-hydroxybutyrate)-based composites as potential replacement for conventional petrochemical plastics. Biomacromolecules 2007;8:2210–8.

[65] Vilaplana F, Karlsson S. Quality concepts for the improved use of recycled polymeric materials: a review. Macromolecular Materials and Engineering 2008;293:274–97.

[66] Lange J-P. Lignocellulose conversion: an introduction to chemistry, process and economics. Biofuels. Bioproducts and Biorefining 2007;1(1):39–48.

[67] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behavior and kinetics of biomass derived materials. Journal of Analytical and Applied Pyrolysis 2002;62(2):331–49.

[68] Matsuzawa Y, Ayabe M, Nishino J. Acceleration of cellulose co-pyrolysis with polymer. Polymer Degradation and Stability 2001;71(3):435–44.

[69] Jiménez A, Ruseckaite R. Binary mixtures based on polycaprolactone and cellulose derivatives. Journal of Thermal Analysis and Calorimetry 2007;88 (3):851–6.

[70] Ruseckaite RA, Jiménez A. Thermal degradation of mixtures of polycaprolactone with cellulose derivatives. Polymer Degradation and Stability 2003;81(2):353–8.

[71] Fraga A, Ruseckaite RA, Jiménez A. Thermal degradation and pyrolysis of mixtures based on poly(3-hydroxybutyrate-8%-3-hydroxyvalerate) and cellulose derivatives. Polymer Testing 2005;24(4):526–34.

[72] Gatenholm P, Mathiasson A. Biodegradable natural composites. II. Synergistic effects of processing cellulose with PHB. Journal of Applied Polymer Science 1994;51(7):1231–7.

[73] Espert A, de las Heras LA, Karlsson S. Emission of possible odourous low molecular weight compounds in recycled biofibre/polypropylene composites monitored by head-space SPME-GC-MS. Polymer Degradation and Stability 2005;90(3):555–62.

[74] Kim H-S, Kim S, Kim H-J, Kim H-G. Physico-mechanical properties, odor and VOC emission of bio-flour-filled poly(propylene) bio-composites with different volcanic pozzolan contents. Macromolecular Materials and Engineering 2006;291(10):1255–64.

[75] Baun A, Hartmann NB, Grieger KD, Hansen SF. Setting the limits for engineered nanoparticles in European surface waters - are current approaches appropriate? Journal of Environmental Monitoring 2009;11(10):1774–81.

[76] Behra R, Krug H. Nanoecotoxicology: Nanoparticles at large. Nat Nano 2008;3(5):253–4.

[77] Handy R, Owen R, Valsami-Jones E. The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges, and future needs. Ecotoxicology 2008;17(5):315–25.

[78] Papp T, Schiffmann D, Weiss D, Castranova V, Vallyathan V, Rahman Q. Human health implications of nanomaterial exposure. Nanotoxicology 2008;2(1):9–27.

[79] Pérez S, Farré Ml, Barceló D. Analysis, behavior and ecotoxicity of carbon-based nanomaterials in the aquatic environment. TrAC Trends in Analytical Chemistry 2009;28(6):820–32.

[80] Quiévy N, Jacquet N, Sclavons M, Deroanne C, Paquot M, Devaux J. Influence of homogenization and drying on the thermal stability of microfibrillated cellulose. Polymer Degradation and Stability 2010;95(3):306–14.

[81] Scheringer M. Nanoecotoxicology: environmental risks of nanomaterials. Nature Nanotechnology 2008;3(6):322–3.

[82] Wiesner MR, Lowry GV, Alvarez P, Dionysiou D, Biswas P. Assessing the risks of manufactured nanomaterials. Environmental Science & Technology 2006;40(14):4336–45.

[83] Ray PC, Yu H, Fu PP. Toxicity and environmental risks of nanomaterials: challenges and future needs. Journal of Environmental Science and Health, Part C: Environmental Carcinogenesis and Ecotoxicology Reviews 2009;27(1):1–35.

[84] Farré M, Gajda-Schrantz K, Kantiani L, Barceló D. Ecotoxicity and analysis of nanomaterials in the aquatic environment. Analytical and Bioanalytical Chemistry 2009;393(1):81–95.

[85] Reijnders L. Cleaner nanotechnology and hazard reduction of manufactured nanoparticles. Journal of Cleaner Production 2006;14(2):124–33.

[86] Marquis BJ, Love SA, Braun KL, Haynes CL. Analytical methods to assess nanoparticle toxicity. The Analyst 2009;134(3):425–39.

[87] Strömberg E. Long-term properties of sustainable polymeric materials: mechanical recycling and use of renewable resources fibre and polymer technology. Stockholm: Royal Institute of Technology (KTH); 2009.

[88] Reijnders L. The release of TiO2 and SiO2 nanoparticles from nanocomposites. Polymer Degradation and Stability 2009;94(5):873–6.

[89] Wallström S, Strömberg E, Karlsson S. Microbiological growth testing of polymeric materials: an evaluation of new methods. Polymer Testing 2005;24(5):557–63.

[90] Chen H, Miao M, Ding X. Influence of moisture absorption on the interfacial strength of bamboo/vinyl ester composites. Composites Part A: Applied Science and Manufacturing 2009;40(12):2013–9.

[91] Jacob M, Varughese KT, Thomas S. Water sorption studies of hybrid biofiber-reinforced natural rubber biocomposites. Biomacromolecules 2005;6(6):2969–79.

[92] Comyn J. Polymer permeability. London: Chapman & Hall; 1985.

[93] Bismarck A, Aranberri-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, et al. Surface characterization of flax, hemp and cellulose fibers; surface properties and the water uptake behavior. Polymer Composites 2002;23(5):872–94.

[94] Espert A, Vilaplana F, Karlsson S. Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. Composites Part A Applied Science and Manufacturing 2004;35(11):1267–76.

[95] Alvarez VA, Ruseckaite RA, Vazquez A. Aqueous degradation of MATER BI Y–Sisal fibers biocomposites. Journal of Thermoplastic Composite Materials 2007;20(3):291–303.

[96] di Franco CR, Cyras VP, Busalmen JP, Ruseckaite RA, Vázquez A. Degradation of polycaprolactone/starch blends and composites with sisal fibre. Polymer Degradation and Stability 2004;86(1):95–103.

[97] Bessadok A, Marais S, Roudesli S, Lixon C, Métayer M. Influence of chemical modifications on water-sorption and mechanical properties of Agave fibres. Composites Part A: Applied Science and Manufacturing 2008;39(1):29–45.

[98] Joseph PV, Rabello MS, Mattoso LHC, Joseph K, Thomas S. Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. Composites Science and Technology 2002;62(10–11):1357–72.

[99] Dhakal HN, Zhang ZY, Richardson MOW. Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Composites Science and Technology 2007;67(7–8):1674–83.

[100] Stark N. Influence of moisture absorption on mechanical properties of wood flour-polypropylene composites. Journal of Thermoplastic Composite Materials 2001;14(5):421–32.

[101] Le Duigou A, Davies P, Baley C. Seawater ageing of flax/poly(lactic acid) biocomposites. Polymer Degradation and Stability 2009;94(7):1151–62.

[102] Beg MDH, Pickering KL. Mechanical performance of Kraft fibre reinforced polypropylene composites: Influence of fibre length, fibre beating and hygrothermal ageing. Composites Part A: Applied Science and Manufacturing 2008;39(11):1748–55.

[103] Chow WS, Bakar AA, Ishak ZAM. Water absorption and hygrothermal aging study on organomontmorillonite reinforced polyamide 6/polypropylene nanocomposites. Journal of Applied Polymer Science 2005;98(2):780–90.

[104] Chen B, Liu S, Evans JRG. Polymeric thermal actuation using laminates based on polymer-clay nanocomposites. Journal of Applied Polymer Science 2008;109(3):1480–3.

[105] Sinha Ray S, Yamada K, Okamoto M, Ueda K. Control of biodegradability of polylactide via nanocomposite technology. Macromolecular Materials and Engineering 2003;288(3):203–8.

[106] Paul MA, Delcourt C, Alexandre M, Degée P, Monteverde F, Dubois P. Polylactide/montmorillonite nanocomposites: study of the hydrolytic degradation. Polymer Degradation and Stability 2005;87(3):535–42.

[107] Zhou Q, Xanthos M. Nanoclay and crystallinity effects on the hydrolytic degradation of polylactides. Polymer Degradation and Stability 2008;93(8):1450–9.

[108] Devi LU, Joseph K, Nair KCM, Thomas S. Ageing studies of pineapple leaf fiber-reinforced polyester composites. Journal of Applied Polymer Science 2004;94(2):503–10.

[109] Varghese S, Kuriakose B, Thomas S. Short sisal fibre reinforced natural rubber composites: high-energy radiation, thermal and ozone degradation. Polymer Degradation and Stability 1994;44(1):55–61.

[110] Srebrenkoska V, Gaceva GB, Avella M, Errico ME, Gentile G. Recycling of polypropylene-based eco-composites. Polymer International 2008;57(11):1252–7.

[111] Beg MDH, Pickering KL. Reprocessing of wood fibre reinforced polypropylene composites. Part I: effects on physical and mechanical properties. Composites Part A: Applied Science and Manufacturing 2008;39(7):1091–100.

[112] Bourmaud A, Baley C. Investigations on the recycling of hemp and sisal fibre reinforced polypropylene composites. Polymer Degradation and Stability 2007;92(6):1034–45.

[113] Kaci M, Hamma A, Pillin I, Grohens Y. Effect of Reprocessing cycles on the morphology and properties of poly(propylene)/wood flour composites compatibilized with EBAGMA terpolymer. Macromolecular Materials and Engineering 2009;294(8):532–40.

[114] Le Duigou A, Pillin I, Bourmaud A, Davies P, Baley C. Effect of recycling on mechanical behaviour of biocompostable flax/poly(l-lactide) composites. Composites Part A: Applied Science and Manufacturing 2008;39(9):1471–8.

[115] Islam T, Khan RA, Khan MA, Rahman MA, Fernandez-Lahore M, Huque QMI, et al. of Gamma-irradiated biocomposites of jute fabric-reinforced poly(caprolactone). Polymer-Plastics Technology and Engineering 2009;48(11):1198–205.

[116] Beg MDH, Pickering KL. Accelerated weathering of unbleached and bleached kraft wood fibre reinforced polypropylene composites. Polymer Degradation and Stability 2008;93(10):1939–46.

[117] Islam MS, Pickering KL, Foreman NJ. Influence of accelerated ageing on the physico-mechanical properties of alkali-treated industrial hemp fibre reinforced poly(lactic acid) (PLA) composites. Polymer Degradation and Stability 2010;95(1):59–65.

[118] Pandey JK, Raghunatha Reddy K, Pratheep Kumar A, Singh RP. An overview on the degradability of polymer nanocomposites. Polymer Degradation and Stability 2005;88(2):234–50.

[119] Pfaendner R. Nanocomposites: Industrial opportunity or challenge? Polymer Degradation and Stability 2010;95(3):369–73.

[120] Qin H, Zhang S, Liu H, Xie S, Yang M, Shen D. Photo-oxidative degradation of polypropylene/montmorillonite nanocomposites. Polymer 2005;46(9):3149–56.

[121] Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo J-E. Polymer biodegradation: mechanisms and estimation techniques – a review. Chemosphere 2008;73(4):429–42.

[122] Flemming H-C. Relevance of biofilms for the biodeterioration of surfaces of polymeric materials. Polymer Degradation and Stability 1998;59:309–15.

[123] Strömberg E, Karlsson S. The effect of biodegradation on surface and bulk property changes of polypropylene, recycled polypropylene and polylactide biocomposites. International Biodeterioration & Biodegradation 2009;63(8):1045–53.

[124] Scaffaro R, Morreale M, Lo Re G, La Mantia FP. Degradation of Mater-Bi®/wood flour biocomposites in active sewage sludge. Polymer Degradation and Stability 2009;94(8):1220–9.

[125] Singh RP, Pandey JK, Rutot D, Degée P, Dubois P. Biodegradation of poly([var epsilon]-caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer. Carbohydrate Research 2003;338(17):1759–69.

[126] Iovino R, Zullo R, Rao MA, Cassar L, Gianfreda L. Biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions. Polymer Degradation and Stability 2008;93(1):147–57.

[127] Ohkita T, Lee S-H. Thermal degradation and biodegradability of poly (lactic acid)/corn starch biocomposites. Journal of Applied Polymer Science 2006;100(4):3009–17.

[128] Wan YZ, Luo H, He F, Liang H, Huang Y, Li XL. Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. Composites Science and Technology 2009;69(7–8):1212–7.

[129] Wu C-S. Assessing biodegradability and mechanical, thermal, and morphological properties of an acrylic acid-modified poly(3-hydroxybutyric acid)/wood flours biocomposite. Journal of Applied Polymer Science 2006;102(4):3565–74.

[130] Kim H-S, Kim H-J, Lee J-W, Choi I-G. Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil. Polymer Degradation and Stability 2006;91(5):1117–27.

[131] Zhao Q, Tao J, Yam RCM, Mok ACK, Li RKY, Song C. Biodegradation behavior of polycaprolactone/rice husk ecocomposites in simulated soil medium. Polymer Degradation and Stability 2008;93(8):1571–6.

[132] Sinha Ray S, Yamada K, Okamoto M, Ueda K. Polylactide-layered silicate nanocomposite: a novel biodegradable material. Nano Letters 2002;2(10):1093–6.

[133] Fukushima K, Abbate C, Tabuani D, Gennari M, Camino G. Biodegradation of poly(lactic acid) and its nanocomposites. Polymer Degradation and Stability 2009;94(10):1646–55.

[134] Pan H, Qiu Z. Biodegradable poly(l-lactide)/polyhedral oligomeric silsesquioxanes nanocomposites: enhanced crystallization, mechanical properties, and hydrolytic degradation. Macromolecules 2010;43(3):1499–506.

[135] Sinha Ray S, Yamada K, Okamoto M, Ogami A, Ueda K. New polylactide/layered silicate nanocomposites. 3. High-performance biodegradable materials. Chemistry of Materials 2003;15(7):1456–65.

[136] Maiti P, Batt CA, Giannelis EP. New biodegradable polyhydroxybutyrate/layered silicate nanocomposites. Biomacromolecules 2007;8(11):3393–400.

[137] Singh NK, Purkayastha BD, Roy JK, Banik RM, Yashpal M, Singh G, et al. Nanoparticle-induced controlled biodegradation and its mechanism in poly (Îµ-caprolactone). ACS Applied Materials & Interfaces 2009;2(1):69–81.

[138] Lee S-R, Park H-M, Lim H, Kang T, Li X, Cho W-J, et al. Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites. Polymer 2002;43(8):2495–500.

[139] Wang S, Song C, Chen G, Guo T, Liu J, Zhang B, et al. Characteristics and biodegradation properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organophilic montmorillonite (PHBV/OMMT) nanocomposite. Polymer Degradation and Stability 2005;87(1):69–76.

[140] Kapanen A, Itävaara M. Ecotoxicity tests for compost applications. Ecotoxicology and Environmental Safety 2001;49(1):1–16.

[141] Jayasekara R, Sheridan S, Lourbakos E, Beh H, Christie GBY, Jenkins M, et al. Biodegradation and ecotoxicity evaluation of a bionolle and starch blend and its degradation products in compost. International Biodeterioration & Biodegradation 2003;51(1):77–81.

[142] Rudnik E, Milanov N, Matuschek G, Kettrup A. Ecotoxicity of biocomposites based on renewable feedstock – preliminary studies. Chemosphere 2007;70 (2):337–40.

[143] Tuominen J, Kylma J, Kapanen A, Venelampi O, Itavaara M, Seppala J. Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact. Biomacromolecules 2002;3(3):445–55.