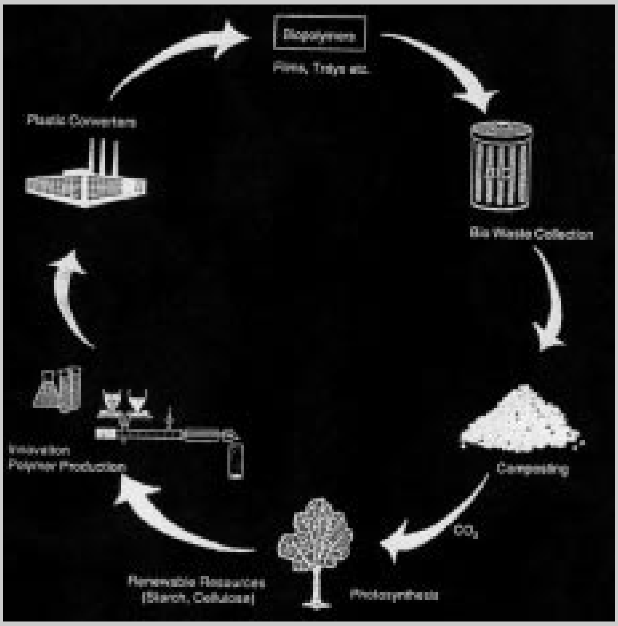
Macromol. Mater. Eng. **276/277,** *1–24 (2000)*

Macromolecular Materials and Engineering

Review: Recently the critical discussion about the preservation of natural resources and recycling has led to the renewed interest concerning biomaterials with the focus on renewable raw materials. Because of increasing environmental consciousness and demands of legislative authorities, use and removal of traditional composite structures, usually made of glass, carbon or aramid fibers being reinforced with epoxy, unsaturated polyester, or phenolics, are considered critically. Recent advances in natural fiber development, genetic engineering and composite science offer significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. The important feature of composite materials is that they can be designed and tailored to meet different requirements. Since natural fibers are cheap and biodegradable, the biodegradable composites from biofibers and biodegradable polymers will render a contribution in the 21st century due to serious environmental problem. Biodegradable polymers have offered scientists a possible solution to waste-disposal problems associated with traditional petroleum-derived plastics. For scientists the real challenge lies in finding applications which would consume sufficiently large quantities of these materials to lead price reduction, allowing biodegradable polymers to compete economically in the market. Today's much better performance of traditional plastics are the outcome of continued R&D efforts of last several years; however the existing biodegradable polymers came to public only few years back. Prices of biodegradable polymers can be reduced on mass scale production; and such mass scale production will be feasible through constant R&D efforts of scientists to improve the performance of biodegradable plastics. Manufacture of biodegradable composites from such biodegradable plastics will enhance the demand of such materials. The structural aspects and properties of several biofibers and biodegradable polymers, recent developments of different biodegradable polymers and biocomposites are discussed in this review article. Collaborative R&D efforts among material scientists and engineers as well as intensive co-operation and co-ordination among industries, research institutions and government are essential to find various commercial applications of biocomposites even beyond to our imagination.



Life cycle of compostable, biodegradable polymers (after ref.[78])

Biofibres, biodegradable polymers and biocomposites: An overview

A. K. Mohanty[a, b], *M. Misra*[a, b], *G. Hinrichsen**

Technical University of Berlin, Institute of Nonmetallic Materials, Polymer Physics, Englische Str. 20, D-10587 Berlin, Germany

(Received: September 27, 1999; revised: March 2, 2000)

Summary of contents

---

[a] Present address: Composite Materials and Structures Center, Michigan State University, 2100 Engineering Building, East Lansing, MI 48824-1226, USA.

[b] Home address: Polymer & Composites Laboratory, Department of Chemistry, Ravenshaw College (Autonomous), Cuttack – 753003, Orissa, India.

1438-7492/2000/0103–0001$17.50+.50/0

1. Introduction

Fibre-reinforced plastic composites began with cellulose fibre in phenolics in 1908, later extending to urea and melamine, and reaching commodity status in the 1940s with glass fibre in unsaturated polyesters. From guitars, tennis racquets and cars to microlight aircrafts, electronic components and artificial joints, composites are finding use in diverse fields. Because of increasing environmental consciousness and demands of legislative authorities, the manufacture, use and removal of traditional composite structures, usually made of glass, carbon or aramid fibres being reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics, are considered critically. The most important disadvantage of such composite materials is the problem of convenient removal after the end of life time, as the components are closely interconnected, relatively stable and therefore difficult to separate and recycle1). In the modern polymer technology it is a great demand that every material should especially be adapted to the environment. In order to successfully meet the environmental and recycling problems, the DLR (Deutsches Zentrum für Luft- und Raumfart e.V.) Institute of Structural Mechanics, applying their knowledge in composite technology in a new broadened way2), developed an innovative idea in 1989.

By embedding natural reinforcing fibres, e.g. flax, hemp, ramie, etc. into biopolymeric matrix made of derivatives from cellulose, starch, lactic acid, etc; new fibre reinforced materials called biocomposites were created and are still being developed2–8). Biocomposites consist of biodegradable polymer as matrix material and usually biofibre as reinforcing element. Since both components are biodegradable, the composite as the integral part is also expected to be biodegradable. Biofibres, i.e., natural polymers, are generally biodegradable but they do not possess the necessary thermal and mechanical properties desirable for engineering plastics. On the other hand, the best engineering plastics are obtained from synthetic polymers, but they are non-biodegradable. A lot of R&D work has been carried out on biofibre reinforced synthetic polymers. The composites of natural fibres and non-biodegradable synthetic polymers may offer a new class of materials but are not completely biodegradable. Government regulations and growing environmental awareness throughout the world have triggered a paradigm shift towards designing materials compatible with the environment9). The biofibres derived from annually renewable resources, as reinforcing fibres in both thermoplastic and thermoset matrix composites provide positive environmental benefits with respect to ultimate disposability and raw material utilization10). Auto makers now see strong promise in natural fiber reinforcements11). We find a number of publications on natural fiber composites in automotive applications12–14). Literature also shows some reviews on cellulosic as well as ligno-cellulosic fiber based composites15–18). Advantages of biofibres over traditional reinforcing materials such as glass fibres, talc and mica are9): low cost, low density, high toughness, acceptable specific strength properties, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery and biodegradability. The main drawback of biofibres is their hydrophilic nature which lowers the compatibility with hydrophobic polymeric matrix during composite fabrications. The other disadvantage is the relatively low processing temperature required due to the possibility of fibre degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures for most of the biofibres are thus limited to about 200 °C, although it is possible to use higher temperatures for short periods19).

The annual disposal of over 10 million tons of plastics in both the US and EC countries has raised the demand for means of managing this non-biodegradable waste stream. The synthetic polymers have displaced metals, glasses, ceramics and wood in many products, especially in the area of packaging. The commodity plastics, the so called “big four” polyethylene (PE), poly(propylene) (PP), polystyrene (PS) and poly(vinyl chloride) (PVC) in a variety of forms such as films, flexible bags and rigid containers have revolutionized the packaging industry. However, once these materials are discarded, they persist in the environment without being degraded thus giving rise to a multitude of ecological and environmental concerns. The important feature of composite materials is that they can be designed and tailored to meet different requirements. Since biofibres are cheap and biodegradable, the biocomposites from biofibre reinforcced biodegradable polymers will render a contribution in 21st century due to serious environmental problem. Now it is a challenge for scientists to examine the properties of different biodegradable polymers available in the market to make sure whether or not they are suited to be used as a matrix system for biocomposites. Keeping above facts into consideration the present review article deals with the current development of biocomposites with a broad outline of discussion on structural parts of some important biofibres, the current development of different biodegradable polymers so as to give a broad idea for the future R&D activities in this challenging field of work.

2. Reinforcing biofibres

In biocomposites the biofibres serve as a reinforcement by enhancing the strength and stiffness to the resulting composite structures. Source, origin, nature as well as physical and chemical composition of different natural fibers have been reviewed20, 21). The conventional fibres like glass, carbon, aramid, etc., can be produced with a definite range of properties, whereas the characteristic properties of natural fibres vary considerably22). This depends on whether the fibres are taken from plant stem or leafs23), the quality of the plants locations24), the age of the plant25) and the preconditioning26, 27). Depending on their origin, the natural fibres may be grouped into: leaf, bast, seed, and fruit origin. The best known examples are: (i) Leaf: Sisal, pineapple leaf fibre (PALF), and henequen; (ii) Bast: Flax, ramie, kenaf/mesta, hemp and jute; (iii) Seed: Cotton; (iv) Fruit: Coconut husk, i.e., coir. The natural fibres are lignocellulosic in nature. Lignocellulosic materials are the most abundant renewable biomaterial of photosynthesis on earth. In terms of mass units, the net primary production per year is estimated to be 2×10^{11} tons28) as compared to synthetic polymers by 1.5×10^{8} tons. Lignocellulosic materials are widely distributed in the biosphere in the form of trees (wood), plants and crops. Cellulose, in its various forms, constitutes approximately half of all polymer utilized in the industry worldwide29).

2.1 Chemical constituents and structural aspects

The major constituents of biofibres (lignocelluloses) are cellulose, hemicellulose and lignin. The amount of cellulose, in lignocellulosic systems, can vary depending on the species and age of the plant/species. Cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1,4-β-bonded anhydroglucose units30) which contains alcoholic hydroxyl groups. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules as well as with hydroxyl groups from the air. Therefore, all of the natural fibres are hydrophilic in nature; their moisture content reaches 8–12.6%22). Although the chemical structure of cellulose from different natural fibres is the same, the degree of polymerization (*DP*) varies. The mechanical properties of a fibre are significantly related to *DP*. Bast fibres commonly show the highest *DP* among approximately 10 000 different natural fibres31).

Lignin is a phenolic compound, generally resistant to microbial degradation, but the pretreatment of fibre renders it susceptible to the cellulose enzyme32, 33). The exact chemical nature of the principal component of biofibre, the lignin, still remains obscure16, 34). The main difficulty in lignin chemistry is that no method has so far been established by which it is possible to isolate the lignin in the native state from the fibre. Although the exact structural formula of lignin in natural fibre has yet not been established, most of the functional groups and units which make up the molecule have been identified. The high carbon and low hydrogen content of lignin suggest that it is highly unsaturated or aromatic in character. Lignin is characterized by its associated hydroxyl and methoxy groups. Ethylenic and sulfur-containing groups have also been found in lignins28). The chemical nature of lignin in lignocellulosic materials has been an important subject of studies35, 36). Lignin is a biochemical polymer which functions as a structural support material in plants. During synthesis of plant cell walls, polysaccharides such as cellulose and hemicellulose are laid down first, and lignin fills the spaces between the polysaccharide fibres, cementing them together. This lignification process causes a stiffening of cell walls, and the carbohydrate is protected from chemical and physical damage. The topology of lignin from different sources may be different but has the same basic composition.

Although the exact mode of linkages in biofibre16) is not well known, lignin is believed to be linked with the carbohydrate moiety through two types of linkages, one alkali sensitive and the other alkali resistant. The alkali sensitive linkage forms an ester-type combination between lignin hydroxyls and carboxyls of hemicellulose uronic acid. The ether-type linkage occurs through the lignin hydroxyls combining with the hydroxyls of cellulose. The lignin, being polyfunctional, exists in combination with more than one neighbouring chain molecule of cellulose and/or hemicellulose, making a crosslinked structure. The lignocellulosic material possesses many active functional groups28) like primary and secondary hydroxyls, carbonyls, carboxyls(esters), carbon-carbon, ether and acetal linkages.

The chemical compositions and structural parameters of some important biofibres are represented in Tab. 1. As it is found from Tab. 1 the various chemical constituents of a specific natural fibre also vary considerably. Such variation may be due to the origin, age, retting (mode of extraction of fibre from the source) process adopted, etc. Among all the natural fibres listed, coir is observed to contain least amount of cellulose but highest percent of lignin.

Tab. 1. Chemical composition and structural parameters of some natural fibres

Type of fibre	Cellulose wt.-%	Lignin wt.-%	Hemicellulose wt.-%	Pectin wt.-%	Wax wt.-%	Micro-fibrillar/spiral angle (Deg.)	Moisture content wt.-%	References
Bast								
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0	12.6	22, 28, 37, 38
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0	10.0	22, 28, 37, 38
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8	22, 28, 37, 38
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0	22, 28, 37, 39
Kenaf	31–39	15–19	21.5	–	–	–	–	28, 40
Leaf								
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	20.0	11.0	22, 28, 37, 41
PALF	70–82	5–12	–	–	–	14.0	11.8	42
Henequen	77.6	13.1	4–8	–	–	–	–	28
Seed								
Cotton	82.7	–	5.7	–	0.6	–	–	43
Fruit								
Coir	36–43	41–45	0.15–0.25	3–4	–	41–45	8.0	37, 41, 44

Tab. 2. Comparative properties of some natural fibres with conventional manmade fibres

Fibre	Density g/cm^3	Diameter μm	Tensile strength MPa	Young's modulus GPa	Elongation at break %	References
Cotton	1.5–1.6	–	287–800	5.5–12.6	7.0–8.0	45, 49
Jute	1.3–1.45	25–200	393–773	13–26.5	1.16–1.5	22, 23, 37, 45, 49
Flax	1.50	–	345–1100	27.6	2.7–3.2	22, 23, 37, 49
Hemp	–	–	690	–	1.6	22, 37
Ramie	1.50	–	400–938	61.4–128	1.2–3.8	22, 37, 46, 49
Sisal	1.45	50–200	468–640	9.4–22.0	3–7	22, 23, 37, 45, 49
PALF	–	20–80	413–1627	34.5–82.51	1.6	45
Coir	1.15	100–450	131–175	4–6	15–40	22, 45
E-glass	2.5	–	2000–3500	70	2.5	22, 47
S-glass	2.5	–	4570	86	2.8	22, 23, 47
Aramid	1.4	–	3000–3150	63–67	3.3–3.7	22, 47
Carbon	1.7	–	4000	230–240	1.4–1.8	22, 47

2.2 *Properties of biofibres*

The natural fibres exhibit considerable variation in diameter along with the length of individual filaments. Quality as well as most of the properties depend on factors like size, maturity as well as processing methods adopted for the extraction of fibres. The modulus of fibre decreases with increase in diameter. The properties such as density, electrical resistivity, ultimate tensile strength, initial modulus, etc., are related to the internal structure and chemical composition of fibres. A comparison of properties of some natural fibres with conventional manmade fibres can be obtained from Tab. 2. The strength and stiffness correlate with the angle between axis and fibril of the fibre, i.e., the smaller this angle, the higher the mechanical properties; the chemical constituents and complex chemical structure of natural fibres also affect the properties considerably. Coir shows least tensile strength among all the natural fibres as listed in Tab. 2 which is attributed to low cellulose content and considerably high microfibrillar angle as evidenced from Tab. 1. Again high tensile strength of flax may be attributed to its high cellulose content and comparatively low microfibrillar angle. However, it is not possible to correlate the fiber strength exactly with cellulose content and microfibrillar angle because of the very complex structure of natural fibres. Filament and individual fibre properties can vary widely depending on the source, age, separating technique, moisture content, speed of testing, history of fibre, etc. The lignin content of the fibres influences its structure[31], properties[31, 37–49] and morphology[50]. The waxy substances of natural fibres, generally influence the fibre's wettability and adhesion charateristics[51, 52].

In terms of specific strength, natural fibres can be compared with well-known glass fibres. The breaking length

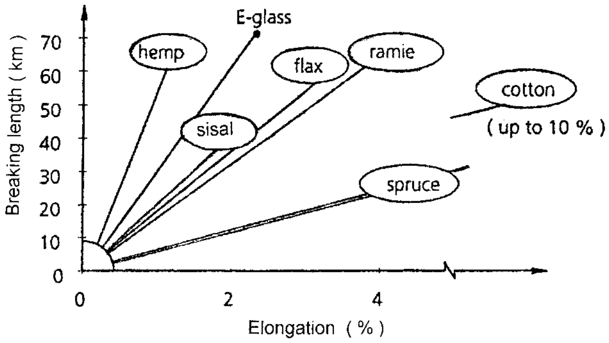


Fig. 1. Breaking length versus elongation of some natural fibers (after ref.[2])

versus elongation of some natural fibres is represented in Fig. 1. As observed, the stiffness of hemp is even higher than that of E-glass. The natural fibres showing best mechanical properties are to be selected[53–56] for composite fabrication. On the other hand the low thermal resistance of natural fibres does not allow an arbitrary choice of polymers as matrix materials. For manufacture of composites with suitable matrix systems, it is very important to know the degradation of mechanical properties when the fibres are exposed to composite processing temperature between 180–200 °C for certain time. The temperature resistance of coir and of different modified jute fibres has been investigated[44, 57, 58]. The surface modification of natural fibre improves the mechanical properties of the fibre[59]. The studies on degradation of tensile strength of elementary ramie fibres due to the influence of temperature and time of exposure reveal[4, 5, 8] that manufacturing conditions at about 200 °C lasting for a period of 10 min make the fibres lose nearly 10% of their strength. The said tests were performed on pure fibres. As fibres are usually surrounded and protected by the matrix when exposed to heat during the composite fabrication, the actual decrease of mechanical properties is expected to be less than reported.

2.3 Degradation properties of biofibres

The lignocellulosic natural fibres are degraded biologically because organisms recognise the carbohydrate polymers, mainly hemicelluloses in the cell wall and have very specific enzyme systems capable of hydrolysing these polymers into digestible units[40]. Fig. 2 demonstrates how the components of lignocellulosics interact in various ways. Biodegradation of the high molecular weight cellulose weakens the lignocellulosic cell wall because crystalline cellulose is primarily responsible for the strength of the lignocellulosics[60]. Due to degradation of cellulose, the strength gets lost. Photochemical degradation by ultraviolet light occurs when lignocellulosics are exposed to outside. This degradation primarily takes place in the lignin component, which is responsible for the characteristic colour changes[61]. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptable to UV degradation. After the lignin is degraded, the poorly bonded carbohydrate-rich fibres erode easily from the surface, which exposes new lignin to further degradative reactions. It is important to note that hemicellulose and cellulose of lignocellulosic fibres are degraded by heat much before the lignin[61]. The lignin component contributes to char formation, and the charred layer helps to insulate the lignocellulosics from further thermal degradation. Biofibres change their dimensions with varying moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups which attract moisture through hydrogen bonding[62]. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and surface of crystalline cellulose also play major roles. Lignocellulosics shrink as they lose moisture.

BIOLOGICAL DEGRADATION

Hemicellulose > > > Acessible Crystalline Cellulose > Non-crystalline Cellulose > > > > Crystalline Cellulose > > > > > Lignin

MOISTURE SORPTION

Hemicellulose > > Accessible Cellulose > > > Non-crystalline Cellulose > Lignin > > > Crystalline Cellulose

ULTRAVIOLET DEGRADATION

Lignin > > > > > Hemicellulose > Accessible Cellulose > Non-crystalline Cellulose > > > Crystalline Cellulose

THERMAL DEGRADATION

Hemicellulose > Cellulose > > > > > Lignin

STRENGTH

Crystalline Cellulose > > Non-crystalline Cellulose + Hemicellulose + Lignin > Lignin

Fig. 2. Cell wall polymers responsible for lignocellulosic properties (after ref.[40])

2.4 Cost aspects, availability and sustainable development of biofibres

The world's supply of natural resources is being depleted, the demand for sustainable and renewable raw materials continues to rise. In 1997, approximately 25 million metric tons of man-made fibres (about 45 million metric tons of man-made and natural fibres) were produced worldwide[63]. So responsible use of available natural fibres has become an inevitable task for scientists. In order to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for biofibres. One such avenue is in the area of fibre reinforced composites. Now we cannot only use our natural renewable resources for applications like for making twines, ropes, cords, etc., where cheap and synthetic PP fibres can be used. The price for biofibres which are feasible for different applications varies a lot depending on the changed economy of the countries where such fibres are widely available. Jute

Tab. 3. (a) Comparison of the price of synthetic and natural fibres (cf. ref.[23])

Fibre	Carbon	Steel	Glass	Sisal	Jute	Coir
Cost (US$/kg)	200	30	3.25	0.36	0.30	0.25
Modulus/cost (GPa kg/$)	2.0	6.7	21.5	41.7	43.3	20.0

Tab. 3. (b) Production of plant fibres in comparison to glass fibres (1993) (cf. ref.[43, 68])

Fibre	Price in comparison to glass fibres (%)	Production (1000 t)
Jute	18	3600
E-glass	100	1200
Flax	130	800
Sisal	21	500
Banana	40	100
Coir	17	100

is the so-called golden fibre from India and Bangladesh[34]; coir is produced in the tropical countries of the world and India accounts 20% of total world production of coir[64]; sisal plant though native to tropical and sub-tropical North and South America, is also widely grown in tropical countries of Africa, the West Indies and Far East[23], Tanzania and Brazil being now the two main producing countries[65]; Kenaf is a crop grown commercially in the U.S[66]; flax is mostly planted in EC although now it is grown in many diverse agricultural systems and environments throughout the world, as far apart as Canada, Argentina, India and Russia, and flax fibre accounts for less than 2% of world consumption of apparel and industrial textiles, despite the fact that it has a number of unique and beneficial properties[67]; hemp is originated from Central Asia, from which it spread to China, and is now cultivated in many countries of the temperature zone[67]; ramie fibres are the longest and one of the strongest fine textile fibres and mostly available and used in China, Japan and Malaysia[67]. For comparison, prices of some natural and synthetic fibres are represented in Tab. 3a and b. From Tab. 3a it is observed that the price of natural fibre is very low as compared to synthetic fibres. For specific price (modulus per unit price), jute is the best. In recent years, prices of natural fibres were not stable, especially for flax fibres[43], being about 30% more expensive than glass fibres (Tab. 3b). For these economical reasons, a substitution of glass fibres by natural fibres seems not to be easily realized. However biofibres offer several advantages, the most important being biodegradibility. Geethamma et al.[69] have reported the cost ratio of some natural fibres as coir : sisal : PALF : jute = 1 : 1.5 : 1.5 : 2. From the above discussion it is found that cost of natural fibres varies a lot depending on the place of origin and changed economy of that place.

Tab. 4. Costs of waste management options in Germany, Belgium and The Netherlands (in US$ per ton) (cf. ref.[70])

Option	Germany	Belgium	The Netherland
Composting	151	80	60
Incineration	486	110	135
Landfilling	402	75	105

3. Biodegradable polymers

The rising oil prices helped to stimulate early interest in biodegradables back in the 1970s and concerns over the dwindling availability of landfill sites are reviving interests in biodegradable materials today. Tab. 4 illustrates some typical prices for composting, incineration and landfilling in three European countries[70]. The difference in cost between the various countries can be partly explained by some reasons such as a different level of technology required, environmental regulations, scale of installation, etc. Biodegradable polymers have offered scientists a possible solution to waste-disposal problems associated with traditional petroleum-derived plastics. First introduced in the 1980s, biodegradable plastics and polymers as used in films, molded articles, sheets, etc., comprise a market that is still in its infancy.

3.1 Definition

According to Albertsson and Karlsson[71] biodegradation is defined as an event which takes place through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc.) and their secretion products. It is also necessary to consider abiotic reactions like photodegradation, oxidation and hydrolysis which may also alter the polymer before, during or instead of biodegradation because of environmental factors. International organizations, such as the American Society for Testing and Materials (ASTM) in connection with the Institute for Standards Research (ISR), the European Standardisation Committee (CEN), the International Standardisation Organisation (ISO), the German Institute for Standardisation (DIN), the Italian Standardization Agency (UNI), the Organic Reclamation and Composting Association (ORCA) are all actively involved in developing definitions and tests for biodegradability in different environments and compostability[72, 73]. A standard world-wide definition for biodegradable polymers although has not yet been established, all the definitions already in place, correlate the degradability of a material to a specific disposal environment and to a specific test method which simulates this environment in a time period which determines its classification[74]. The basic requirements for a material to be declared compostable are based on: 1. Complete biodegradability of

Tab. 5. Classification of biodegradable polymers on the basis of material class (cf. ref.[75])[a]

Material class	Manufacturer	Product name
Cellulose acetate	Mazzucchelli	BIOCETA®
	Planet Polymer	EnviroPlastic®-Z
Copolyester	BASF	Ecoflex
	Eastman	Easter Bio™
Polycaprolactone (PCL)	Birmingham Polymers	Poly(ε-caprolactone)
	Planet Polymer	Enviroplastic®-C
	Solvay	CAPA®
	Union Carbide	TONE®
Poly(ester amide)	Bayer	BAK 1095
		BAK 2195
Poly(ethylene terepthalate) (PET)-modified	DuPont	Biomax®
Polyglycolide (PGA)	Alkermes	Medisorb®
	Birmingham Polymers	Poly(glycolide)
	Boehringer Ingelheim	Resomer®
	PURAC	PURASORB® PG
Polyhydroxyalkanoates (PHA)	Metabolix	PHA
	Biomer	Biomer™
	Monsanto	Biopol®
Poly(lactic acid) (PLA)	Alkemers	Medisorb®
	Birmingham Polymers	Poly(L-lactide) & Poly(DL-lactide)
	Boehringer Ingelheim	Resomer®
	Cargill Dow Polymers	EcoPLA®
	Chronopol	Heplon™
	Hygail	PLA
	Neste	Poly(L-lactide)
	PURAC	PURASORB® PL/PD/PDL
Poly(vinyl alcohol) (PVOH)	Idroplast	Hydrolene®
	Novon	Aqua-NOVON®
	Planet Polymer	Aquadro™
	Texas Polymer	Vinex™
Starch & starch blends	AVEBE	Paragon™
	BioPlastic (Michigan)	Envar™
	BIOTEC	Bioplast®, Bioflex®, Biopur®
	Buna Sow Leuna	Sconacell®
	Earth Shell	Starch-based composite
	Midwest Grain	Polytriticum™ 2000
	Novamont	Mater-Bi™
	Novon	Poly-NOVON®
	Starch Tech	ST1, ST2, ST3
Other blends	Alkermers	Medisorb®
	Bio Plastic (Colorado)	Biocomposite material
	Birmingham Polymers	Poly(DL-lactide-co-caprolactone) & Poly(DL-lactide-co-glycolide)
	Boehringer	Resomer®
	Planet Polymer	EnviroPlastic®-U
	PURAC	PURASORB® PLG, PURASORB® PDLG

[a] Reproduced with permission from Mar Tech, USA (Website: http://www.Mar Tech-Reports.com).

the material, measured by respirometric tests like ASTM D5338-92, ISO/CD 14855 and corresponding CEN draft or the modified Sturm test ASTM D5209, in a time period compatible with the composting technology (some months); 2. No adverse effects on compost quality and in particular no toxic effects of the compost and leachates on the aquatic and terrestial organisms; 3. Disintegration of the material during the fermentation phase; 4. Control of laboratory-scale results on pilot scale composting plants.

3.2 *Classification*

The classification of biodegradable polymers on the basis of material class is represented in Tab. 5. Biodegradable polymers may be classified as: biosynthetic, semi-biosynthetic, and chemosynthetic type. Steinbüchel76) has studied the use of biosynthetic, biodegradable thermoplastics and elastomers from renewable resources. Almost all biosynthetic polymers which are readily available from renewable resources are biodegradable within a reasonable time scale. Many semibiosynthetic and chemosynthetic polymers are also biodegradable if they contain chemical bonds which occur in natural compounds. Thus biodegradability is not only a function of origin but also of chemical structure and degrading environments.

3.3 Importance of biodegradable polymers from renewable resources

When a biodegradable material (neat polymer, blended product, or composite) is obtained completely from renewable resources we may call it a green polymeric material. Biopolymers from renewable resources have attracted much attention in recent years77). Renewable sources of polymeric materials offer an answer to maintaining sustainable development of economically and ecologically attractive technology. The innovations in the development of materials from biopolymers, the preservation of fossil-based raw materials, complete biological degradability, the reduction in the volume of garbage and compostability in the natural cycle, protection of the climate through the reduction of carbon dioxide released, as well as the application possibilities of agricultural resources for the production of bio/green materials are some of the reasons why such materials have attracted the public interest78). The life cycle of compostable biodegradable polymers is represented in Fig. 3. The use of agricultural materials and biomass has been reviewed by Mülhaupt79) who has concluded that, although Germany is at the forefront of green technology and a wide range of biodegradable pharmaceutical and novel surfactant materials can be made from renewable materials, it is only as components of packaging and as natural fibre composites that these materials are currently viable in terms of price and performance. The effect on the US economy of substituting production of corn-based polymer resins for petroleum-based polymers has been analysed by Beach et al.80)

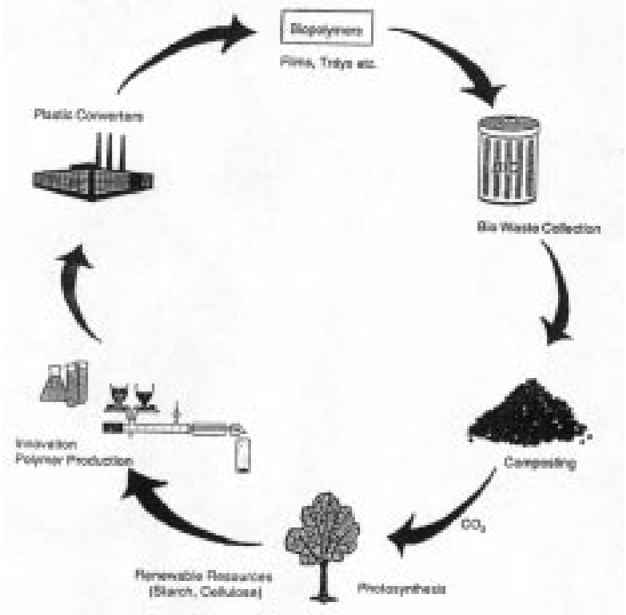


Fig. 3. Life cycle of compostable, biodegradable polymers (after ref.78))

3.4 Structure, synthesis and properties of biodegradable polymers

The best starting point for a correct approach to the production of biocomposites is to know the structure, properties, and function of biodegradable polymers very well, and also how they intercombine or interact with different natural fibres in the formation of biocomposites. Structural aspects and properties of some natural fibres have already discussed in Section 2. In this section the structure, synthesis, and properties of some biodegradable polymers are summarized.

3.4.1 Aliphatic polyesters

Structural effects on the biodegradation of aliphatic polyesters have been reported81). Aliphatic polyesters as biodegradable structural materials are classified into two types regarding the mode of bonding of constituent monomers, i.e., polyhydroxyalkanoates, which are polymers of hydroxy acids, HO-R-COOH, as repeating units and poly(alkylene dicarboxylate)s which are synthesized by polycondensation reaction of diols and dicarboxylic acids. Again hydroxy acids are classified into α-, β- and ω-hydroxy acids in respect of bonding position of the OH group from the COOH end group. All such structures are represented in Fig. 4.

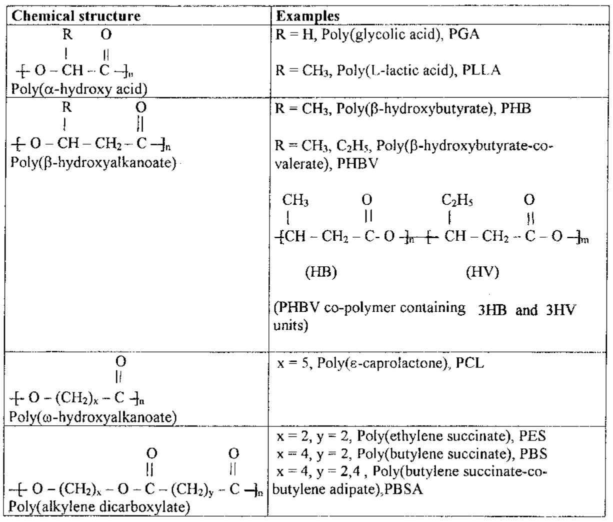
i. Poly(α-hydroxy acid) such as poly(glycolic acid), PGA, or poly(lactic acid), PLA, are crystalline polymers with relatively high melting point. Although recently microorganisms or enzymes that can degrade PLA have been reported, the number of carbon atoms between ester bonds in the main chain may be responsible for the major nonenzymatic hydrolytic degradation of poly(α-hydroxy acid). Recently PLA has been highlighted because of its availability from renewable resources like corn. PLA is a hydrophobic polymer because of the incorporation of the $-CH_3$ side groups when compared to PGA. PLA is synthesized by the condensation polymerization of D- or L-lactic acid or ring opening polymerization of the lactide. Advanced industrial technologies of polymerization have been developed to obtain high molecular weight pure PLA which leads to a potential for structural materials with enough lifetime to maintain mechanical properties without rapid hydrolysis even under humid environment, as well as good compostability. The physical properties and biodegradibility of PLA can be regulated by employing a comonomer component of hydroxy acids or racemization of D- or L- isomer, whereas PLA homopolymer such as poly(L-lactic acid) (PLLA) is a hard, transparent and crystalline polymer having a melting point of 170–180 °C and a glass transition temperature of about 53 °C[81]. PLLA, a highly crystalline polymer, is more resistant than PGA to hydrolysis due to the methyl substituent's steric shielding effect of the ester group. PLA is primarily used for medical applications including sutures, drug delivery, vascular grafts, artificial skin, and orthopedic implants[82]. Synthetic biodegradable PLA, PGA, and copolymers of these, have been manufactured for biomedical applications since the 1970s.

A new range of PLA biodegradable polymers is being offered by Cargill Dow Polymers[83]. All PLA resins are manufactured using renewable agricultural resources, such as corn or sugar beets. They are composed of chains of lactic acid that are produced by converting starch into sugar which is then fermented. By removal of water lactide is formed which is then converted into PLA resins through solvent-free polymerization. Cargill Dow is confident that the new PLA polymers will compete successfully on a cost-performance basis with certain polymers, like polyethylene, poly(propylene) and polyester. Current commercial applications include compostable food and lawn waste bags, yoghurt cartons, seeding mats and nonwoven mulch to prevent weed growth.

DuPont's biodegradable Biomax copolyester resin, a modified form of PET, was launched in 1997. Its properties, according to DuPont, are diverse and customisable, but they are generally formulated to mimic polyethylene or poly(propylene)[83]. Because it is based on PET technology, and can be produced on commercial lines, DuPont believes that Biomax is only marginally more expensive to produce than PET itself, and significantly cheaper to produce than other biodegradable polymers. Biomax has a relatively high melting point for a biodegradable resin, of around 200 °C, which accounts for its wide range of processing options. As a modified PET it can also be processed on equipments designed for the standard polymer. It can be made into films, fibre and non-wovens, as well as being thermoformed and injection moulded. Biomax has a broad range of potential applications including single-use products such as geotextiles, agricultural mulch films, seed mats, plant pots and bags for covering ripening fruits, disposable plates and cups, waste bags, etc. Biomax can be recycled, incinerated, or land-filled, but it is intended mainly for disposal by composting and in-soil degradation. It is hydro/biodegradable as it must undergo hydrolysis first before becoming biodegradable. The large molecules are split by moisture into smaller molecules which are consumed and converted to carbon dioxide and water by naturally occurring microbes.

ii. Poly(*β*-hydroxyalkanoate)s (PHAs), which are synthesized biochemically by microbial fermentation and which may be produced in the future by transgenic plants, represent natural polyesters. Bacteria came first and are still the only real source of these polyesters; it will still require some more years research until transgenic plants will be available for production. Poly(β-hydroxybutyrate) (PHB) (commercial name Biopol®) is a biotechnologically produced polyester that constitutes a carbon reserve in a wide variety of bacteria[84] and has attracted much attention as a biodegradable thermoplastic polyester[85–87]. It can be degraded to water and carbon dioxide under environmental conditions by a variety of bacteria and has much potential for applications of environmentally degradable plastics[88]. However, it suffers from some disadvantages compared with conventional plastics, for example, brittleness and a narrow processability window[89]. To improve these properties, various copolymers containing hydroxyalkanoate units other than 3-hydroxybutyrate (3HB) have been biosynthesized[90]. PHB and the copolymer, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), are produced by Monsanto and sold under the tradename Biopol®. PHBV polymers were first manufactured[88] by ICI in 1983 and were originally intended as biodegradable substitutes for oil-based polyolefins in films, bottles and plastic containers[91]. The actual and potential uses of PHB and PHBV for motor oil containers, film formation and paper-coating materials have been reviewed[92]. In 1990 the manufacture of blow-moulded bottles using Biopol® for packaging shampoo was started in Germany by Wella AG, Darmstadt. The range of possible uses of Biopol® polymers have been summarized by Amass et al.[93] PHBVs are highly crystalline polymers with melting points and glass transition temperature similar to poly(propylene) (PP)[84]. Due to characteristics of biodegradability through non-toxic intermediates and easy processability, PHBV polymers are being developed and commercialized as ideal candidates for the substitution of non-biodegradable polymeric materials in commodity application[94, 95]. However, the prohibitive cost, the small difference between thermal degradation and melting temperature and especially the low impact resistance around the room temperature and below, due to high crystallinity and relatively high glass transition, have prevented its larger commercial application.

With all melt-processed polymers there is the possibility of thermal degradation at temperatures in the region of the melting point (in case of PHB, melting point as calculated is 180 °C)[96]. PHB is known[97–100] to be susceptible to thermal degradation at temperature close to its melting point. This degradation occurs almost exclusively via a random chain scission mechanism involving a six-membered ring transition state[99, 100]. Lehrle and Williams[101] have reported



Chemical structure	Examples
$\left[O - \overset{R}{\overset{\mid}{CH}} - \overset{O}{\overset{\|}{C}} \right]_n$ Poly(α-hydroxy acid)	R = H, Poly(glycolic acid), PGA R = CH₃, Poly(L-lactic acid), PLLA
$\left[O - \overset{R}{\overset{\mid}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} \right]_n$ Poly(β-hydroxyalkanoate)	R = CH₃, Poly(β-hydroxybutyrate), PHB R = CH₃, C₂H₅, Poly(β-hydroxybutyrate-co-valerate), PHBV $\left[\overset{CH_3}{\overset{\mid}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - O \right]_n \left[\overset{C_2H_5}{\overset{\mid}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - O \right]_m$ (HB) (HV) (PHBV co-polymer containing 3HB and 3HV units)
$\left[O - (CH_2)_x - \overset{O}{\overset{\|}{C}} \right]_n$ Poly(ω-hydroxyalkanoate)	x = 5, Poly(ε-caprolactone), PCL
$\left[O - (CH_2)_x - O - \overset{O}{\overset{\|}{C}} - (CH_2)_y - \overset{O}{\overset{\|}{C}} \right]_n$ Poly(alkylene dicarboxylate)	x = 2, y = 2, Poly(ethylene succinate), PES x = 4, y = 2, Poly(butylene succinate), PBS x = 4, y = 2,4 , Poly(butylene succinate-co-butylene adipate),PBSA

Fig. 4. Unit structures of typical types of biodegradable aliphatic polyesters

that under certain conditions random chain scission can not be responsible exclusively for the formation of the observed degradation products. In particular, it was shown that primary products are involved in a number of secondary reactions and isomerizations and, indeed, that tetramer is formed principally as a result of such secondary reactions[102)]. The two monomer units i.e., 3-hydroxypentanoic acid (trivially known as 3-hydroxyvaleric acid or 3HV) and 3-hydroxybutyric acid (3HB) of PHBV copolymer are shown in Fig. 4. The copolymer can be produced by adding propionic acid to the nutrient feedstock supplied to the bacteria. The copolymer compositions containing up to 30 mol-% of 3HV can be produced by controlling the feedstock and the conditions. Biopol® is also produced commercially by a fermentation process using glucose and propionic acid as carbon sources for the microorganisms. The mole percentage of valerate in the polymer sample is limited by the toxicity of the propionic acid to the microorganisms used, *Alcaligenes eutrophus*[101)]. However, polymers with compositions up to 95 mol-% 3HV have been obtained by adding controlled mixture of pentanoic acid and butyric acid to the feedstock[103, 104)]. The copolymer is believed to possess an almost completely random distribution[105–107)]. The comonomer reduces the crystallinity and also the melting point of the homopolymer. The melting point (T_m) of the copolymer decreases from the calculated 180 °C with increasing 3-hydroxyvalerate content and reaches a minimum value of 75 °C at approximately 40 mol-% 3HV. Again, as the 3HV content increases towards pure 3PHV, the melting point increases; thus at 95 mol-% 3HV the melting point increases to 108 °C[88,106,108)]. The impact strength[88)], flexural modulus[109)], melting temperature[106)], and the rate of crystallization[110)] of PHBV copolymers have been shown to be regulated by the content of 3HV units.

There are not only poly(β-hydroxybutyrate) and the copolymer of 3-hydroxybutyrate with 3-hydroxyvalerate that are produced by bacteria, other bacterial polyesters are also available. Steinbuchel and Valentin[111)] have reviewed the diversity of bacterial polyhydroxyalkanoic acids in which an overview is provided on the diversity of biosynthetic polyhydroxyalkanoic acids, and all hitherto known constituents of these microbial storage compounds. The occurrence of 91 different hydroxyalkanoic acids reflects the low substrate specificity of polyhydroxyalkanoic acid syntheses which are the key enzymes of polyhydroxyalkanoic acid biosynthesis. Inspite of the excitement of more than 90 different constituents of biosynthetic PHA, the commercial exploitation of this variety remains limited, since only very few PHA are available in sufficient amounts to allow the evaluation of the physical, chemical and biological material properties of these polyesters. Microbiologists can contribute significantly in the near future to solve this dilemma.

iii. A Poly(ω-hydroxyalkanoate) such as poly(ε-caprolactone), PCL, is a partially crystalline linear polyester with a low T_g of $-60\,°C$ and a low T_m of 60 °C. It is produced by several manufacturers, including Union Carbide, Solvay, and Daicel. PCL is prepared from cyclic ester monomer, lactone, by a ring-opening reaction with a catalyst like stannous octanoate in the presence of an initiator that contains an active hydrogen atom[81)]. PCL is a tough and semi-rigid material at room temperature having a modulus between those of low-density and high-density polyethylene. It has been shown that PCL is degraded by enzymes, lipases, secreted from microorganisms[112, 113)]. Currently, most of its applications are not related to its biodegradability. PCL is compatible with many organic materials and polymers and thus it is used in many polymer formulations as compatibilizers. Its low T_g (high chain flexibility) leads to its use as soft blocks for segmented polyurethanes. Recent findings showing that PCL can provide water resistance in starch-based formulations may lead to future application of large quantities of this polymer in this area[114)].

iv. Poly(alkylene dicarboxylate) type of biodegradable aliphatic polyesters has been developed by Showa Highpolymer under the trade name "Bionolle". Different grades (Fig. 4) of Bionolle are: polybutylene succinate, PBS (#1000 series), poly(butylene succinate-co-butylene adipate), PBSA (#3000 series) and poly(ethylene succinate), PES (#6000 series). Bionolle polymers with high molecular weight ranging from several tens to several hundreads of thousands were invented in 1990 and produced through polycondensation reaction of glycols (such as ethylene glycol and butanediol-1,4) with aliphatic dicarboxylic acids (such as succinic acid and adipic acid and others)[115–117)]. In case of need of higher molecular weight, coupling reaction is carried out with a small amount of coupling agents as chain extenders[118, 119)]. As reported by Fujimaki[115)], Bionolle is a white crystalline thermoplastic with melting point of about 90–120 °C (similar to LDPE), glass transition temperature of about –45 to –10 °C (between PE and PP), density of about 1.25 g/cm^3 (similar to PET), tensile strength between PE and PP, stiffness between LDPE and HDPE and heat of combustion below 6 kcal/g, i.e., about one half of polyolefins. Bionolle has excellent processability and can be processed on polyolefin processing machines at temperature of 160–200 °C, into various products such as injected, extruded and blown ones[120–125)]. A new grade Bionolle (coded #1900 series), which has a long chain branch, and high recrystallization rate, has been developed, to enable to prepare stretched blown bottles and highly expanded bottles as well as foams[126)]. The biodegradability of Bionolle polymers depends upon their structures and also the environment in which they are placed. Biodegradability of different grades of Bionolle buried in activated sludges, soils and compost has been studied [127)]. As per the findings, Bionolle #3000 showed the best biodegradability in soils and a compost, while Bionolle #6000 showed best biodegradability in activated sludges[119)]. Fujikami[126)] has reported the potential and near-future applications of Bionolle.

3.4.2 Polyester amides

Aliphatic polyester amides have been suggested and recently investigated as a potential family of polymers with good mechanical and thermal properties, as well as processing facilities and susceptibility to degradation[128, 129)]. A series of biodegradable aliphatic polyester amides derived from 1,6-hexanediol, glycine, and diacids with a variable number of methylene groups (from 2 to 8) has been synthesized and characterized[130)]. The synthesis and some physicochemical properties of polyester amides derived from 1,6-hexanediol, sebacic acid and an α-amino acid such as glycine, alanine or phenylalanine have been reported[131)]. Saotome et al.[132)] have synthesized a series of polyester amides based on 1,2-ethanediol, adipic acid, and an amino acid as glycine, leucine, or phenylalanine. The degradation studies with proteolitic enzymes (*chymiotripsine* and *elastase*) indicated that only the polymers containing glycine were not degraded by any of the tested enzymes. They also reported[133)] that inclusion of phenylalanine in the glycine-derived polyesteramides enhances their degradability with *chymiotripsine*. As reported by Paredes et al.[130)] the polyester amides derived from diacids with a high number of methylene groups possess adequate molecular weights to give film- and fibre-forming properties. Again the decomposition temperatures of such polyester amides were always higher than the corresponding melting temperatures suggesting that these polymers can be processed from the melt. Enzymatic incubation with *papain* demonstrated the biodegradability of all the polyester amides of the series. In all cases, the polymers showed a high susceptibility to enzymatic degradation.

On a call from the Government of Germany for research and development on biodegradable thermoplastics with good performance and processing behavior, in 1990[134)], Bayer presented its first grade of polyester amide (BAK 1095) to the public, five years later[135)]. During 1997 Bayer, launched another grade i.e. BAK 2195. BAK 1095 is based on caprolactam (Nylon 6), butanediol and adipic acid, whereas BAK 2195 is synthesized from adipic acid and hexamethylene diamine (Nylon 6,6) and adipic acid with butanediol and diethylene glycol as ester components. Since the production process of BAK is solvent- and halogen-free, the polymer is free of halogens, aromatic compounds and toxic heavy metals. Although the processing conditions are similar to polyolefins[136, 137)], the biggest difference being the shape of the granules, the granulation technique is under constant development by Bayer to reach at easily processible granules. BAK 1095 has mechanical and thermal properties resembling to those of polyethylene[138)]. The resin is also noted for its high toughness and tensile strain at break. It can be processed into film and also into extruded or blow-moulded parts. It is suitable for thermoforming and can be colored, printed, hot-sealed and welded. The crystallisation temperature of BAK 1095 is 66 °C and it crystallises relatively slowly and so it is not ideal for injection moulding. BAK 2195 resin is an an injection-moulding grade biodegradable thermoplastic that exhibits greater stiffness. This resin has higher melting point (175 °C) than BAK 1095 (m.p. 125 °C) and also higher crystallisation temperature, i.e., 130 °C. The property profile of BAK 2195 can also be extended through the addition of fillers and reinforcing substances, such as starch, natural fibres, wood flour, and minerals[83)]. The combined performance of both BAK grades and the compounds open a wide range of applications like disposable plant pots, agricultural films, biowaste bags, plant clips, cemetery decoration, one-way dishes and others. BAK 1095 breaks down into water, carbon dioxide, and biomass under aerobic conditions. The degradation rate is comparable to that of other organic materials that are composted[138)]. All the biodegradability tests[139, 140)] demonstrate the complete biodegradability of BAK 1095 and similar tests for BAK 2195 are in process[135)].

3.4.3 Starch plastics

Starch is produced in plants and is a mixture of linear amylose (poly-α-1,4-D-glucopyranoside) and branched amylo-pectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside). The amount of amylose and amylopectin varies with the source. The chemical structure of amylose and amylopectin is shown in Fig. 5. The exact structure of starch granules is not yet fully understood. Amy-

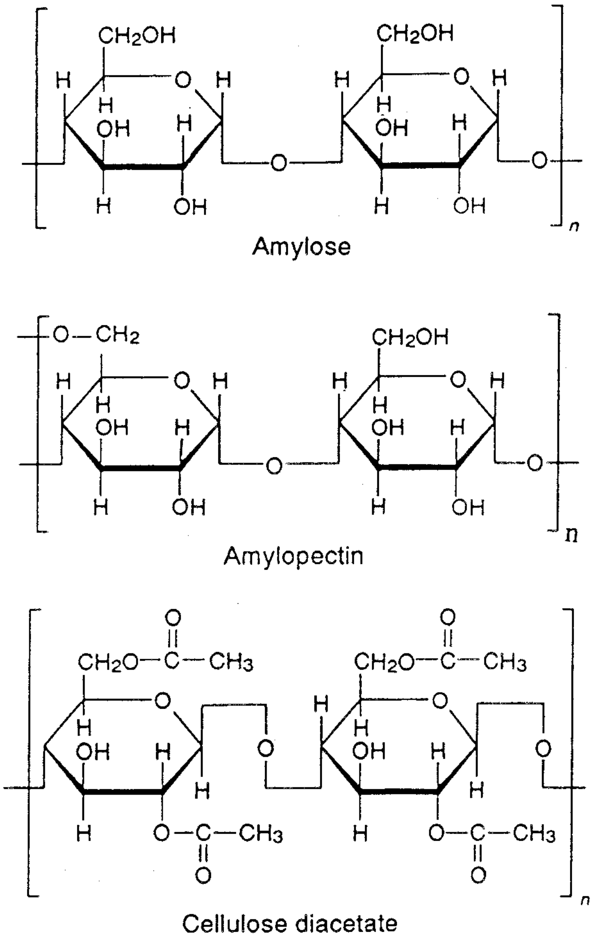


Fig. 5. Chemical structure of some biodegradable polymers: amylose, amylopectin and cellulose diacetate

lose is the minor component of starch ranging from 20 to 30%[141]. The amylopectins are responsible for the crystalline properties of starches. The relative amounts, structures and molar masses of amylose and amylopectin in starches are determined by means of genetic and environmental control during biosynthesis, and hence wide variation occurs among plant raw materials. Corn is the primary source of starch, although potato, wheat and rice starch also have markets in Europe and USA[142]. Up to US$ 1.8×10^{10} worth of corn is produced in the USA annually[114]. Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile biopolymer with immense potential for use in the non-food industries. Of the 6.8 million tons of starch produced in Europe annually, approximately 20% is used in non-food industries[141]. However from a recent report[78] it is found that, starch is industrially processed with a volume of almost 7 million tons/year in Europe, and nearly 50% of the starch produced is used for non-food applications.

Starch converted to thermoplastic material (starch plastics) offers an interesting alternative for synthetic polymers where long-term durability is not needed and rapid degradation is an advantage. The properties and applications of starch and starch plastics have been reviewed recently by Shogren[143]. Starch can be made thermoplastic through destructurization in presence of specific amounts of plasticisers (water and/or poly-alcohols) in specific extrusion conditions[74]. Thermoplastic starch products with different viscosity, water solubility and water absorption have been prepared by altering the moisture content, amylose/amylopectin ratio of raw product and the temperature or the pressure in the extruder[144–148]. Thermoplastic starch alone can be processed as a traditional plastic; however, its sensitivity to humidity, makes it unsuitable for many applications. The thermoplastic starch alone is mainly used in soluble compostable foams, such as loose-fillers, expanded trays, shape moulded parts and expanded layers, as a replacement for polystyrene. BIOTEC of Germany has conducted promising research and development along the lines of starch-based thermoplastic materials. The company‘s three product lines are Bioplast® granules for injection moulding, Bioflex® film, and Biopur® foamed starch. Starch-based biopolymer thermoplastics include, in particular, thermoplastic starches (TPS®)[149] and the group of polymer blends of thermoplastic starches with additional polymer components like aliphatic polyesters e.g. polycaprolacton and bionolle, poly vinyl alcohol, polylactic acid, copolymer from aliphatic diolin and aliphatic as well as aromatic dicarbon acids together with especially biodegradable polyesteramides[78]. The research results for TPS® bioplastics and their production processes are protected by international patents or have patents pending[150–153]. Under the Mater-Bi trademark, Novamont of Italy today produces four classes of biodegradable materias Z, Y, V, and A, all containing starch and differing in synthetic components[74]. Each class is available in several grades and has been developed to meet the needs of specific applications. The current production capacity of Novamont is 8000 tons/year. Mater-Bi can be processed using conventional plastic technologies such as injection moulding, blow moulding, film blowing, foaming, thermoforming and extrusion. The physical-mechanical properties of Mater-Bi are similar to those of conventional plastics like polyethylene and polystyrene. Mater-Bi is not only recyclable but also as biodegradable as pure cellulose. The biodegradability of Mater-Bi products has been measured according to standard test methods approved by International Organizations (ISO, CEN, ASTM). The compostability of some Mater-Bi grades has been certified by the “Ok Compost” label. Mater-Bi can be used in a wide range of applications such as disposable items (plates, cutlery, cup lids etc.), packaging (wrapping film, film for dry food packaging, board lamination etc.), stationery (pens, cartridges, pencil sharpeners etc.), personal care and hygine (sanitary napkins, soluble cotton swabs etc.)

and a lot others like toys, shopping bags, mulch film etc. Various starch plastics with different trade names (Tab. 5) are now available in the market. Buna Sow Leuna (BSL) of Germany has developed a line of biodegradable polymers based on esterified starch with the trade names Sconacell S, Sconacell A, and Sconacell AF. Compared to common thermoplastics, however, biodegradable products based on starch still reveal many disadvantages which are mainly attributed to the highly hydrophilic character of starch polymers. Inspite of many positive results, thermoplastic starch-based materials are still at an early stage of development and the markets for such products are expected to increase in future as the properties are more improved, prices still decline, and an infrastructure for composting becomes more established.

3.4.4 Cellulose acetate

Cellulose esters, e. g., cellulose acetate (CA) are considered as potentially useful polymers in biodegradable applications[154–160]. CA is a modified polysaccharide synthesized by the reaction of acetic anhydride with cotton linters or wood pulp. The structure of cellulose diacetate is represented in Fig. 5. The production of cellulose esters from recycled paper and sugar cane has also been demonstrated[161]. Historically, there has been considerable confusion regarding the biodegradation potential of CA. It was generally accepted that cellulose esters with a degree of substitution (*DS*) less than 1.0 will degrade from the attack of microorganisms at the unsubstituted residues of the polymers, and that the ether linkages in the cellulose backbone are generally resistant to microbial attack[162, 163]. It is also reported that CA is a poor substrate for microbial attack[164]. Early evidence as to the biodegradation potential of CA is reported by Cantor and Mechales[165] who demonstrated that reverse-osmosis membranes prepared from CA with $DS = 2.5$ suffers losses in semipermeability due to microbial attack. Gardner et al.[156] showed, basing on film disintegration and on weight loss, that cellulose acetates, having DS less than approximately 2.20, compost at 53 °C and 60% moisture at rates comparable to that of PHBV. Komarek et al.[155] provided via aerobic biodegradation of radiolabeled CA, that in CA with a *DS* of 1.85 more than 80% of the original ^{14}C-polymeric carbon was biodegraded to $^{14}CO_2$. The studies on biodegradation of CA although have been given much attention in recent times; scarce attention has been paid to the biodegradation of formulated resins consisting of cellulose acetate and diluents. This should be taken into account seriously, as the melt processing temperature of the cellulose acetates exceeds that of its decomposition temperature, which implies that most cellulose acetates must be plasticized if they are to be used in thermoplastic applications[166]. Effect of plasticizer on biodegradation of CA films has been reported by Jiang and Hinrichsen[167]. In that work, biodegradation of plasticized cellulose acetate (PCA) film was evaluated by the ways of percent conversion of carbon to CO_2. A strong loss of 20% in weight occured within the first two weeks of degradation. It was concluded that the fractions of lower molecular weight or lower substitution portion of PCA were biodegraded and removed preferentially from the film. CA of various *DS* are now being widely used as films and coatings. Commercially available CA has a *DS* between 1.7 and 3.0. CA films have a tensile strength comparable to polystyrene, which makes the polymer suitable for injection moulding[82]. CA is used to produce clear adhesive tape, tool handles, eyeglass frames, textiles and related materials. Mazzucchelli of Italy and Planet polymer of USA manufacture biodegradable plastics based on cellulose acetate under the trade names, BIOCETA® and EnviroPlastic® Z respectively. BIOCETA® is targeted for the manufactures of biodegradable packaging films, retractable films, tubes, and containers for oils, powders, and other products. EnviroPlastic® Z materials are also aimed at use in products in the packaging and the industrial markets.

3.4.5 Soy plastic

The production, structure, and composition, physicochemical properties, processing for plastics, industrial applications and biodegradable nature of soy protein biopolymer have been reviewed[168]. In US, soybeans provide over 60% of the fats and oils used for food and the majority of the feed protein. Soybeans typically contains about 20% oil and 40% protein. Protein levels as high as 55% have been observed in soybeans. Soybeans consist of discrete groups of proteins (polypeptides) that span a broad range of molecular sizes and are comprised of approximately 38% of non-polar, non-reactive amino acid residues, while 58% are polar and reactive. Modifications that take advantage of water solubility and reactivity are exploited in improving soy protein for use in plastics and other biomaterials[169, 170]. Soy protein plastics of different compositions have been prepared by injection moulding[171]. Compression moulding is also used for soy plastic processing. Less than 0.5% of the available soy protein is used for industrial products[172, 173]. Soy protein has unusual adhesive properties. Soy plastics have been used for manufacturing automobile parts by Ford company[168]. Dried soy plastics display an extremely high modulus, 50% higher than that of currently used epoxy engineering plastics[174]. So with proper moisture-barrier, soy protein is a potential starting material for engineering plastics. Blending the biodegradable soy protein plastic with polyphosphate filler greatly reduced its water sensitivity, allowing new uses in moist and load-bearing environments where the unfilled plastic was not useable[175]. Development of affordable soy-based plastics, resins, and adhesives is reviewed recently[176)]. The reaction product of soybean, a carbohydrate filler, a reducing agent, water and additives resulted in an improved biodegradable plastic[177)] having high degree of flowability for processing by extrusion and injection moulding into solid articles with a high degree of tensile strength and water resistance.

3.5 Biodegradable plastics vs. traditional plastics

The growing environmental concern has made plastics a target of criticism due to their lack of degradability. Of all the packaging wastes discarded in the United States, plastics account for about 20% by volume[178)]. Annual expenditure on packaging increased by more than 4% to US$ 111 billion between 1994 and 1996, according to a report[179)] from Pira, the UK packaging consultancy. Plastic's share of the total packaging expenditure remained constant over the same period, at 29%, second in terms of sector importance behind paper and board, which accounted for 41% of the market in 1996. So there has been a lot of interest in research committed to the design of biodegradable plastics[180)]. The concept of environmentally conscious materials (ecomaterials) is being rapidly accepted by countries all over the world[181)]. Biodegradable polymers are considered as an environmental waste-management option[182)]. They constitute a loosely defined family of polymers that are designed to degrade through action of living organisms and offer a possible alternative to traditional non-biodegradable polymers where recycling is unpractical or not economical. The two main reasons for the interest in biodegradable materials are: the growing problem of waste thereby resulting general shortage of landfill availability and the need for the environmentally responsible use of resources together with the CO_2 neutrality aspect[183)]. Interest in biodegradable plastics is being revived by new technologies developed by major companies, such as Bayer, DuPont, and Dow Cargill[83)]. Demands for biodegradables are forecast to grow nearly 16% per annum[184)]. Performance limitations and high costs have restricted the adoption of such plastics to very small niches up to now. For scientists, the real challenge lies in finding applications which would consume sufficiently large quantities of these materials to lead to price reduction, allowing biodegradable polymers to compete economically in the market. The challenge in replacing conventional plastics by biodegradable materials is to design materials that exhibit structural and functional stability during storage and use, yet are susceptible to microbial and environmental degradation upon disposal, without any adverse environmental impact. The design of appropriate biodegradable materials will require a clear understanding of factors influencing material properties and performance as well as biodegradability, so that appropriate trade-off can be made. The balancing of degradability and performance of biodegradable materials is reviewed[82)]. The performance of biodegradable materials must be maintained during processing, storage and use in order to ensure that they can carry out their intended functions.

The blending of biodegradable polymers is a method of reducing the overall cost of the material and offers a method of modifying both properties and degradation rates. However a blend, particularly with a non-biodegradable polymer, can even reduce or even inhibit the degradation of the biodegradable component[93)]. In recent years, the biodegradable polymers have offered scientists a possible solution to the waste-disposal problems associated with traditional petroleum-derived plastics. Most of the biodegradable polymers were intended to be used in packaging industries, in farming and also in specialized bio-medical applications. A lot of research work has been done on blending of biodegradable polymers.

The main constraint on the use of biodegradable polymers is the difference in the price of these polymers compared to bulk produced oil-based plastics[93)]. The cost of Biopol® is approximately 8000 UK pounds per ton (1000 kg), compared with the UK prices of commodity polymers of between 500 pound/ton (PVC and PP) and 600 pound/ton (HDPE and high-impact PS). According to a recent report[185)], Monsanto says it will cease production and research, as it can not sustain the money-losing business. According to Mar Tech report of July 1998, a larger market for biodegradable plastics and polymers is not expected to open up until prices drop below US$ 2/lb; which is not likely to occur until products can be mass marketed. The prices in US$/lb of some biodegradable and traditional plastics are represented in Tab. 6. As can be observed from the table, biodegradable plastics can cost up to ten times more than commodity plastics. Mayer and Kaplan[82)] have also reviewed the cost (US$/lb) of polymers such as, starch (0.15–0.8), cellulose acetate (1.70), PHBV (6–8), PVOH (1.5–2.5), polycaprolactone (2.7) and PLA (1–3). According to these values PHBV costing 6.00–8.00 US$/lb is about four to ten times more expensive than starch which costs only 0.15–0.8 US$/lb. First prices of BAK of 7.00 DM/kg (ca. 2 US$/lb) are subject of further quantities per delivery and annual demand[187)]. The product costs of different grades of Sconacell will depend on the production scale and as speculated by the producer BSL, Germany[188)], the costs will be in the range 0.6–1.1 US$/lb. Starch-based and PLA-based polymers have occupied the major market of biodegradable plastics today. Cargill Dow officials say that PLA will initially be priced in the 50 cts – $ 1/lb range, but that will come down as greater scale and process efficiencies are achieved[189)]. The market potential for biodegradable products in the next five years can be estimated at approximately 30000–40000 tons/year[74)] in Europe. American and Japanese markets are of great potential, but are still at a very early stage of development, with the

Tab. 6. Biodegradable vs. traditional plastics – cost comparison (cf. ref.[186])[a)]

Material		Average cost $//lb.
Biodegradable plastics	PLA (Cargill Dow Polymers)	1.50–3.00
	Starch-based resins (Novon/Novamont)	1.60–2.90
	PHA (BIOTEC/Monsanto)	4.00–6.30
Commodity petrochemical plastics	PP	0.33
	LDPE	0.41
	HDPE	0.37
	PS	0.39
	PVC	0.28
	Polyester	0.52
	PVOH	1.40
	Polycarbonate	1.60

[a)] Reproduced with permission from Mar Tech, USA (Website: http://www.Mar Tech-Reports.com).

exception of starch-based loose-fillers. The demands of certain biodegradable products are at the rising level. A pilot plant of Bionolle by Showa Highpolymer[115)] with a capacity of 10 tons/year was built in 1991, whereas a plant with a capacity of 3000 tons/year was constructed only after three years, i.e., in 1993. Cargill's existing PLA facility near Minneapolis, in US, having 3600 tons/year capacity during the beginning of 1998, expanded to 7200 tons/year towards the end of the year. A new 140000 tons/year commercial plant[83)] is also planned for 2001. The production capacity of starch-based materials by Novamont[74)] is 8000 tons/year. The market potential for bioplastics has been studied by EC Commission GD XII[190)]. 1.1 million tons/year of bioplastics with an increase in economic value and job potential of four billion DM and 20000 new jobs respectively is predicted. This optimistic forecast appears to be unbelievably high when the current production amounts of bioplastics are taken into account[78)]; however, in comparison with the current production data from plastic industry: 32 million tons/year in Europe and 120 million tons/year worldwide displays realistic estimates for the future technology. Up to the year 2000 an average increase in the consumption of plastics of about 5% per annum is expected[191)]. In USA, people primarily use recycling and landfill to dispose the plastic materials; composting is also being debated, especially in Europe for disposing of plastics and in Japan, where the land is expensive and not available for landfilling, combustion to carbon dioxide and water and reuse of the energy seems to be only choice[192)]. Today's much better performance of traditional plastics are the continued R&D efforts of several years. Most of the biodegradable polymers came to public only few years back and from around 1990 onwards the market and production for biodegradable materials have taken a marching form. Prices of biodegradables can be reduced only on mass scale production; and such mass scale production by companies will be feasible through constant R&D efforts of scientists to improve the performance of biodegradable plastics. In any case, the potential market for biodegradable plastics is significant, even if they only manage to capture a small segment of the commodity plastics market. Over the next several years, demand for biodegradable plastics is expected to grow fastest in Europe, due to European directives that encourage the use of biodegradable polymers for compostable packaging. The German Federal Government and the German Parliament have agreed on an amendment to the Packaging Regulation with a rule for compostable plastic packaging. This special provision is valid for compostable packaging materials that contain mainly biodegradable materials based on renewable resources[78)]. In near future because of serious environmental threat whole world will take a serious look towards use of biodegradable polymers. The market for biodegradable plastics in North America and Europe from 1997 to 2006 (Fig. 6) is quite encouraging.

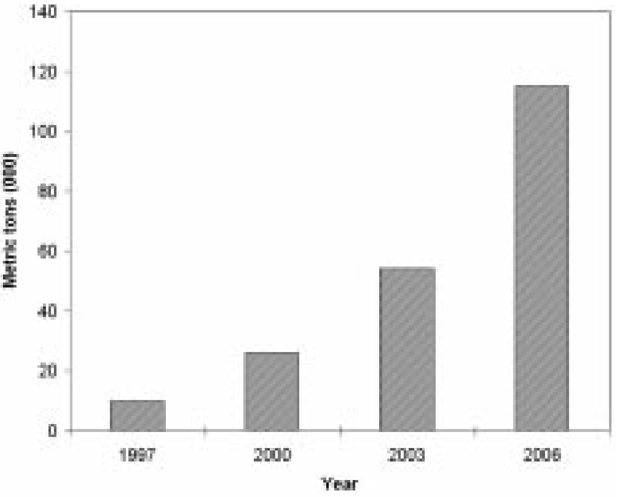


Fig. 6. Market for biodegradable plastics in North America & Europe (1997 – 2006) (after ref.[75)], reproduced with permission from MarTech, http://www.Mar Tech-Reports.com)

4. Biocomposites

The literature survey reveals that only little work has yet been done on biocomposites. The developments of biocomposites started in the late 1980s, and most of the biodegradable polymers as discussed in Section 3, not yet satisfying each of the requirements for biocomposites, are now available in the market. The biodegradable polymers like Biopol®, polycaprolacton, Bioceta, Mater Bi, Sconacell, etc.[8, 193)] have been tested, in order to examine their properties with special emphasis on the suitability of such polymers for use as matrix material for the fabrication of biocomposites. The low viscosity of these matrix polymers at the processing temperature, good mechanical properties of both the matrix and reinforceing fibre as well as good fibre-matrix adhesion are required to obtain high-quality biocomposites.

4.1 *Cellulose fibre based biocomposites*

The study of polymer composites that contain cellulosic materials has been recognised as an important area of research for over a decade. Cellulosic materials are used in the polymer industry for a wide range of applications, including: laminates, fillers and panel products, composites, alloys and blends, and cellulose derivatives[29)]. Interest is growing in the field of cellulose-reinforced thermoplastics[194–197)]. Graft co-polymers of the matrix material and the addition of a polar group have been used successfully to improve the mechanical properties of cellulose-polymer composites[198, 199)]. Cellulosic fibres are also finding applications as reinforcement in most common thermoset polymers[200–202)] like polyester, epoxy, amino and phenolic resins. Short cellulosic fibre-reinforced elastomer composites have gained practical and economic interest in the rubber industry[203, 204)]. However, all the above mentioned cellulose-based composites are not fully biodegradable because of non-degradable synthetic matrix components.

The structure and physical properties of bacterially synthesized polyesters have been reviewed[205)]. The processing and properties of biodegradable composites of bacteria-produced polyesters (Biopol®) reinforced with wood cellulose have been reported by Gatenholm et al.[206)] Although cellulose fibres improved the strength and stiffness of the polyhydroxybutyrate (PHB), the composites were very brittle. At a high proportion of HV, the tensile modulus is reduced up to 30%, whereas elongation at break increases to about 60%. The effect on the tensile modulus (*TM*) by the incorporation of cellulose fibres into three different thermoplastics like PP, PS (polystyrene), and PHB has also been investigated, which revealed that the tensile modulus increased for each composite with increasing fibre content. The stiffening effect of cellulose fibre in PHB was in the same order as in PS. From the studies of dynamic mechanical properties of PHB copolymers of varying composition and of cellulose-filled composites it was observed that the introduction of cellulose resulted in a decreased mechanical loss factor owing to restrictions of chain mobility in the amorphous phase, while an improvement in the dynamic modulus was noticed. An excellent dispersibility of cellulose fibres was achieved in the PHB matrix as compared with synthetic matrices such as PP or PS. The degree of dispersibility was strongly dependent on processing conditions and related to the fibre-length reduction. The microscopic investigations on the fibres extracted from composite showed defibrillation characteristics, suggesting a possible hydrolysis of cellulose by crotonic acid formed in situ as a result of thermal decomposition of the PHB matrix. The synergistic effects during the processing of cellulose with Biopol® have been reported[207)]. Lignocellulosic straw fibre-reinforced PHB generally leads to expect good mechanical properties of such composites as reported by Avella et al.[208)]

4.2 *Flax, hemp, and ramie based biocomposites*

As discussed under Section 2, flax, hemp and ramie are the most interesting biofibres to be used as reinforcement in composite structures. Flax fibre-reinforced PP composites have attracted much attention[209–211)]. The results of a research project of a German company (Daimler-Benz A.G.) suggests[212)] that flax and sisal based composites are used for making vehicle interior parts. The reinforcement of polyisocyanate-bonded particleboards with flax fibres led to products comparable to those of carbon and glass fibre-reinforced particleboards[213)].

As far as biocomposites are concerned, Herrmann et al.[2)] have reported the tensile strength and stiffness[214, 215)] of unidirectional-laminates from hemp, ramie and flax each combined with a matrix of Sconacell A and ramie embedded in a shellac based resin[193)]. The stiffness of ramie/Sconacell A and flax/Sconacell A were about 50%, whereas tensile strengths were about 60% as compared to E-glass-epoxy composites (GFRP). The stiffness of ramie/shellac laminates was quite comparable with GFRP, while the tensile strength was only 43%. Hemp/Sconacell biocomposite showed 143% of the stiffness and 60% of tensile strength as compared to GFRP. These values of mechanical properties reveal that biocomposites can in many cases replace GFRP in structural applications. Several publications[4–7, 216, 217)] report about the comparability of mechanical properties of biocomposites with well-known glass fibre reinforcd plastics. Tests with different flax fibre-reinforced biodegradable matrix polymers by Hanselka et al.[4)] showed that the tensile strength and Young’s modulus of these biocomposites were clearly influenced by particular matrix and adhesion between fibre and matrix. The mechanical properties of extruded flax fibre-reinforced thermoplastic starch (structured with water or glycerin) showed increased values, especially for tensile strength and Young's modulus because of addition of green-flax fibre rovings. The literature on this subject suggests that from the point of view of the mechanical properties, such biocomposites are suitable construction materials; however, limitations must be seen where excessive environmental conditions exist. Major prospects for these material systems are, therefore, lining elements with support function in the automobile, rail car, and furniture industries[4]. The tensile strength and stiffness of biocomposites mainly meant for use as panellings i. e. non-woven fabrics from flax reinforced with Sconacell A, Bioceta, shellac and some newly investigated matrix systems (yet confidential) and also from Lyocell (a man made cellulosic fibre), embedded in Sconacell have been reported[2]. The fibre volume content was 30% with the exception of an additional flax/shellac sample containing 45% fibres by volume. As reported, flax/newly developed matrix system and flax/shellac compounds gave good values of tensile strength which were in the range from 80 to 93 MPa or even 109 MPa with increased fibre volume content of flax/shellac composites from 30 to 45%. A considerable improvement in tensile strength was achieved by using Lyocell instead of flax fibres each embedded in Sconacell A; the corresponding values being 57 and 80 MPa, respectively. Strucural biocomposites are reinforced by multilayer or woven fabrics, mainly from yarns or slivers for strength and stiffness requirements, whereas panellings are usually made from non-woven fabrics from relatively short fibres for a better draping. Biocomposites containing natural fibres and biodegradable matrices are patented[218] for applications as building materials. The title materials contain natural fibres, e.g., flax, hemp, ramie, sisal or jute and a biodegradable matrix such as cellulose diacetate, or a starch derivative. While reviewing the chances and limitations of biodegradable polymers based on renewable raw materials, Fritz et al.[219] have reported that some destructurized polysaccharides can form the polymer matrix of flax fibre-reinforced composites.

4.3 Jute based biocomposites

Jute is one of the most common agro-fibres having high tensile modulus and low elongation at break. If the low density (1.45 g/cm^3) of this fibre is taken into consideration, then its specific stiffness and strength are comparable to the respective quantities of glass fibre[220–223]. The specific modulus of jute is superior to glass fibre, and on a modulus per cost basis, jute is far superior. The specific strength per unit cost of jute approaches that of glass fibre. There are many reports about the use of jute as reinforcing fibres for thermosets[224–229] and thermoplastics[223, 230–232]. Mohanty and Misra[16] have reviewed jute reinforced thermosets, thermoplastic, and rubber based composites. To reduce the moisture regain property of jute, it is essential to pretreat jute so that the moisture absorption would be reduced and wettability of the matrix polymer would be improved. Recently, Mitra et al.[233] have reported the studies on jute-reinforced composites, their limitations and some solutions through chemical modifications of fibres. Flexural strength, flexural modulus and the dynamic strength of chemically modified jute-PP composites increased by 40, 90 and 40% respectively as compared to unmodified jute-PP composites[234] due to the chemical modification of jute with maleic anhydride grafted polypropylene. The reinforcement of jute with biodegradable matrix has not been studied to a great extent. The effect of different additives on performance of biodegradable jute fabric-Biopol® composites has been reported[235]. In absence of any additive, both tensile strength (*TS*) and bending strength (*BS*) of composites were found to increase around 50% whereas elongation at break reduced only 1% as compared to pure Biopol® sheet. In order to study the effects of additives, the jute fabrics were soaked with several additive solutions of different concentrations. During such treatments dicumyl peroxide (DCP) was used as the initiator. The effects of various surface modifications of jute on performance of biodegradable jute-Biopol® composites as prepared by hot-press technique, have been reported very recently[236, 237]. The surface modifications of jute, involving dewaxing, alkali treatment, cyanoethylation and grafting are made with the aim to improve the hydrophobicity of the fibre so as to obtain good fibre-matrix adhesion in the resulting composites. Differently chemically modified jute yarn-Biopol® composites[236] showed maximum enhancement of mechanical properties like tensile strength (*TS*), bending strength (*BS*), impact strength (*IS*) and bending-modulus (*Bmf*) by 194, 79, 166 and 162% respectively in comparison to pure Biopol®. With 10% acrylonitile (AN) grafted yarn, the *TS* of composite enhanced by 102%, whereas with 25% grafted yarn, TS enhanced by 84% in comparison to pure Biopol®. Thus with increase of grafting percent the mechanical properties were found to decrease. The composites made from alkali treated yarns produced better mechanical properties than dewaxed and grafted yarns. Orientation of jute yarn played an important role on the properties. The enhancement of mechanical properties of composites are noticed only when the properties of composites were measured along the yarn wrapping direction.

Unlike jute yarn, the enhancement of mechanical properties of jute fabric-Biopol® composites do not show any variation with the direction of measurement of properties[237]. More than 50% enhancement of *TS*, 30% of *BS* and 90% of *IS* of resulting composites as compared to pure Biopol® sheets were observed under the experimental conditions used. Scanning electron microscopy (SEM) showed that the surface modifications improved the fibre-matrix adhesion. The superior strength of alkali treated jute may be attributed to the fact that alkali treatment improves the adhesive characteristics of jute surface by removing natural and artificial impurities thereby producing a rough surface topography[238]. In addition, alkali treatment leads to fibre fibrillation, i.e., breaking down of fabrics fibre bundle into smaller fibres. This increases the effective surface area available for contact with matrix polymer. An effective method of natural fibre chemical modification is graft copolymerization[34, 239–241]. It is observed that the composite prepared from 10% AN grafted jute fabric shows superior properties as compared to untreated fabric[237]. AN-grafting exhibited comparatively better properties of the composites than methyl methacrylate (MMA) grafting. Similar results have also been reported in the literature[221]. From the compost degradation studies it was observed that about 34% weight loss occurred for neat Biopol®, while dewaxed, alkali treated, 19% AN-grafted, and 30% AN-grafted jute fabric-Biopol® composites decreased their weights by about 56, 42, 37 and 34% after 150 d of degradation. Higher percent weight loss of dewaxed sample as compared to alkali treated sample was attributed to the fact that there was a week fibre-matrix adhesion which might have boosted the degradation. A lower degradation rate of AN-grafted based composites was noticed because of the non-biodegradability behavior of polyacrylonitrile.

Keeping in view the broader applications of commercial biodegradable polyester amide (BAK), different surface modified jute fabrics were used as reinforcing component in biodegradable composites[242] based on BAK 1095. Among the chemically modified jute (dewaxed, bleached, alkali treated, cyanoethylated and grafted), the alkali treated, cyanoethylated and low percent grafted samples based composites produced comparatively better properties than their untreated and dewaxed counterparts. The effect of different types of surface modifications of jute fabrics on the mechanical properties of composites are represented in Fig. 7. More than 40% improvement in TS of BAK 1095 occurred as a result of the reinforcement with alkali treated jute. Jute content also affected the properties of composites and about 30 wt.-% jute gave optimum mechanical properties. Among MMA and AN grafted samples, the low percent, i.e., 10% AN-grafted jute showed comparatively better improvement of mechanical properties of the composites than high percent grafted counterparts. SEM investigations demonstrated that fibre pull out from composite sample was reduced as a result of the fibre surface modification. From degradation studies it was found that about 5–10% weight loss and about 11 to 45% decrease of bending strength of differently surface modified jute-BAK composites took place after 15 d of compost degradation. The loss of weight as well as the decrease of BS of degraded composites were more or less directly related to each other.

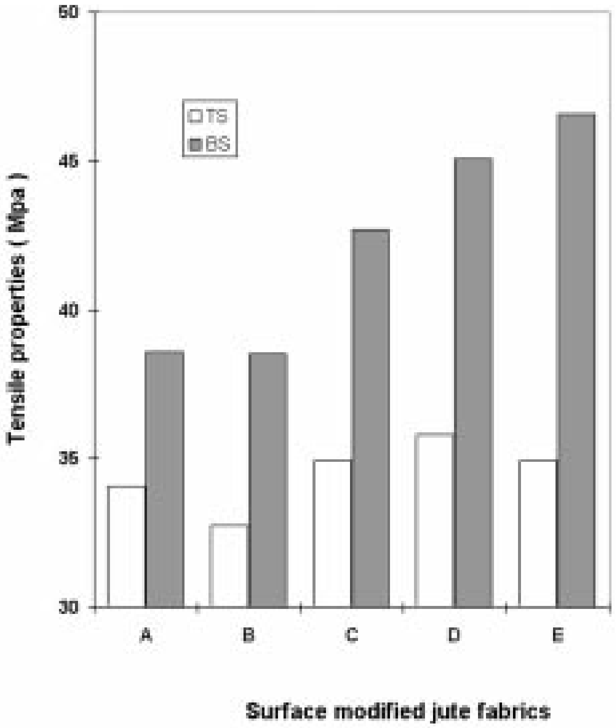


Fig. 7. Effect of different surface modifications of jute fabrics on tensile properties of the composites: (A) bleached; (B) detergent washed; (C) dewaxed; (D) alkali treated; (E) cyanoethylated (after ref.[242])

4.4 *Miscellaneous biocomposites*

A nonwoven fabric sheet and a film both from Bionolle 1030 were laminated and bonded to give composite sheet materials[243] showing good water resistance, flexibility, and decomposition in soil after 6 months. The first sheet, i.e., nonwoven fabrics of melt-spun continuous long fibres from polyesters comprising glycols and derivatives of dicarboxylic acids, were bonded with the second sheet comprising films (obtained from same polyester) on one side to give the title products useful for disposable diapers, etc. It has been shown that aliphatic polyesters like polycaprolactone (PCL) and PHBV can be used to form biodegradable composites with polysaccharides reinforcing materials[244]. The naturally occuring polysaccharides have relatively high strength in the dry state, however, their physical properties weaken when plasticized and/or swollen by water. When used as reinforcing materials, they are protected by hydrophobic polyester matrices. The polarity and hydrophilicity of polysaccharides provide gas barrier properties to the composites. Cross-linking was necessary to provide dimensional stability and creep resistance to the composites and it was observed that such cross-linking did not affect the biodegradability of the composite material. It is also reported that compatibilizers and reactive oligomers can be used to provide better bonding of the PCL and polysaccharide components, thereby increasing the strength and rigidity of the composites, and the use of oligomers can also increase the ease of processing of the composites.

Relatively water-resistant biodegradable soy-protein composite is resulted[245)] through blending of special bioabsorbable polyphosphate fillers, biodegradable soy protein isolate, plasticizer, and adhesion promoter in a high-shear mixer followed by compression moulding. To develop affordable, stiff, strong bioabsorbable polyphosphate filler/soy protein polymer composites, along with methods for making practical shapes from these products are under current investigations[245–248)]. The degradable composite films composed of soy protein isolate (SPI) and fatty acids[249)] as well as SPI and propyleneglycolalginate (PGA)[250)] have been prepared. Incorporation of fatty acids into SPI resulted in films which were thicker, more whitish, and less susceptible to shrinkage upon drying than the control SPI films. The composite films with more than 20% of fatty acids were heat sealable and also showed improved tensile strength. The incorporation of PGA into SPI also resulted in composite films of modified physical properties. Suo and Netravali[251)] have reported the mechanical and thermal properties of bio/green composites obtained from pineapple leaf fibers (with fiber content up to 28%) and Biopol®, i.e., PHBV resin. The tensile strength and modulus of the biocomposites increased significantly as compared to pure PHBV resin, in the longitudinal direction but decreased in the transverse direction with increase of fiber content. The flexural strength and modulus of the biocomposites along the longitudinal direction increased with increase of fiber content whereas the flexural strength along the transverse direction decreased and the flexural modulus in the transverse direction showed little change with the increase of fiber content. The interfacial and mechanical properties of PALF-PHBV green composites with 20 to 30 wt.-% content of fibers placed in a $0^\circ/90^\circ/0^\circ$ fiber arrangement have also been reported[252)]. The tensile and flexural properties of those green composites in comparison with different types of wood specimens showed that although the tensile and flexural strength and moduli of the former specimens were lower along the grain direction of testing, they were significantly higher perpendicular to grain direction than the corresponding wood specimens. SEM photographs of the fracture surface of the biocomposites showed fiber pull-out indicating week fiber-matrix adhesion. More investigations on such biocomposites are needed to improve fiber-matrix interactions.

4.4 Applications of biocomposites

Recent work on biocomposites reveals that in most cases the specific mechanical properties of biocomposites are comparable to widely used glass fibre reinforced plastics. Various complex structures, i.e., tubes, sandwich plates, car door interior panellings, etc; have been made of biocomposites[2, 4–7)]. A new vertical drainage product made of coconut and jute fibres is being introduced in Europe by Horman[252)]. Vertical drainage is needed to accelerate consolidation of soft compressible clay soils. With the right preservation of the fibre the product has a predicted lifetime, and after the consolidation process this environmentally friendly product will decompose as claimed by the company. A resin made out of soy bean oil on reinforcement with glass-fibre produced a new product developed at the University of Delaware as to be used in parts of newest tractors produced by John Deere[253)]. The replacement of GFRP by biocomposites in many applications has been proved from the results of several investigations[3–8, 193)]. Apart from satisfactory mechanical properties, there are very often applications demanding additional features. Since biocomposites are organic materials, they are combustible. So, one of the most important requirements for biocomposites as to be used for panellings in railways or aircraft is a certain degree of flame resistance. In the modern polymer industry the different types of polymer flame retardants based on halogens (Cl, Br), heavy and transition metals (Zn, V, Pb, Sb), or phosphorus organic compounds may reduce risk during polymer combustion and pyrolysis, yet may present ecological issues. The use of halogenated flame retardants is still showing an up-ward trend, and the environmental concerns have started a definite search for environmentally friendly polymer additives. The new aspects of ecologically friendly polymer flame retardant systems have been reported[254)]. When regarding the latest results of examinations on natural fibre and matrix combinations and environmentally compatible flame retardants, biocomposites can replace glass fibre reinforced plastics in many cases[2)]. The new construction materials are well suited for anisotropic and specially tailored lightweight structural parts as well as for panelling elements in cars. The potential applications of biocomposites in railways, aircraft, irrigation system, furniture industries, sports and leisure items are under current reseach activities[2)].

5. Conclusion

The persistence of plastics in the environment, the shortage of landfill space, concerns over emissions during incineration, and entrapment and ingestion hazards from these materials have spurred efforts to develop biodegradable materials. In order to be competitive, biodegradable plastics must have the same desirable properties as obtained in conventional plastics. Existing biodegradable product lines need to be broadened to meet specific end-use physical property requirements and polymer formulations must be further researched and modified so that degradation timing can be easily manipulated to account for climate differences and performance requirements.

There is broad agreement in the industry that there is the room, and the need for different biodegradable technologies, but there is still much work to be done if the use of biodegradables is to accelerate. The most important factors to the formation of a successful biodegradable polymer industry include cost reduction as well as public and political acceptance. Government should encourage the use of biodegradable materials by tax reduction. Germany is fore-runner in the field of green technology. The market although is increasing significantly in Europe, but lags behind USA.

Existing biodegradable polymers are mainly blended with different materials with an aim to reduce cost and to tailor the product for some specific applications. Application of biodegradable polymers in natural fibre-reinforced composites will broden their uses. The world‘s supply of natural resources is being depleted. The demand for sustainable and renewable materials continues to rise. Natural resource development and agriculture will continue to be key sectors for the developing countries but research has become so globalized and complex through trade, finance, and electronic development that no country can escape globalization’s embarce. As already discussed, biodegradable polymers may be obtained from renewable resources or by synthetic routes. Since certain biocomposites have proven to be a very interesting alternative to traditional GFRP, the new or existing biodegradable polymers should be continuously developed with a close co-operation with such polymers producers to satisfy the special demand of biocomposites. Because of the very complex structure of biofibres, more data on properties of biocomposites are required to establish confidence in their uses. Training must have priority to accelerate the acceptance of biocomposites for various applications. The structural aspects and properties of various biofibres and biodegradable polymers, recent development of different biodegradable polymers and biocomposites as discussed in this review article and appropriate knowledge might be used with proper R&D efforts, for the commercialization of biocomposites products for various applications. An intensive co-operation among industries, research institutes and governments is essential for achieving this.

Acknowledgement: One of the authors, A. K. Mohanty, is thankful to the *Alexander von Humboldt Foundation*, Germany, for an AvH fellowship. The helps rendered by Prof. *R. P. Wool*, University of Delaware, USA; Prof. *Anil N. Netravali*, Cornell University, USA; Dr. *C. Bastioli*, Novamont SpA, Italy; Dr. *R. Kakuschke*, BSL, Germany; Mr. *J. Hierschmann*, Bayer Corp. USA; Mrs. *H. Schmidt*, Mrs. *Erhardt* and Dr. *H. Springer*, of Technical University of Berlin, Germany are gratefully acknowledged.

[1] G. Menges, W. Michaeli, M. Bittner, Eds., “*Recycling von Kunststoffen*”, C. Hanser, München 1992

[2] A. S. Herrmann, J. Nickel, U. Riedel, *Polym. Degrad. Stab*. **59**, 251 (1998)

[3] A. S. Herrmann, H. Hanselka, H. Nickel, U. Riedel, “*Biodegradable fibre reinforced plastics based upon renewable resources*”, TECNITEX, Torino-Lingotto, November 1996

[4] H. Hanselka, A. S. Herrmann, “*Bio-Verbund: Biologisch abbaubare Konstruktionswerkstoffe auf der Basis nachwachsender Rohstoffe*”, Techtextil Symposium 94, Frankfurt, June 1994

[5] A. S. Herrmann, H. Hanselka, “*Biologisch abbaubare Konstruktionswerkstoffe auf der Basis nachwachsender Rohstoffe*”, 26. Int. AVK-Tagung, September 1994

[6] H. Hanselka, A. S. Herrmann, E. Prömper, “*Automobil-Leichtbau durch den Einsatz von (biologisch abbaubaren) Naturfaser-Verbundwerkstoffen*”, VDI Berichte Nr. 1235, 1995

[7] G. Niederstadt, A. S. Herrmann, H. Hanselka, “*Faserverbundwerkstoffe – nach Gebrauch auf den Kompost, Spektrum der Wissenschaft*”, February 1995

[8] A. S. Herrmann, H. Hanselka, G. Niederstadt, “*Faserverbundwerkstoffe und Verfahren zur Herstellung von Strukturbauteilen*”, DE 44 20 817, June 1994, August 1995

[9] R. Karnani, M. Krishnan, R. Narayan, *Polym. Eng. Sci*. **37**, 476 (1997)

[10] R. Narayan, in: “*Emerging Technologies for Materials and Chemicals from Biomass*”, R. M. Rowell, T. P. Schultz, R. Narayan, Eds., *ACS Symp. Ser.* **476**, 1 (1992)

[11] P. Mapleston, “*Modern Plast.*”, April 1999, p. 73

[12] *Daimler-Benz High Tech Report* 2, The Corporate Units in the Daimler-Benz Group (1995)

[13] A. L. Leao, R. Rowell, N. Tavares, “*Application of natural fibers in automotive industry in Brazil – Thermoforming process*” in: *Science and Technology of Polymers and Advanced Materials*, P. N. Prasad, J. E. Mark, S. Kandil, Z. H. Kafafi, Eds., Plenum Press, New York 1998, p. 755

[14] B. Dahlke, H. Larbig, H. D. Scherzer, R. Poltrock, *J. Cellular Plast*. **34**, 361 (1999)

[15] R. Kozlowski, M. Helwig, *Recent Adv. Flame Tetard. Polym. Mater.* **9**, 180 (1998)

[16] A. K. Mohanty, M. Misra, *Polym. Plast. Technol. Eng*. **34**, 729 (1995)

[17] D. Maldas, B. V. Kokta, *Compos. Interf.* **1(1)**, 87 (1993)

[18] R. M. Rowell, in: “*Science and Technology of Polymers and Advanced Materials*”, P. N. Prasad, J. E. Mark, S. Kandil, Z. H. Kafafi, Eds., Plenum Press, New York 1998, p. 463

[19] A. R. Sanadi, R. M. Rowell, D. F. Caulfield, *Polym. News* **20**, 7 (1996)

[20] J. N. McGovern, “*Fibers, Vegetable*”, in: *Encyclopedia of Polymer Science and Engineering*, vol. 7, John Wiley & Sons, New York 1987, p. 17

[21] S. K. Batra, “*Other long vegetable fibers*” in: *Handbbok of Fiber Chemistry*, 2nd Edn., M. Lewin, E. M. Pearce, Eds., Marcel Dekker, Inc., New York 1998, p. 505

[22] A. K. Bledzki, S. Reihmane, J. Gassan, *J. Appl. Polym. Sci*. **59**, 1329 (1996)

[23] E. T. N. Bisanda, M. P. Ansell, *J. Mater. Sci*. **27**, 1690 (1992)

[24] B. C. Barkakaty, *J. Appl. Polym. Sci*. **20**, 2921 (1976)

[25] N. Chand, S. A. R. Hashmi, *Met. Mater. Proc.* **5(1)**, 51 (1993)

[26] K. K. Chawa, A. C. Bastos, *Int. Conf. Mech. Beh. Mat*. **3**, 191 (1979)

[27] P. K. Ray, A. C. Chakravarty, S. B. Bandyopadhyay, *J. Appl. Polym. Sci*. **20**, 1765 (1976)

[28] D. N.-S. Hon, *Polym. News* **17(4)**, 102 (1992)

[29] D. Maldas, B. V. Kokta, *TRIP* **1(6)**, 174 (1993)

[30] H. Li, P. Zadorecki, P. Flodin, *Polym. Composites* **8**, 199 (1987)

31) L. M. Lewin, E. M. Pearce, "*Handbook of Fiber Science and Technology*", Volume IV Fiber Chemistry, Marcel Dekker, New York 1985

32) C. David, R. Fornasier, *Macromolecules* **19**, 552 (1986)

33) M. Paillet, A. Peguy, *J. Appl. Polym. Sci*. **40**, 427 (1990)

34) A. K. Mohanty, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **27 (3&4)**, 593 (1987–88)

35) R. L. Crawford, "*Lignin Biodegradation and Transformation*", Wiley, New York, 198

36) T. K. Kirk, T. Higuchi, H. M. Chang, "*Lignin Biodegradation: Microbiology, Chemistry and Potential Applications*", CRS Press, Orlando, FL, 1980

37) S. C. O. Ugbolue, *Text. Inst*. **20 (4)**, 1 (1990)

38) M. S. Kucharyov, *Tekst. Prom*. **8–9**, 23 (1993)

39) E. W. Wuppertal, "*Die textilen Rohstoffe (Natur und Chemiefasern)*", Dr. Spohr-Verlag/Deutscher Fachverlag, Frankfurt, 1981

40) R. M. Rowell, in: "*Emerging Technologies for Materials and Chemicals*", R. M. Rowell, T. P. Schultz, R. Narayan, Eds., **476**, 12 (1992)

41) D. S. Varma, M. Varma, I. K. Varma, *Text. Res. Inst*. **54 (12)**, 821 (1984)

42) P. S. Mukherjee, K. G. Satyanarayana, *J. Mater. Sci*. **21**, 51 (1986)

43) A. K. Bledzki, J. Gassan, in: "*Handbook of Engineering Polymeric Materials*", N. P. Cheremisinoff, Ed., Marcel Dekker, Inc. New Jersey 1997, p. 787

44) D. S. Varma, M. Varma, I. K. Varma, *Thermochim. Acta* **108**, 199 (1986)

45) N. Chand, P. K. Rohatgi, in: "*Natural Fibres and Composites*", Periodical Experts Agency, Delhi, India, 1994, p. 55

46) S. H. Zeronian, *J. Appl. Polym. Sci*. **47**, 445 (1991)

47) H. Saechtling, "*International Plastics Handbook*", Hanser, Munich 1987

48) B. C. Barkakaty, *J. Appl. Polym. Sci*. **20**, 2921 (1976)

49) A. K. Bledzki, J. Gassan, *Prog. Polym. Sci*. **24**, 221 (1999)

50) E. T. N. Bisanda, M. P. Ansell, *Compos. Sci. Technol*. **41**, 165 (1991)

51) S. H. Zeronian, H. Kawabata, K. W. Alger, *Text. Res. Inst*. **60 (3)**, 179 (1990)

52) V. V. Safonov, "*Treatment of Textile Materials*", Legprombitizdat, Moscow 1991

53) G. Satlow, S. Zaremba, B. Wulfhorst, "*Flachs sowie andere Bast- und Hartfasern*", Chemiefasern/Textilindustrie, 44/96, Vol. 11/12, 1994

54) H. Hanselka, I. Koltermann, "*Mechanische Modelle zur Beschreibung des Werkstoffverhaltens naturfaserverstärkter Biopolymere*", IB 131 – 96/2, DLR Braunschweig 1996

55) DIN EN ISO 5079: "*Textilien-Faser-Bestimmung der Höchstzugkraft und Höchstzugkraftdehung*", Deutsches Institut für Normung, Berlin, February 1996

56) DIN 53816: "*Zugversuch an Einzelfasern, Haaren, Borsten*", Deutsches Institut für Normung, Berlin, June 1976

57) A.K. Mohanty, B.C. Singh, *J. Appl. Polym. Sci*. **37**, 1423 (1989)

58) A. K. Mohanty, S. Pattnaik, B. C. Singh, M. Misra, *J. Appl. Polym. Sci*. **37**, 1171 (1989)

59) J. Rout, M. Misra, A. K. Mohanty, *Polym. Adv. Technol*. **10**, 336 (1999)

60) R. M. Rowell, G. R. Esenther, J. A. Youngquist, D. D. Nicholas, T. Nilsson, Y. Imamura, W. Kerner-Gang, L. Trong, G. Deon, in: "*Proc. IUFRO wood protection subject group*", Honey Harbor, Ontario, Canada; Canadian Forestry Service, 1988, p. 238–266

61) R. M. Rowell, Ed.: "*The Chemistry of Solid Wood*", *Adv. Chem. Ser.* **207**; American Chemical Society, Washington, DC, 1985

62) R. M. Rowell, W. B. Banks, *Gen. Tech. Rep*. FPL-GTR-50; USDA Forest Service, Forest Products Laboratory, Madison, WI, **1985**, p. 24

63) P. Barghoorn, U. Stebani, M. Balsam, *Adv. Mater.* **10 (9)**, 635 (1998)

64) K. G. Satyanarayana, C. K. S. Pillai, K. Sukumaran, S. G. K. Pillai, P. K. Rohatgi, K. Vijayan, *J. Mater. Sci*. **17**, 2453 (1982)

65) N. Chand, R. K. Tiwary, P. K. Rohatgi, *J. Mater. Sci*. **23**, 381 (1988)

66) A. R. Sanadi, D. F. Caulfield, R. E. Jacobson, R. M. Rowell, *Ind. Eng. Chem. Res*. **34**, 1889 (1995)

67) J. E. G. van Dam, G. E. T. van Vilsteren, F. H. A. Zomers, W. B. Shannon, I. T. Hamilton, ''*Increased application of domestically produced plant fibres in textiles, pulp and paper production, and composite materials*", Directorate-General XII Science Research and Development, EUR 16101 EN, ATO-DLO Wageningen, The Netherlands, 1994

68) H. Baumgartl, A. Schlarb, "*Nachwachsende Rohstoffe-Perspektiven für die Chemie*", 2. Symposium, Frankfurt, May 5–6, 1993

69) V. G. Geethamma, K. T. Mathew, R. Lakshminarayanan, S. Thomas, *Polymer* **39 (6–7)**, 1483 (1998)

70) B. D. Wilde, J. Boelens, *Polym. Degrad. Stab*. **59**, 7 (1998)

71) A.-C. Albertsson, S. Karlsson, in: "*Chemistry and Technology of Biodegradable Polymers*", Blackie, Glasgow, 1994, p. 48

72) "*ASTM standards on environmentally degradable plastics*", 1993 ASTM publication code number (DCN): 03-420093-19

73) CEN TC 261 SC4 W62 draft "*Requirements for packaging recoverable in the form of composting and biodegradation, test scheme for the final acceptance of packaging*", March 11, 1996

74) C. Bastioli, *Polym. Degrad. Stab*. **59**, 263 (1998)

75) "*Biodegradable Polymers in North America & Europe*", (PO81): Mar Tech New York, July 1998

76) A. Steinbüchel, *J. Macromol. Sci., Pure Appl. Chem*. **A32 (4)**, 653 (1995)

77) "*Biopolymers from Renewable Resources; Macromolecular Systems – Materials Approach*", D. L. Kaplan, Ed., Springer-Verlag, Berlin, Heidelberg 1998

78) J. Lörcks, *Polym. Degrad. Stab*. **59**, 245 (1998)

79) R. Mülhaupt, *Chimia* **50**, 191 (1996)

80) E. D. Beach, R. Boyd, N. D. Uri, *Appl. Math. Model*. **20**, 388 (1996)

81) M. Mochizuki, M. Hirami, *Polym. Adv. Technol*. **8**, 203 (1997)

82) J. M. Mayer, D. L. Kaplan, *TRIP*, **7(2)**, 227 (1994)

83) D. Marshall, *Eur. Plast. News*, March 1998, p. 23

84) M. Avella, B. Immirzi, M. Malinconico, E. Martuscelli, M. G. Volpe, *Polym. Int.* **39**, 191 (1996)

85) P. A. Holmes, in: "*Development of Crystalline Polymers*", Vol. 2, D. C. Bassett, Ed., Elsevier, London 1988, p. 1

86) Y. Doi, "*Microbial Polyesters*", VCH Publishers, New York 1990

87) L. Zhang, X. Deng, S. Zhao, Z. Huang, *Polym. Int.* **44**, 104 (1997)

88) P. A. Holmes, *Phys. Technol*. **16**, 32 (1985)

89) P. J. Barham, A. Keller, *J. Polym. Sci., Polym. Phys. Ed.* **24**, 69 (1986)

90) Y. Doi, *Macromol. Chem. Phys., Macromol. Symp*. **98**, 585 (1995)

91) R. Pool, *Science* **245**, 1187 (1989)

92) P. J. Hocking, R. H. Marchessault, "*Chemistry and Technology of Biodegradable Polymers*", Blackie, 1994, p. 48

93) W. Amass, A. Amass, B. Tighe, *Polym. Int*. **17**, 89 (1998)

94) P. P. King, *J. Chem. Technol. Biotechnol*. **32**, 2 (1982)

95) R. S. Lehrle, R. J. Williams, *Macromolecules* **27**, 3782 (1994)

96) E. R. Howells, *Chem. Ind. (London)* **7**, 508 (1982)

97) N. Grassie, E. J. Murray, P. A. Holmes, *Polym. Degrad. Stab*. **6**, 47 (1984)

98) N. Grassie, E. J. Murray, P. A. Holmes, *Polym. Degrad. Stab*. **6**, 127 (1984)

99) N. Grassie, E. J. Murray, P. A. Holmes, *Polym. Degrad. Stab*. **6**, 95 (1984)

100) M. Kunioka, Y. Doi, *Macromolecules* **23**, 1933 (1990)

101) R. S. Lehrle, R. J. Williams, *Macromolecules* **27**, 3782 (1994)

102) R. S. Lehrle, R. Williams, C. French, T. Hammond, *Macromolecules* **28**, 4408 (1995)

103) Y. Doi, M. Kunioka, Y. Nakamura, K. Soga, *Macromolecules* **21**, 2722 (1988)

104) M. Kunioka, Y. Nakamura, Y. Doi, *Polym. Commun*. **29**, 174 (1988)

105) Y. Doi, M. Kunioka, Y. Nakamura, K. Soga, *Macromolecules* **19**, 2860 (1986)

106) T. L. Bluhm, G. K. Hamer, R. H. Marchessault, C. A. Fyfe, R. P. Veregin, *Macromolecules* **19**, 2871 (1986)

107) Y. Doi, M. Kunioka, A. Tamaki, Y. Nakamura, K. Soga, *Macromol. Chem*. **189**, 1077 (1988)

108) M. Kunioka, A. Takami, Y. Doi, *Macromolecules* **22**, 694 (1989)

109) A. J. Owen, *Colloid Polym. Sci*. **263**, 799 (1985)

110) S. Bloembergen, G. K. Hamer, T. L. Bluhm, R. H. Marchessault, *Macromolecules* **19**, 2865 (1985)

111) A. Steinbüchel, H. E. Valentin, *FEMS Microbiol. Lett*. **128**, 219 (1995)

112) J. E. Potts, R. A. Clendinning, W. B. Ackart, W. D. Niegisch, *Polym. Sci. Technol*. **3**, 61 (1973)

113) Y. Tokiwa, T. Suzuki, *Nature* **270**, 76 (1977)

114) "*Biodegradable Polymers*", in: "The Encyclopedia of Advanced Materials", Vol. 1, D. Bloor, M. C. Flemings, R. J. Brook, S. Mahajan, Eds., Pergamon, 1994 p. 238

115) T. Fujimaki, *Polym. Degrad. Stab*. **59**, 209 (1998)

116) E. Takiyama, N. Harigai, T. Hokari, *Japanese Patent* No. H5-70566, 1993

117) E. Takiyama, S. Seki, *Japanese Patent* No. H5-70572, 1993

118) T. Fujimaki, E. Takiyama, *Polym. Prep., Symp. Polym.*, Society of Polymer Sience, Japan **43 (11)**, 3993 (1994)

119) E. Takiyama, T. Fujimaki, in: "*Biodegradable Plastics and Polymers*", Vol. 12(3), Y. Doi, K. Fukuda, Ed., Elsevier, Amsterdam 1994, p. 150

120) Y. Yasuda, E. Takiyama, *US Patent* No. 5391644, 1995

121) M. Imaizumi, M. Kotani, R. Kamei, E. Takiyama, *US Patent* No. 5658627, 1997

122) T. Taka, Y. Yasukawa, E. Takiyama, *US Patent* No. 5324794, 1994

123) M. Imaizuki, M. Kotani, H. Kondo, T. Iwasa, E. Takiyama, *US Patent* No. 5314969, 1994

124) T. Takahasi, R. Kamei, S. Terazono, T. Takahasi, A. Nakamura, E. Takiyama, *US Patent* No. 5310872, 1994

125) Y. Moteki, N. Fujiwara, Y. Furuichi, E. Takiyama, *US Patent* No. 5360663, 1994

126) T. Fujimaki, *Sen'I Gakkaishi* **52 (8)**, 320 (1996)

127) M. Nishioka, T. Tuzuki, Y. Wanajyo, H. Oonami, T. Horiuchi, in: *"Biodegradable Plastics and Polymers"*, Vol. 12 (3), Y. Doi, F. Fukuda, Eds., Elsevier, Amsterdam, 1994, p. 584

128) R. J. Gaymans, J. L. de Haan, *Polymer* **34**, 4360 (1994)

129) I. Arvanitoyamis, A. Nakayama, N. Kawasaki, N. Yamamoto, *Polymer* **36**, 857 (1995)

130) N. Paredes, A. Rodriguez-Gala'n, J. Puiggali, *J. Polym. Sci., Part A: Polym. Chem*. **36**, 1271 (1998)

131) L. H. Ho, S. J. Huang, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **33 (2)**, 94 (1992)

132) Y. Saotome, T. Miyazawa, T. Endo, *Chem. Lett*. 21 (1991)

133) Y. Saotome, T. Miyazawa, T. Endo, *Chem. Lett*. 153 (1991)

134) *Bundesanzeiger Nr.* 20, 30. 1. 1990, p. 513

135) G. Grigat, R. Koch, R. Timmermann, *Polym. Degrad. Stab*. **59**, 223 (1998)

136) E. Grigat, K. Salewski, R. Timmermann, *Kunstoffe Plast. Eur.*, 19 January 1997

137) E. Grigat, W. Littek, W. Schulz-Schlitte, *Kunstoffe Plast. Eur.*, 21 May 1997

138) *Polym. News* **23**, 129 (1998)

139) "*Prüfung der Kompostierbarkeit von polymeren Werkstoffen*", E DIN 54900 (Gelbdruck)

140) *Quote*, e. g. ISO 14855

141) K. Poutanen, P. Forssell, *TRIP* **4 (4),** 128 (1996)

142) O. B. Wurzburg, *"Modified Starches: Properties and Uses"*, CRS Press, 1986

143) R. L. Shogren, *"Biopolymers from Renewable Resources (Macromolecular systems, materials approach)"*, D. L. Kaplan, Ed., Springer-Verlag, Berlin Heidelberg 1998, p. 30

144) C. Mercier, P. Feillet, *Cereal Chemistry* **52 (3)**, 283 (1975).

145) J. W. Donovan, *Biopolymers* **18**, 263 (1979)

146) P. Colonna, C. Mercier, *Phytochemistry* **24 (8)**, 1667 (1985)

147) J. Silbiger, J. P. Sacchetto, D. J. Lentz, *Eur. Pat*. Appl. 0 404 728, 1990

148) C. Bastioli, V. Bellotti, G. F. Del Tredici, *Eur. Pat*. Appl. WO 90/EP1286, 1990

149) I. Tomka, WO 90/05161/US 5,362,777/EP 0397819, *"Thermoplastically Processable Starch And A Method Of Making It"*

150) I. Tomka, EP 0 542 155, US 5 280 055, *"Biodegradable Polymerblend"*

151) I. Tomka, EP 596 437, *"Biodegradable Polymerblends*"

152) J. Loercks, W. Pommeranz, H. Schmidt, WO 96/19599, *"Technical And Non-Technical Textile Products And Packaging Materials*"

153) J. Loercks, W. Pommeranz, H. Schmidt, WO 96/31561, *"Biologically Degradable Polymer Mixture"*

154) C. M. Buchanan, R. M. Gardner, R. J. Komarek, *J. Appl. Polym. Sci*. **47**, 1709 (1993)

155) R. J. Komarek, R. M. Gardner, C. M. Buchanan, S. C. Gedon, *J. Appl. Polym. Sci*. **50**, 1739 (1993)

156) R. M. Gardner, C. M. Buchanan, R. J. Komarek, D. D. Dorschel, C. Boggs, A. W. White, *J. Appl. Polym. Sci*. **52**, 1477 (1994)

157) C. J. Rivard, W. S. Adney, M. E. Himmel, D. J. Mitchell, T. B. Vinzant, K. Grohmann, L. Moens, H. Chum, *Appl. Biochem. Biorech*. **34/35**, 725 (1992)

158) J.-D. Gu, D. Eberiel, S. P. McCarthy, R. A. Gross, *J. Environ. Polym. Degrad*. **1**, 143 (1993)

159) J.-D. Gu, M. Gada, G. Kharas, D. Eberiel, S. P. McCarthy, R. A. Gross, *J. Am. Chem. Soc., Polym. Prepr.* 1992, p. 351

160) C. M. Buchanan, R. M. Gardner, R. J. Komarek, S. C. Gedon, A. W. White, in: *"Fundamentals of Biodegradable Materials and Packaging*", D. Kaplan, E. Thomas, C. Ching, Eds., Techomic Publishing Co; Lancaster, Pennsylvania, 1993, p. 133

161) G. R. Elion, *US Patent* 2,244,945, 1993

162) U. Kasulke, H. Dautzenberg, E. Polter, B. Philipp, *Cellul. Chem. Technol*. **17**, 423 (1983)

163) A. S. Perlin, S. S. Bhattacharjee, *J. Polym. Sci. Part C* **36**, 506 (1971)

164) F. Stutzenberger, G. Kahler, *J. Appl. Bacteriol*. **61**, 225 (1986)

165) P. A. Cantor, B. J. Mechales, *J. Polym. Sci. Part C* **28**, 225 (1969)
166) C. M. Buchanan, S. C. Gedon, A. W. White, M. D. Wood, *Macromolecules* **26**, 2963 (1993)
167) L. Jiang, G. Hinrichsen, *Angew. Makromol. Chem*. **253**, 193 (1997)
168) Y. T.-P. Ly, L. A. Johnson, J. Jane, "Soy Protein as Biopolymer" in: *Biopolymers from Renewable Resources, Macromolecular Systems-Materials Approach*, D. L. Kaplan, Ed., Springer-Verlag, Berlin Heidelberg 1998, p. 144
169) S. J. Huang, "Plant proteins as materials", in*: Identifying new industrial uses of soybean protein. Special Rep 95*, C. P. Baumel, L. A. Johnson, C. A. Greiner, Eds., Iowa Agriculture and Home Economics Experiment Station, Iowa State University, Ames, IA, USA, 1994
170) S. F. Thames, "Soybean polypeptide polymers" in: *Identifying new industrial uses of soybean protein. Special Rep 95*, C. P. Baumel, L. A. Johnson, C. A. Greiner, Eds., Iowa Agriculture and Home Economics Experiment Station, Iowa State University, Ames, IA, USA, 1994
171) J. Jane, S. Wang, *US Patent* 5,523,293, 1996
172) D. Myers, Cereal Foods World **38**, 278 (1993)
173) D. J. Myers, "Past, present and potential uses of soy proteins in nonfood industrial applications", in: *Proceeding of the AOCS World Conference & Exposition on Oilseeds Technology and Utilization*, T. H. Applewhite, Ed., AOCS Press, Champaign, IL. 1993
174) S. Wang, H.-J. Sue, J. Jane, *J. Macromol. Sci., Pure Appl. Chem*. **33**, 557 (1994)
175) J. U. Otaigbe, H. Goel, T. Babcock, J. Jane, *J. Elastomers Plast*. **31 (1)**, 56 (1999)
176) R. P. Wool, *Chemtech* **29 (6)**, 44 (1999)
177) J. Jane, S. Wang, *US Patent* Appl. US 94–248994 940525
178) *European Plastic News*, July/August 1998, p. 14
179) R. H. Yocum, *Plastics Engineering*, June 1998, p. 14
180) K. E. Gonsalves, P. M. Mungara, *TRIP*, **4 (1)**, 25 (1996)
181) T. Harada, T. Hirata, K. Setoyama, M. Ohkoshi, "Advanced Materials '93 V/A Ecomaterials", R. Yamamato, Ed., *Trans. Mater. Res. Soc.* Vol. 18A, Elsevier Science, 1994, p. 2
182) G. Swift, *Polym. News* **19,** 102 (1994)
183) J. Saimon, H. Müller, R. Koch, V. Müller, *Polym. Degrad. Stab*. **59**, 107 (1998)
184) *Polym. News* **18 (10)**, 312 (1993)
185) *Chemical Week*, December 9, 1998, p. 5
186) "*Biodegradable Polymers in North America & Europe (PO81)*", Mar Tech, USA, July 1998, p. 21
187) *Personal letter* from Bayer, 16 October 1998
188) *Personal letter* from BSL, 8 February 1999
189) R. Westervelt, *Chemical Week*, January 19, 2000, p. 9
190) European Commission, "*Study on production of thermo-bioplastics and fibres mainly on biological materials",* Directorate-General XII, Science, Research and Development, EUR 16102
191) P. Barghoorn, U. Stebani, M. Balsam, *Adv. Mater.* **10 (9)**, 635 (1998)
192) O. Vogl, *J. Macromol. Sci., Pure Appl. Chem*. **A33 (7)**, 963 (1996)
193) U. Riedel, M. Chowanietz, "*Faserverbundwerkstoff und Verfahren zu seiner Herstellung*", DE Akz. 196 47 671.2–44, November 1996
194) G. E. Myers, I. S. Chahyadi, C. A. Coberly, D. S. Ermer, *Int. J. Polym. Mater.* **15**, 21 (1991)
195) J. M. Felix, P. Gatenholm, in: "*Controlled Interphases in Composite Materials*", H. Ishida, Ed., 1990, p. 267, Elsevier Science Publisher
196) G. S. Han, N. Shiraishi, *Mokuzai Gakkaishi* **37**, 241 (1991)
197) J. M. Felix, P. Gatenholm, *J. Appl. Polym. Sci*. **4**, 609 (1991)
198) J. M. Felix, P. Gatenholm, *J. Appl. Polym. Sci*. **52**, 689 (1991)
199) H. Kishi, M. Yoshioka, A. Yamanoi, N. Shiraishi, *Mokuzai Gakkaishi* **34**, 133 (1988)
200) P. Flodin, P. Zadorecki, in: "*Composite Systems from Natural and Synthetic Polymers*", L. Salmen, A. de Ruvo, J. C. Seferis, E. B. Stark, Eds., Elsevier Science Publishers, 1986, p. 59
201) P. Zadorecki, H. Karnerfors, S. Lindenfors, *Compos. Sci. Technol*. **27**, 291 (1986)
202) L. Hua, P. Flodin, T. Rönnhult, *Polym. Compos*. **8**, 203 (1987)
203) D. K. Setua, in: *Polym. Sci. Technol.*, Vol. 33, E. Carraher Jr; L. H. Sperling, Eds., Plenum Press, 1986, p. 275
204) P. Flink, B. Stenberg, *Brit. Polym. J*. **22**, 147 (1990)
205) Y. Inoue, N. Yoshie, *Prog. Polym. Sci*. **17**, 571 (1992)
206) P. Gatenholm, J. Kubat, A. Mathiasson, *J. Appl. Polym. Sci*. **45**, 1667 (1992)
207) P. Gatenholm, A. Mathiasson, *J. Appl. Polym. Sci*. **51**, 1231 (1994)
208) M. Avella, R. dell'Erba, "*Proceeding of the 9th International Conference on Composite Materials*", Vol. II Madrid, July 12–16, 1993, p. 864
209) K.-P. Mieck, A. Nechwatal, C. Knobelsdorf, *Angew. Makromol. Chemie*. **224**, 73 (1995)
210) K.-P. Mieck, A. Nechwatal, C. Knobelsdorf, *Angew. Makromol. Chemie*. **225**, 37 (1995)
211) P. R. Hornsby, E. Hinrichsen, K. Tarverdi, *J. Mater. Sci*. **32**, 1009 (1997)
212) S. Haager, *Energie* **47(5)**, 50 (1995)
213) M. Barbu, T. Fritz, "Flax Fibre-reinforced Particleboard", in Symp.: *Pokroky Vyrobe Pouziti Lepidiel Drevopriem* 1995, 12th; p. 57. *Chem. Abstr.* **124**, 292690s (1996).
214) **DIN 53452**: "*Prüfung von Kunststoffen-Biegeversuch*", Deutsches Institut für Normung, Berlin
215) **DIN 53455**: "*Prüfung von Kunststoffen-Zugversuch*", Deutsches Institut für Normung, Berlin
216) K. Moser, "*Faser-Kunststoff-Verbund*", VDI-Verlag, Düsseldorf 1992
217) A. S. Herrmann, H. Hanselka, J. Nickel, U. Riedel, "*Biodegradable fibre reinforced plastics based upon renewable resources*", TECNITEX, Torino-Lingotto, November 1996
218) A. S. Herrmann, H. Hanselka, G. Niederstadt, *Eur. Pat. Appl*. EP 687,711 (Cl. C08L97/02), 20 Dec. 1995, *DE Appl*. 4,420,817, 16 June 1994
219) H. G. Fritz, W. Aichholzer, T. Seidenstuecker, B. Widmann, *Starch/Staerke* **47(12),** 475 (1995)
220) S. R. Ranganathan, P. K. Pal, *Popular Plast*. **30**, 41 (1985)
221) P. Ghosh, P. K. Ganguly, *Plast. Rubber Compos. Proc. Appl*. **20**, 171 (1993)
222) P. J. Rao, M. P. Ansell, *J. Mater. Sci*. **20**, 4015 (1985)
223) A. C. Karmaker, J. Youngquist, *J. Appl. Polym. Sci*. **62**, 1147 (1996)
224) S. Sahoo, D. Pati, M. Misra, S. S. Tripathy, S. K. Nayak, A. K. Mohanty, "*International Symposium: Polymers 1999*", Polymers beyond A. D. 2000 A. K. Ghosh, Ed., Society of Polymer Science , India, January 1999, p. 542–545
225) J. Gassan, A. K. Bledzki, *Polym. Compos*. **18 (2)**, 179 (1997)
226) A. K. Bledzki, J. Gassan, *Angew. Makromol. Chemie* **236**,129 (1996)
227) M. A. Semsarzadeh, *Polym. Plast. Technol. Eng*. **24**, 323 (1985–86)
228) P. K. Pal, *Plast. Rubber Proc. Appl*. **3**, 4 (1984)
229) A. N. Shah, S. C. Lakkad, *Fibre Sci. Technol*. **15**, 41 (1981)

[230] A. K. Rana, A. Mandal, B. C. Mitra, R. Jacobson, R. Rowell, A. N. Banerjee, *J. Appl. Polym. Sci*. **69**, 329 (1998)

[231] A. C. Karmakar, G. Hinrichsen, *Polym. Plast. Technol. Eng*. **30**, 609 (1991)

[232] G. Hinrichsen, A. C. Karmaker, B. Wuttke, "*Proc. BMFT Seminar*", Bonn-Bad Godesberg, FRG, 1991, p. 285

[233] B. C. Mitra, R. K. Basak, M. Sarkar, *J. Appl. Polym. Sci*. **67**, 1093 (1998)

[234] J. Gassan, A. K. Bledzki, *Composites Part A*, **28A**, 1001 (1997)

[235] M. A. Khan, K. M. I. Ali, G. Hinrichsen, C. Kopp, S. Kropke, *Polym. Plast. Technol. Eng*. **38(1)**, 99 (1999)

[236] A. K. Mohanty, M. A. Khan, G. Hinrichsen, *J. Mater. Sci*. (2000) in press

[237] A. K. Mohanty, M. A. Khan, G. Hinrichsen, *Compos. Sci. Technol*. (2000) in press

[238] E. T. N. Bisanda, M. P. Ansell, *Compos. Sci. Technol*. **41**, 165 (1991)

[239] P. C. Tripathy, M. Misra, S. Parija, S. Mishra, A. K. Mohanty, *Polym. Int*. **48**, 868 (1999)

[240] J. I. Kroschwitz, Polymers: "*Fibers and Textiles*", John Wiley & Sons, New York 1990.

[241] A. K Mohanty, M. Misra, *Angew. Makromol. Chem*. **225**, 1 (1995).

[242] A. K. Mohanty, M. A. Khan, G. Hinrichsen, *Composites Part A* **31(2)**, 143 (2000).

[243] T. Hata, M. Kamya, *Jpn. Kokai Tokkyo Koho* JP 08,132,566 [96, 132, 566] (Cl. B32B27/12), 28 May 1996, Appl. 94/272,288, 7 Nov. **1994**.

[244] S. J. Huang, M. F. Koenig, M. Huang, "Design, synthesis and properties of Biodegradable Composite", in: *Biodegradable Polymers and Packaging,* C. Ching, D. Kaplan, E. Thomas, Eds., Technomic Publishing Company Inc., 1993, p. 97

[245] J. U. Otaigbe, *Plast. Eng.*, April 1998, p. 37

[246] J. U. Otaigbe, J.-L. Jane, *J. Environ. Polym*. **5**, 75 (1997)

[247] J. U. Otaigbe, D. O. Adams, *J. Environ. Polym*. **5**, 199 (1997)

[248] S. Wang, in: "*Polymers from Agricultural Coproducts*", *ACS Symp. Ser.* **575**, 92 (1994)

[249] J. W. Rhim, Y. Wu, C. L. Weller, M. Schnepf, *Sci. Ailments* **19 (1)**, 57 (1999)

[250] J. W. Rhim, Y. Wu, C. L. Weller, M. Schnepf, *J. Food Sci*. **64 (1)**, 149 (1999)

[251] S. Luo, A. N. Netravali, *Polym. Compos*. **20 (3)**, 367 (1999)

[252] S. Luo, A. N. Netravali, *J. Mater. Sci*. **34**, 3709 (1999)

[253] *Green-Tech*® News letter, Vol. 1, No. 1, February 1998

[254] G. E. Zaikov, S. M. Lomakin, *Polym. Plast. Technol. Eng.* **36 (4)**, 647 (1997)