Biomaterials

Pieter van Mourik, Jaap van Dam*, Stephen J. Picken*, Bob Ursem+*
(Delft University of Technology, Faculty of Applied Sciences, Section Advanced Soft Matter)*
(+ Delft University of Technology, Faculty of Applied Sciences, Botanical Garden)

Summary
The metabolic pathways of living organisms produce biomaterials. Hence, in principle biomaterials are fully sustainable. This does not mean that their processing and application have no impact on the environment, e.g. the recycling of natural rubber remains a problem. Biomaterials are applied in a wide range of consumer products, varying from clothing via temporary packaging materials to car parts. Examples are the paper we print on, the wooden table we sit around and the jeans we wear. This survey is based on the corresponding chapter of the textbook *Materials Science in Design and Engineering* (Van Mourik et al., 2012) and deals with three important groups: biopolymers, wood and paper and fibres and textiles.

Biopolymers

Based on the chemical constituents, several classes of biopolymers are distinguished:

Polysaccharides are carbohydrates and are the most widespread biopolymers in nature. They are composed of sugar units, monosaccharides. They are sensitive to aqueous acid, by which they are hydrolysed into their monosaccharide constituents. The most widespread are cellulose and starch, both long chain homopolymers of (1→4) linked glucose units (see Figure 1).

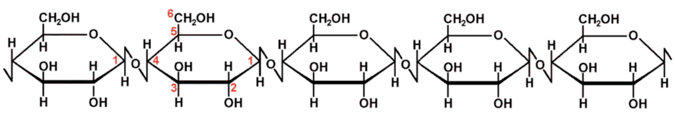

Figure 1. Structure of cellulose showing the β(1→4) linkage.

Cellulose fibres form the major constituent of wood, paper and boards, and some commercial textile fibres (cotton, flax-linen and hemp). They can also be used as reinforcing fibres in thermoplastic composites. Cellulose filaments (rayon) are used to reinforce high-speed car tyres. *Cellophane* is a film of cellulose and applied as packaging for food, flowers and luxury goods, and as a carrier for self-adhesive tapes. The affinity to water of polysaccharides and hence their tendency to undesired biodegradation, has led to the development of many derivatives. These can have thermoplastic properties and can be used as surfactants, coatings and adhesives. *Celluloid* is one of the first man-made polymers, based on cellulose nitrate esters and it was the breakthrough for cinema films. Other polymers now largely replace it, because it is highly flammable. Only for ping-pong balls no substitute with the same performance has been found.

Proteins are used as textiles since ages; common protein-based fibres are silk and wool. They still maintain a strong market position. Since ancient times, proteins have also been used in glues, paints and coatings. As proteins have both hydrophilic and hydrophobic parts, they have surface active and emulsifying properties and can be used as colloidal foaming agents, in films and edible coatings. Protein-based bio-plastics commonly require cross-linking and stabilizing with biochemical or chemical agents to impart water resistance and to avoid rapid microbial attack and des-integration.

Lignin is mainly derived from the woody or bark tissues in plants, where they play a role as a glue and matrix for cellulose fibres, giving strength and stiffness. Liquefaction of lignin/wood at elevated temperatures results in thermosetting resins that can be converted into moulded products, adhesives or carbon fibres. In contrast to most biopolymers lignin is non-linear and not composed of distinct repeating structural elements. The bonds in lignin can be of ester or ether type but also aliphatic or aromatic carbon-carbon linkages occur.

Biopolyesters are natural polymers of hydroxyalkanoic acids that are linked by ester bonds. Biopolyesters can be fully synthesized by micro-organisms or produced as monomer by fermentation and chemically polymerized. Polyhydroxyalkanoates or polyhydroxyalkanoic acids (PHAs) form a class of polyesters that can be used as thermoplastics or as elastomeric polymers. These polyesters are biodegradable and biocompatible. Figure 2 shows the general structure of PHAs; R can stand for a number of side groups, e.g. hydrogen and methyl. Table 1 lists some physical properties of PHAs.

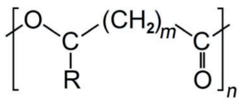

Figure 2. General formula of PHAs, m may be 1, 2 or 3, yet m = 1 is most common.

The effect of the side-chain length is clear. PHB is a semicrystalline thermoplastic resin with properties that are often compared to those of polypropylene, although the E-modulus of PHB is higher than that of PP and the strain at break of PHB is much lower (6%) than that of PP (450%).

Polylactic acid (PLA) is not a naturally occurring polymer, but the precursor, lactic acid (CH_3-CH(OH)-COOH), can readily be produced by fermentation of biomass like corn starch or cane sugar and subsequent polymerization. PLA is fully biodegradable and is mainly suited for medical implants and controlled drug release, although broader applications (packaging and consumer goods) are envisaged. PLA is a glossy colourless thermoplastic with properties similar to polystyrene. The properties of PLA depend very much on the molecular weight and stereochemistry of the main chain. The crystallinity of PLA can reach 80%. It appears that PLA provides ample opportunities for a wide variety of copolymers (see Kaplan (1998)), each with effects on stereochemistry, crystallinity, mechanical and physical properties. PLA suffers from thermal degradation above 200ºC. PLA can be processed by common plastic processing techniques. Table 2 compares some relevant properties of PLA with those of polypropylene and polystyrene.

Wood and paper

Wood properties depend on the species concerned. Balsa wood (relative density only 0.16!) finds application in (model) aeroplanes, and is easy to cut and relatively strong. The heavy black ebony (relative density of above 1) is very strong and hard, causing heavy wear of saws and chisels. Ornamental objects, musical instruments and fine cabinets are produced from it. Structural wood is mainly derived from a limited number of species especially suitable for commercial timber processing, mostly coniferous trees, industrially known as softwoods.

PHA	glass transition temperature (ºC)	melting temperature (ºC)	relative density	side group R
PHB	5	180	1.24	methyl
PHV	-11	105 – 108	1.20	ethyl
PHC	-25	–	–	propyl
PHH	-33	45	–	butyl
PHO	-36	61	1.02	pentyl
PHN	-39	54	1.03	hexyl
PHD	-40	54	1.03	heptyl

Table 1. Some physical properties of PHAs (Kaplan (1998)).

Polymer	PP	PS	PLA
crystallinity (%)	70		up to 80
melting point (ºC)	170	–	170-180
glass transition temperature (ºC)	-15	95	57-60
E-modulus (GPa)	1.4	3.3	3.7
tensile strength (MPa)	50	55	54

Table 2. Some relevant properties of PLA compared with PS and PP.

Softwoods are commonly cheaper than hardwoods because they grow faster. Hardwoods are from deciduous trees (loosing their leaves in winter or dry season) or evergreen (tropical) trees. Hardwoods are not necessarily strong. Willow, birch and poplar, for example, are hardwoods of low strength and of little use as structural material. Willow wickers are applied in mats, covered with stones (Dutch: zinkmatten) for dike protection. Large volumes of softwood timber (pine, spruce, lark, cedar and fir) are used in building and furniture. Oak is highly appreciated for furniture. Beech is favoured in furniture industries because of its consistency and ease of working. Ash wood is typically used where high mechanical endurance is demanded such as in handles of tools (hammers) and broomsticks. Certain tropical hardwoods (meranti, merbau) are favoured for window and door frames as they have excellent weather resistance.

Figure 3. A garden house with walls of unpainted 'red cedar', children's garden De Papaver in Delft, The Netherlands (architect Frank Heyligers, constructed in 1994, photo taken in 2008).

Wood consists of fibre cells that are built up of cellulose fibrils glued together with hemicellulosic polysaccharides and lignin. 'Hemicelluloses' is a generic term for non-cellulosic polysaccharides present in wood cell walls. So, wood is a composite of cellulose fibrils and lignin and hemicelluloses (see Figure 7). The orientation of the fibre cell determines the grain structure of the wood. Cut pieces of timber therefore can show different patterns depending on the angle of sawing. The homogeneity of the wood, the grain orientation and the absence of defects largely determine the quality and thus the value of the sawn timber. Untreated wood will become gray when exposed to light and weathering. Most wood-based products require good protection against decay. There is a great difference between conserving hardwood of deciduous and evergreen trees and coniferous hardwood. The latter always possesses hollow fibres, with a diameter of about 50 µm. Therefore coatings are able to impregnate these coniferous woods due to a radial transport of the preserving materials through pores and hollow lignified fibres. The hardwood of evergreen trees has solid lignified fibres and can only be coated on the surface. To reduce the flammability of wood products fire retardant chemicals are frequently applied. There are a few species that can be used without any protective coating because of their high tannin contents. Among these are 'red cedar' (*Thuya plicata*), juniper (*Juniperus communis*) and chestnut (*Castanea sativa*), wood species that are favoured in outdoor applications such as fences, cladding and shingles. Teak is hard and very durable, and hence pre-eminently suited for decks of sailing yachts and garden furniture.

The strength properties of wood vary much more than those of other materials, due to natural variability and moisture effects. The bearing capability of a wooden column can be very different in directions parallel and perpendicular to the grain. The compression strength parallel to the grain in timber is commonly more than twice that in perpendicular directions.

wood species			relative density		bending strength (MPa)		E-modulus (GPa)	
common name (English)	common name (Dutch)	Latin or botanical name	wet	dry	wet	dry	wet	dry
silver fir	dennen	*Abies alba*	0.58	0.45	43	79	8.1	9.8
Norway spruce	vuren	*Picea abies*	0.53	0.42	39	72	7.4	10.2
Scots pine	grenen	*Pinus sylvestris*	0.63	0.51	46	89	7.3	10.0
merbau	merbau	*Intsia species*	0.66	0.51	53	83	7.4	9.0
meranti	meranti	*Shorea species*	0.61	0.48	67	88	9.7	10.5
oak	eiken	*Quercus petraea, Quercus robur*	0.83	0.69	57	97	8.3	10.1

Table 3. Properties of some wood species (Verver (1996)).

Temperature variation, moisture swelling, ageing and chemical treatment may considerably affect the strength and the E-modulus. The bending and flexural behaviour of a wooden beam determines its suitability to support a structure. Therefore, the bending strength of wood, which is more or less equal to the tensile strength parallel to the trunk direction, is often taken as characteristic for the mechanical properties of wood. Table 3 gathers some indicative values, where 'wet' and 'dry' indicate moisture volume fractions of 50% and 12%, respectively. The maximum number of storeys of a wooden building remains normally restricted to two or three, because of the increasing compression loads and lack of stability.

Plywood, already invented in the 1850s, consists of at least three layers, plied and glued together with the grain running crosswise to add strength and resilience in all directions (Dutch: *triplex* and *multiplex*). As a result, plywood allows higher loading and longer spans and thus a novel design in constructions such as beams. It is also a key material for designers of furniture. The breakthrough was Gerrit Rietveld's 1927 chair with a one-piece plywood screwed on a tubular steel frame (Figure 4).

Figure 4. Rietveld's 1927 plywood chair (collection Gemeentemuseum The Hague).

Most of the paper stems from the pulp of softwoods. Paper sheets are composed of a microscopic web of cellulose fibres that are entangled and linked to each other when the sheets are dried. The stiffness and length of the fibres are of direct influence on the paper sheet properties such as tear, bending strength and folding endurance. The purity of the fibre obtained from the pulping process and the fibrillation degree affect the colour and smoothness of paper. These properties of the cellulosic fibres depend on a combination of tree-inherited features and pulp processing conditions. Additives (fillers, surfactants, adhesives) are used to improve strength, water resistance, gloss and printability. Cellulose pulp can be transformed in many three-dimensional forms by adding glue (starch) or another adhesive and forming it by hand or in a mould. After drying (e.g. by pressing), a rather firm material results. The craft to mould the paper paste into any shape is not only fun on children's parties but this 'papier mâché' is also a useful material for artistic purposes (puppeteers!) and the packaging industries (e.g. egg boxes). Cellulose-based products are in general sensitive to moisture and require protection if a longer functional lifetime is desired. Papers often are coated with glossy top layers or laminated with a synthetic polymer (Figure 5).

Figure 5. Paper packaging.

Specialty papers (cigarette papers, tea bags and banknotes) are made from non-wood cellulose pulps composed of long fibres such as cotton, flax and hemp. Constructive products made of paper and cardboards are used in separation walls or temporary constructions. Between two layers of boards a honeycomb structure provides high mechanical strength and stiffness. For the design of lightweight structures cardboard tubes have been shown to provide a cheap and strong skeleton (Figure 6).

Figure 6. Skeleton of a lightweight structure made of cardboard tubes (Japanese Pavilion, Expo 2000, Hanover, Germany).

Fibres and Textiles

Wood, and thus woody fibre, is a composite of cellulose fibrils and lignin and hemicelluloses (Figure 7). The amount of cellulose depends on the species: ranging from 90% cellulose in cotton, via about 75% in flax and hemp bast fibres to about 40% in wood fibres. Cellulosic fibre-reinforced composites with synthetic polymers such as PP and PE have been extensively investigated and are now applied as lightweight car interior parts (see Figure 8).

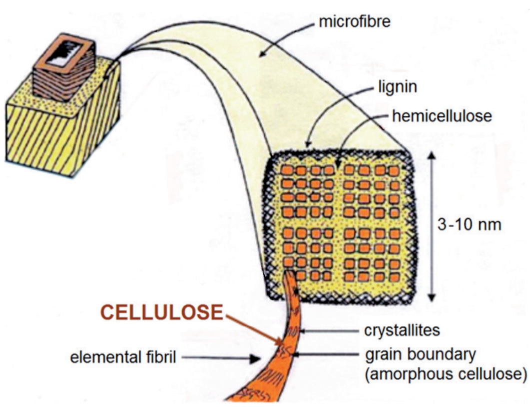

Figure 7. Fibre structure of the woody part of plants.

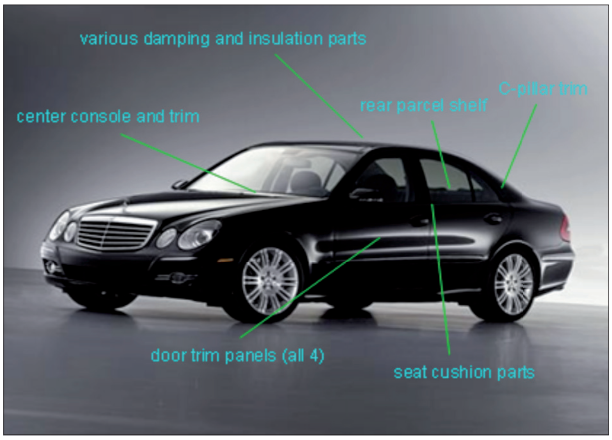

Figure 8. Applications of natural fibre composites in the Mercedes-Benz E-Class.

Of the protein materials, silk is by far the most used in human history. There are numerous insects producing silk. Only one of them, however, has gained commercial importance: the domesticated silkworm, *Bombyx mori*. Silk can be characterized as semi-crystalline with a crystallinity of about 60%. Silk is insoluble in dilute acids and dilute alkali, resistant to many enzymes, but is hydrolysed by concentrated sulphuric acid. Further, it is hygroscopic with moisture absorption of about 10-15%. Table 4 gathers some mechanical properties of silk produced by *Bombyx mori* and the American golden orb-web spider *Nephila clavides* in comparison with some other fibres. The mechanical properties of silk depend on the variety of silk concerned, on the moisture content and on the elongation rate. For most materials the strength and the modulus increase with increasing loading rate, whereas the elongation at break decreases. With silks, the elongation at break increases with the loading rate. This implies that the energy to break is a function of the loading rate. Summarizing, silks are highly oriented semi-crystalline polymers that exhibit high tensile strengths and a good extensibility. The outstanding mechanical properties of silk, its feeling and ease of dyeing explain its ongoing popularity.

The properties of a textile may range from a light transparent gauze used as veils or wound dressing to strong and impermeable canvas used for the sails of ships or coarse geotextiles applied in civil engineering. The process of manufacturing the yarn into a fabric makes a lot of difference for the flexibility, elasticity and drapability of the product. Due to the nature of the weaving process the woven fabric consists of a two-dimensional network of horizontal (warp) and vertical (weft) yarns forming long strokes of limited width.

fibre	elongation at break (%)	E-modulus (GPa)	tensile strength (MPa)	energy to break (kJ/kg)
spider silk *(Nephila clavipes)*	10 – 30	1 - 30	300 – 1800	30 – 100
silkworm silk *(Bombyx mori)*	15 – 35	5	600	70
nylon	18 – 26	3	500	80
cotton	6 – 7	6 – 11	300 – 700	5 – 15
Kevlar	4	100	4000	30
steel	8	200	2000	2

Table 4. Mechanical properties of silk and some other fibres (Byrom (1991)).

One of the most outspoken properties of textile is colour. A striking example of attractive, intricate colour patterns are those on the dresses worn by women in many West African countries, which are known as '*Véritable Hollandais*' (Khoe and Van den Boomen (2007)), see Figure 9. In this wax resist process the patterns are imprinted by an elaborate batik method.

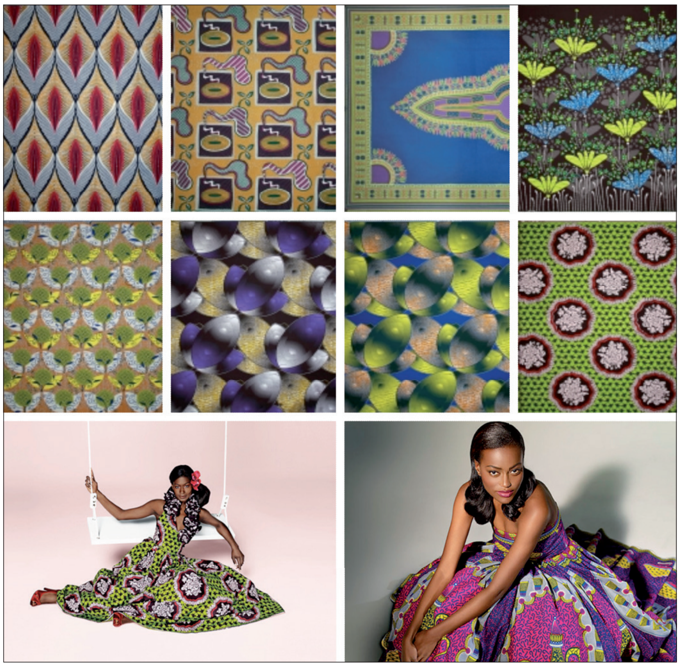

Figure 9. 'Véritable Hollandais' by VLISCO®.

References and further reading

Byrom, D. (ed), *Biomaterials, Novel Materials from Biological Sources,* Stockton Press/MacMillan, New York USA/Basingstoke UK, 1991

Horrocks, A.R., S.C. Anand (eds), *Handbook of Technical Textiles,* The Textile Institute, Woodhead Publishing, Cambridge UK/CRC Press, NW Boca Raton USA, 2000

Iterson Jr., G. van, *Hevea brasiliensis as a Producer of Rubber,* The International Rubber Journal, December 1936, January 1937

Kaplan, D.L. (ed), *Biopolymers from Renewable Resources,* Springer, Berlin BRD, 1998

Khoe, H., T. van den Boomen, *Magazine M NRC Handelsblad,* Rotterdam NL, 2007, 12, p. 17-25

Morton, W.E., J.W.S. Hearle, *Physical Properties of Textile Fibres,* The Textile Institute, Manchester UK, 3rd ed, 1993

Mourik, Pieter van, Jaap van Dam, Stephen Picken, *Materials Science in Design and Engineering,* VSSD, Delft NL, 2012

Verver, M.W., *Materiaalkunde voor Bouwkunde en Civiele Techniek,* Stam Techniek, Houten NL, 1996

Vigo, T.L., *Textile Processing, Preparation, Dyeing, Finishing and Performance,* Elsevier Science BV, Amsterdam NL, 1994

www.fao.org provides statistical data on wood and timber production

Yates, M., Textiles, *a Handbook for Designers,* W.W. Norton & Company, New York USA, 1996