TECHNOLOGY WATCH: BIOPOLYMERS

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About biopolymers.

For the purpose of this Technology Watch, the term “biopolymers” is loosely defined as *polymeric materials consisting for, at least a significant part, out of biological components*. Where “biological” means (recently) produced by living organisms, i.e. not produced from petroleum. Biopolymers can be thermoplastic or thermoset, they can be composites or homogeneous and they can be biodegradable or not.

> ***Biodegradability****: the ability of a substance to be broken down my (micro-)organisms.*
> ***Compostability****: the ability of a substance to be broken down by (micro-) organisms under very specific and standardized conditions (e.g. according to European Standard EN 13432). Not all biodegradable substances are compostable and not all biopolymers are biodegradable*

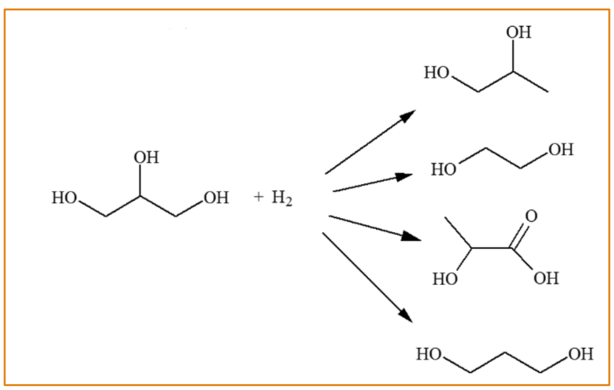
“Classical” Biopolymer	Main Component
Natural Rubber	Polyisoprene
Wood	Cellulose, Lignin
Wool	Protein
Silk	Protein
Cotton	Cellulose
Silk	Protein

Biopolymers have been known since the dawn of civilization: leather, cotton, wool, natural rubber and cork are all biopolymers. While these materials are still popular for specific applications, most polymeric materials in use today are synthetic and based on petroleum-derived resources.

> *A definition for biopolymers sometimes found in patent literature is based on the amount of “modern carbon” that needs to be present in a biopolymer. “Modern carbon” is defined in the ASTMD6866 standard and is about carbon that contains a specific minimum amount of the C14 isotope. In this way it can be proven that the carbon in the material is not from fossil origin*

In recent years the research and development of biopolymers has been gaining significant momentum, driven by “green chemistry” and sustainability principles which are increasingly adapted in the industry. The increased research and development of renewable energy sources, specifically of bio-fuels like bio-ethanol which is produced from grains or biomass and biodiesel which is produced from plant oils, also drives the development of biopolymers. Biodiesel, for example, is produced by reacting plant oils with methanol, resulting in fatty acid methylesters, which is the actual biodiesel, and large amounts of glycerol as a by-product. The glycerol can be converted to di-functional compounds, which in turn can be used as monomers in biopolymer production.

While some biopolymers like polylactic acid (PLA) are already becoming commonplace as ‘green’ and biodegradable packaging materials, others biopolymers are more esoteric. An example is BioSteel™ which are protein fibers produced from milk from goats that had been genetically modified with spider silk genes. The polymers are reportedly up to 10 times stronger than steel for the same weight.

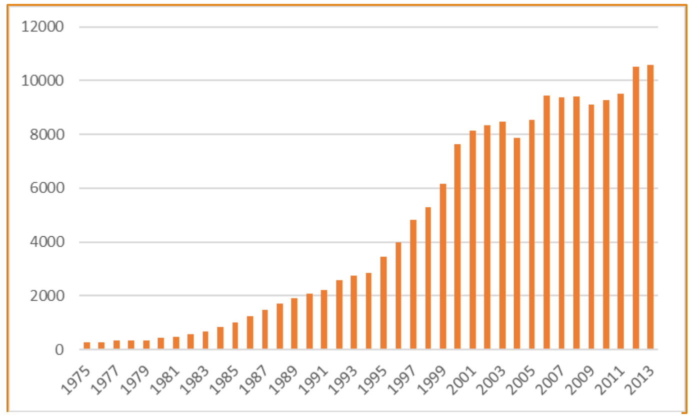


CONVERSION OF GLYCEROL TO GLYCOLS

Currently biopolymers constitute only a relatively small part of industrial polymeric materials, but judging by the sheer amount research and development on the subject a lot of growth can be expected in the near future.

Technology watch: the recent patent literature

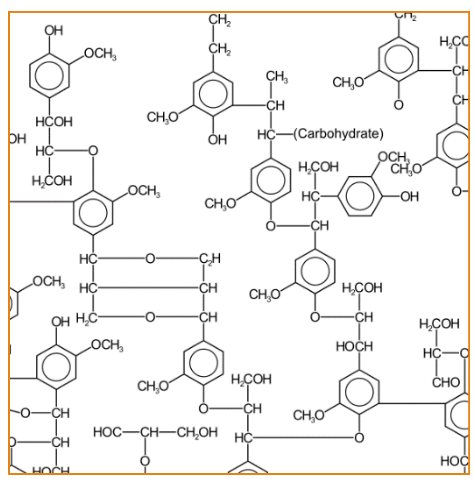
A very large –and growing- number of patent applications related to biopolymers in general is filed every year. For this Technology watch, only the most important and recent (arbitrarily taken as having a priority date of January 1st 2010 or later) patent literature was considered. Not surprisingly these are still many hundreds of patent applications. Below are only some of the most important trends together with some representative examples.



NUMBER OF BIO-POLYMER RELATED PATENT FAMILIES VS PRIORITY YEAR (A VERY ROUGH ESTIMATE!)

In general there are three ways to produce biopolymers, which are reflected in the patent literature:
- Polymers directly extracted or removed from biomass such as some polysaccharides and proteins.
- Polymers produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates, bacterial cellulose, etc.
- Polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as polylactic acid (PLA).

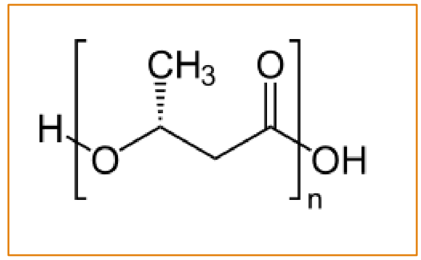
One important trend in the production of biopolymers is the direct extraction of biopolymers from different types of waste streams. Waste streams like waste water[1], “distillers grains”[2] which is a by-product of the (bio-)ethanol production, feathers[3], pineapple mass[4] etc. can all be used to extract biopolymers from. By far the most abundant waste streams are lignin and ligno-cellulose which are available in huge quantities as by products from the paper and agricultural industries. Some specialized companies like Renmatix[5] (US) and Vertichem[6] (Canada) are very active in the field of **lignin** production. Another important waste stream is chitin, which is a polysaccharide found in the shells of shrimp and other crustaceans. Chitin[7] can be converted into **chitosan[8]** which is a useful biopolymer. Biopolymers can also be directly extracted from protein sources like milk[9] or other polysaccharide sources like starch. An edible bioplastic can be made from seaweed[10].



LIGNIN STRUCTURE ©WIKIPEDIA

One of the most important fields of research are the **polyhydroxyalkanoates** (PHA) which are biopolymers produced biochemically by genetically modified microorganisms or modified plants. The resulting polymers are often copolymers form 3- and 4- **hydroxybutyric acid** and/or **hydroxyvaleric acid**. Companies like Metabolix[11,12,13] and Novomer[14] file patents on this topic. Using the correct bacteria PHAs can be produced from wastewater as shown in a number of patent applications or from

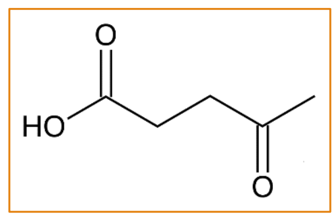
waste fish- or palm oil[15] or from biogas[16] (e.g. from a landfill digesters). PHA can also be produced from glycerol[17], algae[18] or even aromatic sources[19]. Poly(3-hydroxybutyrate) or PHB can also be produced from transgenic plants[20]. An example of a plant that can be genetically engineered to produce PHB are grasses like switchgrass. These grasses are also studied for the bioethanol production in the US.
Most research into improved PHA compositions is about using novel genetically engineered organisms[21] and improved bioreactors[22] . Other application are about improving properties of PHA e.g. by incorporation carbodiimides to improve hydrolysis stability[23].



A Polyhydroxyalkanoate

Recent bio-polymer related patent literature covers a lot of different types of bio-monomers which can be turned into polymers using classical chemical synthesis. For example, quite some research is be done on bio-based "polymer grade" **acrylic acid** and **methacrylic acid**[24,25] which can e.g. be produced from bio-derived glycols and polyols like glycerol and sorbitol. Other bio-monomers commonly associated with classical polymers are

- **Styrene**[26] which can be derived from cinnamic acid
- **Butadiene**[27], 1,4- **butanediol**[28], **hydroxybutyric acid**[29] all of which can be produced from biomass using genetically modified organisms
- 1,3-**propanedio**l[30] which is produced by DuPont (Bio-PDO™) but also studied by Arkema a.o.
- **Isoprene**[31] which can be prepared from acetic acid
- **Isobutylene**[32] from bio butanol
- **Terephthalic acid** from sugar chemistry (furan chemistry)[33] or using genetically modified organisms[34]
- **Succinic acid**[35] by fermentation or by sugar chemistry[36]
- and of course **lactic acid**[37,38].



Levuliniv acid

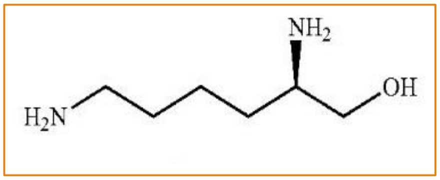
Less common monomers are **levulinic acid** (Segetis)[39], **ketoacids**[40] , **lysinol**[41], **cyclohexadiene**[42] from plant oils. Sugar chemistry research results in **aldaric acid**, furan derivatives like furfural and the like[43,44,45].

Not surprisingly a lot of research is still done on the most common biopolymer i.e. polylactic acid (PLA). The research is often focused on improving polymer properties like increasing toughness, crystallinity, impact modification etc. Companies like Metabolix[46], PURAC[47], Arkema[48], Biovation[49] and others[50,51] are active in this field.

Bio-**polyamides** are also a subject of industrial research, e.g. by DuPont with co-polyamides prepared from plant oils[52], Invista with polyamide terpolymer[53] and Rhodia[54]. Other bio-polymers are **polyacrylates** (P&G)[55,56] , **polyketal esters** (Segetis)[57], **phenolics** (Solvay)[58], **epoxies**[59], **polycaprolacton**[60] and **alkyd esters**[61]. **Bio-polypropylene**[62] is –at least partially- made from renewable resources using methanol and metathesis chemistry.

Bio-polyurethanes[63,64,65,66,67] are an example of a bio-polymer which is only partly prepared from renewable resources. Usually only the 'polyol' part is –partly- replaced by bio-based materials, mostly plant-oil based, while the isocyanate remains petroleum based. Although there is also some research into bio-based **isocyanates**, e.g. by BASF[68].

While there are many types of biopolymers, the applications remain rather limited, at least judging from the recent patent literature. Patents on applications of bio-materials are often related to biodegradable films or sheets, bottles and other types of disposable packaging, but also quite often to adhesives and coatings compositions. For example PLA-based hotmelt adhesives as shown by 3M[69] and pressure sensitive adhesives based on plant oils[70]. PLA-based fibers for nonwovens have been filed by NatureWorks[71] and P&G[72]. Bio-foams can be made from phenolics (Hexion)[73] and compostable polyesters[74]. Other applications include toners[75], automotive panels[76] etc. Another type of application wherein biopolymers are frequently used are medical applications[77] like implants, drug delivery systems, wound dressings and the like, materials which often need specific biodegradation qualities. These materials will be the subject of another Essenscia Technology Watch.



R-Lysinol

A special type of 'application' are the bio-composites. These are mostly fiber-reinforced composites. Obviously the well-known and popular 'composite wood products' like oriented strandboard (OSB) or medium density fiberboard (MDF) are bio-composites. In many cases research into these products is focused on improving the environmental properties of the binder, especially on reducing formaldehyde emissions[78]. For the production of fiber reinforced bio-composites all kinds of natural fibers fibers can be used, like flax[79], bamboo[80], natural wool[81], agave[82] and many others that can be bonded together to form useful composites. Alternatively fiberglass can be bonded with bio-based adhesives like shown by Owens Corning[83]. Apart from fiber-reinforced biocomposites, also particle reinforced biocomposites have been studied[84,85]. Other materials used in biocomposites are e.g. sunflower husks[86] and animal proteins[87]. Of course nano-composites are also represented, consisting of bio-based matrix reinforced with nano-clay or nano-metaloxide particles[88,89].

Conclusion

The global trend towards sustainability, green chemistry and renewable energy and raw materials also has a big impact on the research and development of polymers. A large number of patent applications relating to bio-polymers are being filed, covering an impressive amount of new polymers and monomers. While real-life applications appear to be limited still, this research can be the basis for a strong growth in the near future.

References

The references below are linked to patent bibliography and full text documents on FreePatentsOnline (http://www.freepatentsonline.com).
For a more complete list of relevant patent applications or for other questions please contact me at http://PURpatents.com/contact

1 WO/2014/193748
2 US20150048534
3 US20130072598
4 US20150259370
5 US20140275501
6 WO/2013/173316
7 US20140027938
8 WO/2015/126269
9 WO/2013/068597
10 WO/2014/108887

[11] US20150147929
[12] WO/2014/210535
[13] US20150240273
[14] WO/2013/033209
[15] WO/2015/133887
[16] US20130071890
[17] WO/2013/072541
[18] US20130344550
[19] WO/2014/027129
[20] US20120060413
[21] US20140302572
[22] WO/2012/024406
[23] US20120101200
[24] US20140206831
[25] US20130165690
[26] US20150274944
[27] WO/2014/106122
[28] US20140275465
[29] US20140371417
[30] WO/2015/117967
[31]US20150239803
[32] US9126877
[33] WO/2015/065722
[34] US20150080547
[35] US20130072714
[36] US20140343305
[37] US20150118722
[38] US8772440
[39] US20140316161
[40] WO/2015/089127
[41] US8933189
[42] US20130324688
[43] US20150191560
[44] WO/2015/156802
[45] WO/2014/180979
[46] US20130065046
[47] US20140235777
[48] WO/2015/031315
[49] US20120013037
[50] US20150218367
[51] US9040614
[52] US20130052384
[53] US20120301659
[54] US20150175745
[55] US20130273384
[56] US20130274697
[57] US20150291721
[58] WO/2015/055662
[59] US20120148740
[60]US20150240028
[61] WO/2015/019020
[62] US20150141605
[63] WO/2015/128373

[64] WO/2014/114758
[65] US20140107311
[66] US20150031848
[67] US20140275305
[68] US2012302786
[69] WO/2015/153226
[70] US20130330549
[71] US20150126091
[72] US20130023608
[73] US20140303269
[74] US20120007267
[75] US20150268575
[76] US8497333
[77] US20130184429
[78] WO/2015/086034
[79]WO/2015/125009
[80]US20150041081
[81] US8754152
[82] US20130099029
[83]US20140033950
[84] US20150101509
[85] US8507588
[86] US20140325715
[87] WO/2014/071517
[88] US20150038611
[89] WO/2013/079760