Trends of Biodegradable Polymers

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POLYMERS are commonly known as plastics. Polymeric materials are very important for mankind. This is because polymeric materials are lightweight, durable and cheap to produce compared to metal, wood or ceramic. Many people assume that polymers are the materials for modern applications. In fact, humans have been using polymers for thousands of years. For instance, early man first used natural plant gum to stick together pieces of wood to build houses. This gum, known as dammar gum, is obtained from the *Dipterocapaceae* family of trees in India and East Asia, which is a source of natural polymer.

The first synthetic polymer was invented by Leo Hendrik Baekeland in 1907, a thermosetting-phenol-formaldehyde resin called Bakelite. In just a century, the rapid development of polymer technologies has brought lots of convenience to mankind with the highly effective catalytic polymerization process. When commodity polymers such as polyethylene, polypropylene, polystyrene and polyvinyl chloride became available cheaply, people started to exploit polymers for the production of disposable packaging products. Unfortunately, this has resulted in polymer pollution becoming a serious issue globally as petroleum-derived commodity synthetic polymers required hundreds of years to fully degrade into harmless compounds. For instance, a phone top-up card takes over 100 years to degrade naturally while an apple core will be naturally transformed into organic fertiliser in just 3 months.

Basically, most biodegradable polymers are produced by a family of polyester as shown in Figure 1. Biodegradable polymer can be divided into two categories, i.e. petroleum- and microorganism-derived types. The former type such as polyvinyl alcohol (PVOH) which is a non-polyester family, uses ethylene to produce vinyl acetate for polymerisation of polyvinyl acetate and is further hydrolysed into PVOH. This polymer is very sensitive to the volatility of crude oil prices and is not environment friendly as the production involves substantial emission of greenhouse gases.

On the other hand, microorganism-derived biodegradable polymers utilise the bio-activity of bacteria to convert plant products such as starch, into the starting chemical for polymerization. Polylactic acid (also known as polylactide – PLA) is the first biodegradable polymer found to be viable for mass production and is produced with the activity of microorganisms to yield lactic acid as the input for polymerization. PLA is currently widely used to produce products such as containers and fibre for making textile, packaging, casing, etc. (refers Table 1). Polyhydroxylalkanoate is also a product of bacteria fermentation. These polymers consume renewable feedstock and the productions create carbon credit.

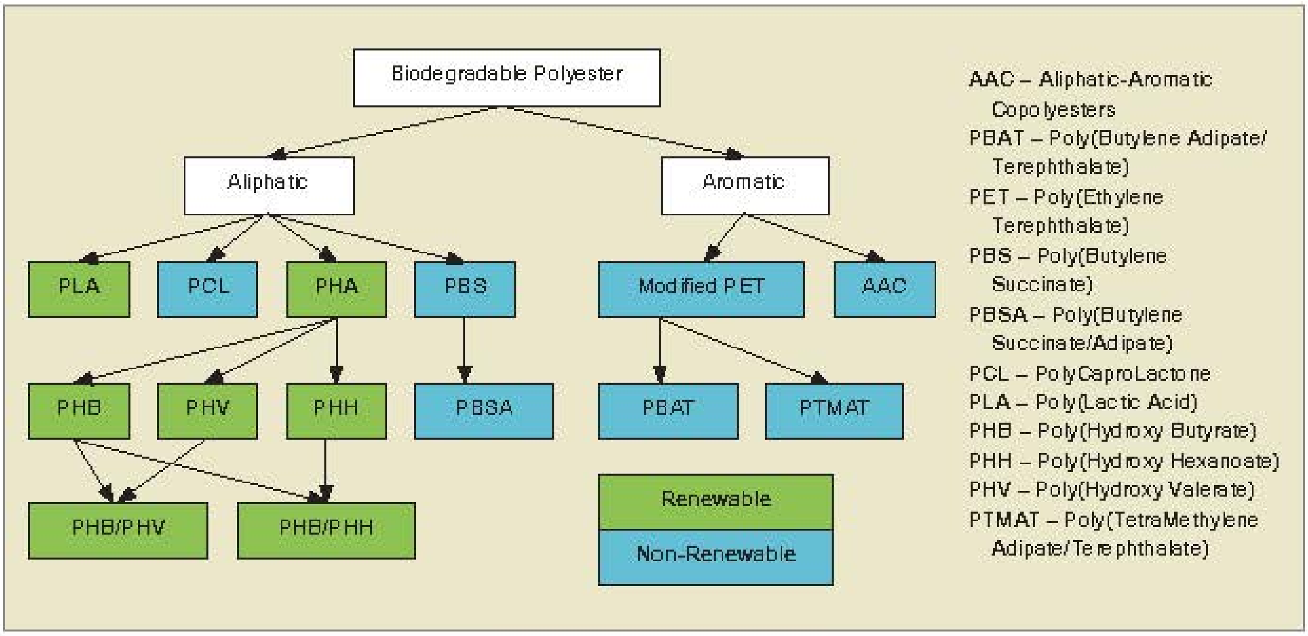


Figure 1: Biodegradable polyester family

In addition, there are also polymer products in the market called oxo-biodegradable plastic. This so-called "biodegradable" plastic has caused controversy among environmentalists as it is actually degraded using a controlled catalyst to kick-start a chain-scissioning reaction to attack the polymer macromolecules. This catalyst is made of series of active organo transition metals. When the oxo-biodegradable polymers are exposed to the ultra-violet and free oxygen attacks, the chain-scissioning reaction occurs extensively and finally reduces the plastics into carbon dioxide (CO_2). In the market, the oxo-degradation additives are mostly added to polyethylene and polypropylene. This additive is applied in very little amount (<1%) for its high effectiveness. Nevertheless, controversy also arises about this type of "eco-friendly" plastic because it is still derived from petroleum-based product and its degradation still generates CO_2 which is against the principle of carbon credit products. In short term consideration, it can help to reduce the burden of landfills. However, the use of such oxo-biodegradable can also cause other serious environmental problems, the most serious of which is that it also takes time to be fully degraded into CO_2. During the early breakdown process, fragmentation of the plastics will pollute the soil and can be accidentally consumed by the soil habitant organisms.

Various types of eco-packaging are available in the market and such eco-plastics products need to undergo a series of test to verify its biodegradability and compostability. In the European Union, the compostable packaging must fulfill the requirement of EN 13432, while other countries have respective standards to be achieved before they are allowed to use the compostable logo on their products (Table 2).

Table 1: Examples of PLA Product Applications

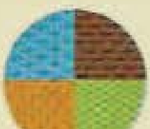
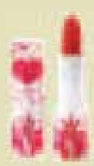
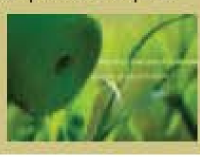
Company	Area of Application	Market Products
CL Chemical Fibers	Spun-bond fabrics	Medical applications, shopping bags, and landscape textiles 
Dyne-A-Pak	Foam meat trays	Dyne-A-Pak Nature™ tray 
Bodin (France)	Foam tray	Tray for meat, fish and cheese 
CDS srl	Food service ware	Cutlery 
Cargo Cosmetics	Casings	Casings for cosmetics 
DS Technical Nonwoven	Exhibition grade carpeting	Ecopunch® carpets 

Table 2: Certification of compostable plastic for respective countries

Certification Body	Standard of Reference	Logo
Australia Bioplastics Association (Australia) *www.bioplastics.org.au*	EN 13432: 2000	
Association for Organics Recycling (UK) *www.organics-recycling.org.uk*	EN 13432: 2000	
Polish Packaging Research and Development Centre (Poland) *www.cobro.org.pl/en*	EN 13432: 2000	
DIN Certco (Germany) *http://www.dincertco.de/en/*	EN 13432: 2000	
Keurmerkinstituut (Netherlands) *www.keurmerk.nl*	EN 13432: 2000	
Vincotte (Belgium) *www.okcompost.be*	EN 13432: 2000	OK compost VINÇOTTE
Biodegradable Products Institute (USA) *www.bpiworld.org*	ASTM D 6400-04	COMPOSTABLE
Japan BioPlastics Association (Japan) *www.jbpaweb.net*	Green Plastic Certification System	グリーンプラ

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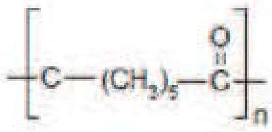
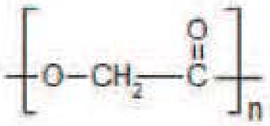
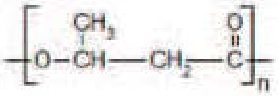
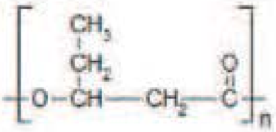
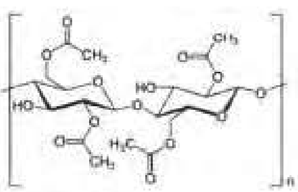
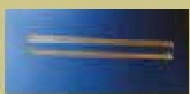
Table 3: Biopolymer producers and applications

Polymer	Chemical Composition	Producer	Applications	Biodegrability
Polycaprolactone (PCL)		DURECT Corporation-Lactel® Daicel Chemical Industry-Celgreen® Union Carbide Corporation-TONE® Solvay Group-CAPA® Purac-Purasorb® PC 12	Ethicon-Monocryl®-Suture Capronor®-Contraceptive implant Agrotec-Agrothane®-Paint and metal protection film	> 12 months
Polyglycolide or Polyglycolic acid (PGA)		Purac-Purasorb® PG 20 Teleflex Incorporated Kureha Corporation	Dolphin-Petcryl®-Sutures Bondek®-Sutures DexonTM S-Sutures DemeTech®-Sutures	> 3 months
Polyhydroxyalkanoate-Polyhydroxybutyrate (PHB) and Polyhydroxylvalerate (PHBV)	 (PHB)  (PHV)	Metabolix/ADM-Telles Mirel™ Ningbo Tianan Biologic Material-Enmat™ Copersucar-Biocycle® Biomer-Biomer®	Compost Bags Consumer packaging Agriculture/Horticulture film Rubbermaid®, Calphalon®, Paper Mate® BioTuf™ EcoGen™	3 -12 months
Polydioxanone (PDO)		Ethicon Samyang	DemeTech® sutures Duracryl® sutures D-Tek® sutures Surgeasy® sutures Ethicon® PDS® II sutures OrthoSorb® pin	< 7 months
Cellulose acetate		Celanese Rhodia	Cigarette filter Textile Spectacle frames Film media Wound dressing-ADAPTIC™ Bioceta® Toothbrush	< 24 months Depend on acetate content

Apart from PVOH and PLA, other commercial biodegradable polymers are only produced on a small scale, either for exploration of commercial potential or mainly for biological applications (refer to Tables 3 and 4). Polycaprolactone (PCL), polyglycolic acid (PGA), and polydioxanone (PDO) are the common biodegradable medium for sutures, pins and drug carrier implants. Normally PGA and PDO are preferable materials over PCL in bio-medical application because PCL takes longer time *in vivo* resabsorbable. A clinical study of PCL-based implantable biodegradable contraceptive indicates that Capronor® containing levonorgestrel remains intact during the first year of use and is finally degraded and absorbed by the body after two years (Darney, 1989). Both PHB and PHBV belong to polyhydroxyalkanoates (PHA) and are developed using biological fermentation of dextrose. Metabolix and ADM joint venture under Telles produces PHB with the trade name of Mirel™. PHB compost bags need 6-12 months to be naturally degraded. International stationary manufacturer Sanford uses PHB in its famous PaperMate® product range. PHB is not easily degraded under normal condition of usage or even storage under humid environment but when buried under soil and compost, the PHB-made PaperMate® pen decomposes in about a year.

Table 4: PLA in biomedical applications

Polymer	Area of Application	Products
Poly (lactide)	Orthopedic surgery, oral and maxillofacial surgery 	Takiron: Osteotrans™ MX, Fixsorb™ MX (screws, nails, pins) Gunze: Grandfix® Neofix® (screws, nails, pins) Arthrex: Bio-Tenodesis® interference screw, Bio-Corkscrew® suture anchor Conmed Linvatec: SmartScrew® SmartNail® SmartTack® SmartPin® BioScrew® Stryker: Biosteon® Biozip® interference screw, anchor Zimmer: Bio-statak® (suture anchor) prostatic stent, suture anchor, bone cement plug Dermik Laboratories: Sculptra® injectable facial restoration Kensey Nash: EpiGuide®
Poly (D,L-lactide-co-glycolide) Poly (D,L-lactide-co-glycolide) 85/15 Poly (D,L-lactide-co-glycolide) 82/18 Poly (D,L-lactide-co-glycolide) 10/90	Suture Drug delivery Oral, and maxillofacial surgery General surgery Suture, periodontal surgery, general surgery 	USS Sport Medicine: Polysorb™ sutures Instrument Makar: Biologically Quiet™ Interference Screw, Staple 85/15 Biomet: ALLthread™ LactoSorb®, screw, plates, mesh, surgical clip, pins, anchor Ethicon: Vicryl suture, Vicryl Mesh
Poly (L-lactide-co-D,L-lactide) 98/2 Poly (L-lactide-co-D-lactide) 98/4 Poly (L-lactide-co-D,L-lactide) 50/50 Poly (L-lactide-co-D,L-lactide) 70/30 Poly (D-lactide-co-D,L-lactide-co-L-lactide)	Orthopaedic surgery Oral and maxillofacial surgery 	Phusiline® Interference Screw, Sage ConMed: Bio-Mini Revo® Sulzer: Sysorb® Screw (50/50) Geistlich: ResorPin® 70/30 Kensey Nash: Drilac® Surgical dressing
Poly (D,L-lactide-co-caprolactone)	Nerve Regeneration 	Ascension Orthopedics: Neurolac® Polyganics: Vivosorb®

Cellullose acetate is commonly used as cigarette filter, textile, spectacle frames and film media. Since the early 20th Century, cellulose acetate is a very important base material for the film industry. Over the decades the application of cellulose acetate has changed and today, a modified cellulose acetate is suitable to be injection moulded to produce biodegradable plastic articles. Some series of sunglasses marketed by Louis Vuitton are made of cellulose acetate. This material comes in a wide variety of colours and textures. They can be adjusted easily, but tend to get brittle with time.

Knitted cellulose acetate fabric treated with specially formulated petrolatum emulsion helps to protect open wounds and prevents the dressing from adhering to the wound. However, prolong exposure to moisture, heat or acids will reduce acetyl (CH_3C) groups that are attached to the cellulose. The degradation process causes the release of acetic acid, which is known as "vinegar syndrome". This is because when cellulose acetate film is stored under hot and humid conditions, the release of saturation acetic acid emits a smell. This will also further attack the polymer chain and deteriorate the cellulose. A study of cellulose acetate, reported by Buchanan *et al.* (1993), showed that cellulose acetate can be biodegraded in waste-water treatment assay approximately 70% at 27 days of cellulose diacetate with the rate of degradation also depending on the degree of substitution of acetate. A high degree of substitution of acetate requires longer exposure.

Besides that, most of the mentioned biodegradable polymers belong to the polyester group (Figure 1). This is due to ester containing covalent bond with reactive polar nature. It can be broken down easily by hydrolysis reaction. The biodegradable polyester can be divided into aliphatic and aromatic group with some of the members derived from renewable and non-renewable sources. PLA and PHA are both aliphatic polyester using renewable agricultural sources while PCL and PBS/PBSA are aliphatic polyester produced from non-renewable feedstock. Most of the PCL in the market are used in biomedical application whereas PBS/PBSA, as marketed by Showa Denko under the tradename Bionolle, is supplied to local Japanese government programmes for packing domestic solid waste before collection.

Generally, all aromatic polyesters are produced from petroleum. Some people think that petroleum-based biodegradable polymers are more feasible than bio-based biodegradable polymers. The reason is that bio-based polymers has raised the issue of competition between food supply and plastic production, especially as there is still a shortage of food among many Third World countries. However, do not let this be an obstacle to developing bio-based polymers because a small step in developing renewable technology today can lead to a giant leap in reducing our dependence on fossil resources.

Besides, BASF has introduced an AAC product named Ecoflex®. This material is widely used to produce compostable packaging and films. According to BASF, the annual production capacity of Ecoflex® has expanded to 60,000 MT to capture the demand of biodegradable plastics which is growing at a rate of 20% per year. BASF also blends polyester with PLA for another product called Ecovio®. The high melt strength polyester-PLA can be used directly and processed by conventional blown film lines without the incorporation of additives. Furthermore, Ecovio® has extraordinary puncture-and-tear-resistant as well as weldability characteristics. Another company, Eastman, also produced AAC with the tradename of Eastar Bio® which has a highly linear structure while Ecoflex® contains long-chain branching. A study reported by BASF shows that AAC of the Ecoflex® has comparable biodegradability as cellulose biomass which is able to achieve 90% compostable in 180 days as per CEN EN 13432. Thus, petroleum-based biodegradable polymer can also be as good as natural material in term of degradability.

The conventional polyethylene terephthalate (PET) takes centuries to be naturally degraded. However, PET with appropriate modification such as copolymerization with co-monomer ether, amide or aliphatic monomer will increase biodegradability. Such modified PET materials include polybutylene adipate/terephthalate (PBAT) and polytetramethylene adiphate/terephthalate (PTMAT). Dupont has commercialized Biomax® PTT 1100 with the plastic melting point of 195°C which makes it suitable for use as fast-food disposable packaging and cups for hot food and drinks.

In conclusion, the research and development of biopolymers have been carried out for many years. Nevertheless, many people lack knowledge about the applications of biopolymers. But with NGOs and government agencies promoting the use of biopolymer as environment-friendly materials for a sustainable future, it is expected that the use of biopolymers will grow tremendously in the near future. ■

REFERENCES

[1] Buchanan, C.M., Gardner, R.M., Komarek, R.J. (1993). Aerobic biodegradation of cellulose acetate. Journal of Applied Polymer Science, 47, 1709-1719.

[2] Darney, P.D., Monroe, S.E., Klaisle, C.M., and Alvarado, A. (1989). Clinical evaluation of the Capronor contraceptive implant: Preliminary report. American Journal of Obstetrics and Gynecology. 160, 1292-1295.

Further reading materials:

1. Lee Tin Sin, A.R. Rahmat, W.A.W.A. Rahman. (2013). Polylactic Acid: PLA Biopolymer Technology and Applications. William Andrew-Elsevier. ISBN 9781437744590. Online access at ScienceDirect.
2. Ebnesajjad S. (ed.), Handbook of Biopolymers and Biodegradable Plastics. United States: William Andrew-Elsevier. pp. 11-54. ISBN 978-4557-2834-3. Online access at ScienceDirect.