PETITION FOR A SYNTHETIC MATERIAL TO BE ADDED TO THE NATIONAL ORGANIC SUBSTANCE LIST

7 CFR 205.601: Synthetic substances allowed for use in organic crop production

Submitted by:

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1. Substance Name:

Trade Name:	CAPA® 6400
Common Name:	Polycaprolactone, PCL, aliphatic polyester
Chemical Name:	poly-epsilon-caprolactone, 2-oxepanone homopolymer
CAS #:	24980-41-4

2. Manufacturer:

> Solvay Corporation
> 3333 Richmond Avenue
> Houston, TX 77098
> Telephone: (713) 525-6584
> jeffrey.neidinger@solvay.com

3. Intended Use of Substance:

The intended use of this unique biodegradable polymer, polycaprolactone (an aliphatic polyester), is to function as a controlled release matrix for insect pheromones or repellents in products that will be used in agricultural and forestry to control pest insect populations without the use of conventional pesticides. These products will be applied to crops or forests in the form of small granules or "flakes." The pheromone or repellent that is incorporated into the polymer will be released passively for 30-90 days after application, depending on environmental conditions. The released pheromone interferes with the chemical communications the males of the species depend on to locate females for mating, thereby reducing insect reproduction and subsequent population levels. If a repellent is used, pest insects will be diverted from attacking susceptible crops, trees, or forests.

Presently the polymer is used in the manufacturing industry for shoe inserts and other items, and in implantable medical devices such as sutures and bone supports.

4. List of crops for which the substance will be used:

The polymer with the contained insect pheromone or repellent will be used on agricultural crops such as fruit and nut orchards or in forestry situations. Examples of crops where this polymer will be used include orchards such as apple, apricot, plum, peach, cherry, walnut, pecan, and pistachio. Treatments using this polymer will be applied to forested areas or pine plantations where the target insect may be gypsy moth or other defoliators, or various bark beetles species.

5. Source of the substance and a detailed description of its manufacturing or processing procedures:

PCL is typically derived by chemical synthesis from crude oil and can be prepared by ring opening polymerization of e-caprolactone using a catalyst. The manufacturer, Solvay, will be submitting a more detailed processing procedure following guidelines for submitting CBI.

6. Summary of previous reviews:

The controlled-release of insect pheromones or repellents is a new use for this biodegradable polymer, therefore there are no other reviews by State or Private Certification programs that Hercon is aware of.

7. Information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers:

EPA: A petition to place this polymer (PCL CAPA 6400) on the EPA polymer list (40 CFR 180.960) was submitted by the manufacturer, Solvay Corporation, on November 7, 2007. The polymer is being reviewed by EPA's Inert Assessment Branch and the Biopesticide Registration Branch. The polymer is intended to be used in a pheromone product in the emergency eradication program for the Light Brown Apple Moth in California. A **Section 18 Emergency Registration** is required for the product, therefore EPA has expedited its review of this inert. Once this polymer is approved it will be exempt from tolerance requirements for use on food and feed crops. An additional requirement of this program is an approved organic certification for products that will be used; therefore it is important that this petition be reviewed as quickly as possible so that it can be approved for use in organic certified production.

FDA: This Agency has extensive information on this biodegradable polymer and has approved its use in medical devices such as sutures, scaffolding and bone supports for implantation within the human body. PCL is degraded by hydrolysis of its ester linkages in physiological

conditions such as found in the human body. Some examples of the medical uses of PCL are drug delivery devices, sutures (Monocryl™), adhesion barriers, and scaffold for tissue repair. A variety of drugs have been encapsulated using PCL for controlled release and targeted drug delivery (see *Anomalous Release of Hydrophilic Drugs from Poly(e-caprolactone)*, authors: R. Rosenberg, W. Devenney, S. Siegel and N. Dun. Matrices, *ASAP Mol. Pharmaceutics* Oct 26, 2007, attachment 1).

Other uses for PCL have been in dental composites (Resilon™) used as a root canal filling. A review of biopolymers, including PCL, in medicine has been written by John C. Middleton and Arthur J. Tipton, *Synthetic Biodegradable Polymers as Medical Devices* in *Medical Plastics and Biomaterials Magazine*, published March 1998 (attachment 2).

State Regulatory: No State registration reviews have been processed at this time. When we receive the Section 18 for the product containing this polymer (Hercon Disrupt Bio-Flake LBAM) from EPA, the State of California will then expedite its registration review. The review for organic use approval will also be expedited in California.

Other Regulatory Information: PCL has been granted a Regulatory Compliance Statement for Food Contact Materials (as the interfacial agent) in accordance with European Directive 2002/72/EC, applicable to EU Member States and to Norway and Switzerland for use in finished film-type food packaging materials. It is also compliant with US FDA Regulations under 21 CFR 177.1520 (b), Canadian Health Protection Branch and with the Japan Hygienic Olefin and Styrene Plastics Association (see DuPont VITON® FREEFLOW™ News Bulletin, attachment 3).

8. Chemical Abstract Service Number (CAS#):
The CAS# of this polymer is 24980-41-4.

9. Physical properties and chemical mode of action:

OPPTS No.	OPPTS Guideline Name	Observation
830.6302	Color	White
830.6303	Physical state	Solid
830.6304	Odor	Odorless
830.6313	Stability to normal/elevated temps, metals & metal ions	Stable under normal conditions
830.6314	Oxidation/reduction: Chemical incompatibility	Non-oxidizing.
830.6315	Flammability	Non-flammable
830.6316	Explodability	NA

830.6319	Miscibility	This inert is not an emulsifiable liquid and is not to be diluted with petroleum solvents.
830.6320	Corrosion characteristics	The inert polymer is non-corrosive. This polymer lacks extreme pH and lacks reactivity with packaging and other materials.
830.6321	Dielectric breakdown voltage	NA
830.7000	pH	NA
830.7050	UV/visible absorption	NA
830.7100	Viscosity	315000mPa-s@ 212^{0}F (100^{0}C)
830.7200	Melting point/melting range	136-140^{0}F (58-60^{0}C)
830.7220	Boiling point/boiling range	Not determined
830.7300	Density/relative density/bulk density	1.10 grams/cm^3 @ melting point
830.7550	Partition coefficient (*n*-octanol/water):	Not determined
830.7860	Water solubility	Not soluble in water
830.7950	Vapor pressure	No data

(a) Chemical interaction with other substances, especially substances used in organic production:

This is a stable inert polymer therefore no chemical interaction with other substances is known or expected.

(b) Toxicity and environmental persistence:

This is a non-toxic biodegradable polymer approved by the Food & Drug Administration (FDA) for use in medical applications for devices such as sutures and scaffolding for bone and skin graphs. Under optimal conditions this polymer can break down into carbon dioxide and water in several days. Little or no biomass will remain once the material biodegrades. Burial tests were preformed using a film sample (25μm X 200 mm X 15 mm) of the polymer buried in soil (moisture content 30%) for 16 days. Tensile strength of the sample was used as an indicator of degradation and after 16 days the tensile strength was zero (see Technical Bulletin: Biodegradable CAPA® Thermoplastics from Solvay Chemicals. Issue 2, Jan 2001 pp 1-8, attachment 4).

In granular form the polymer will degrade much slower but will eventually break down to CO_2 and water. The resulting by-products of the degradation (by-products such as caproic acid that can be found in goat's milk) are non-toxic to humans and the environment.

(c) Environmental impacts from its use and/or manufacture:
None known

(d) Effects on human health:
Effects on human health are expected to be minimal since this polymer is approved for use in sutures and other implantable medical devices that eventually biodegrade in the human body (see *Toxicity screening of biodegradable polymers. II. Evaluation of cell culture test with medium*

extract, M. H. Dang, F. Birchler and E. Wintermantel, *Journal of Polymers and the Environment*, Vol 5, No 1 January 1997 pp 49-56, attachment 5).

(e) Effects on soil organisms, crops or livestock: The degradation of this polymer depends on decomposition by microbes in the soil. No adverse effects are expected on soil organisms. No adverse effects have been noted on crops during efficacy testing on food and forestry crops nor are they expected. This polymer is used in drug delivery systems and as a coating for some medicines, so the no adverse effects from ingestion by humans or livestock are expected.

10. Safety information:
The manufacturer's, Solvay's, Material Safety Data Sheet (MSDS) is attached, however a substance report has not been generated (attachment 6).

11. Research Information about the Substance including research reviews and bibliographies:

Toxicological safety of PCL evidenced by its medical uses:

a)   *Synthetic Biodegradable Polymers as Meidcal Devices*, John C. Middleton and Arthur J. Tipton, *Medical Plastics and Biomaterial Magazine, 1998* (attachment 2)

b)   Polycaprolactone (PCL), Bio Engineering J. E. Gough, P. Christian, published in *Encyclopedia of Biomaterials and Biomedical Engineering*, August 15, 2006. The abstract indicates that PCL is degraded by hydrolysis in physiological conditions. PCL is now one of several degradable polymers approved for use in the human body as drug delivery devices, adhesion barriers, sutures, and staples (attachment 7).

Biodegradability of PCL:

a)   *Preparation and Biodegradation of Starch/Polycaprolactone Films*, Yavuz H., Babac, C., *Journal of Polymers and the Environment*, Volume 11 number 3, July 2003 pp. 107-113. Polycaprolactone is a biodegradable aliphatic polyester that has a low melting point of $60^{0}C$. PCL is derived by chemical synthesis from crude oil, a naturally occurring substance (attachment 8).

b)   Technical Bulletin: Biodegradable CAPA® Thermoplastics from Solvay Chemicals. Issue 2, Jan 2001 pp 1-8. This gives general information and biodegradable studies conducted by Solvay on the CAPA 6000 series product line which has various molecular weights of polycaprolactone. All are fully biodegradable, non-toxic, low melting and used in a variety of applications (attachment 4).

General Information on PCL:

a)   A review paper on biopolymers and their applications (attached): *Biopolymers: overview of several properties and consequences on their applications*, K.Van de Velde, P. Kiekens, *Polymer Testing 21* (2002) pp 433-442. This shows that the PCL has a low melting point making it ideal for mixing with temperature-sensitive pheromones (attachment 9).

b)   Material Safety Data Sheet (MSDS) for CAPA Thermoplastics 6000 series (attachment 6)

12. Petition Justification:
Why this synthetic is necessary for the production or handling of an organic product:

a)   To provide the protective controlled-release matrix required to permit pheromones and other volatile active agents to be used in economical and effective pest insect control products:

Currently there are no known organic materials that function as effectively as certain inert synthetic polymers in providing the protective controlled-release carrier function required to permit volatile insect pheromones, attractants, and repellents to be used practically and economically in commercial or governmental pest insect control programs.

Synthetic polymers already approved for organic production, specifically for the wall material used in certain microencapsulated pheromone-based pest insect control products, have limitations which render them uneconomical and impractical to use in large area pest insect control programs (see below).

PCL is the only synthetic polymer we have found to date that combines the necessary protective controlled-release effect with biodegradability and the ability to manufacture in product forms required for practical use.

b)   For use in major area-wide pest control programs requiring aerial applications of pheromone-based products over agricultural areas including organic production sites:

The Light Brown Apple Moth (LBAM) Eradication Program is scheduled to commence mid-2008 in central California to combat this new invasive pest species. LBAM poses a threat to most of California's major agricultural crops and native vegetation, including redwood trees. If left uncontrolled, LBAM could not only spread throughout most of California, but could also eventually infest 80% of the U.S.

Starting mid-2008, the LBAM Eradication Program is currently planning to make aerial applications of a non-toxic pheromone-based LBAM mating disruptant to about 500,000 acres of agricultural and urban land already infested with LBAM in central costal California. This area also includes numerous organic production sites of various sizes, therefore the product that will be used must have approval for use on such sites since they cannot be avoided during application, and to do so would unacceptably diminish the effectiveness of the treatments.

Most common treatment options are impractical for economical, rapid, and effective pheromone-based mating disruption of LBAM on a large scale. Microencapsulated products can be applied rapidly by air, but their short field-life and susceptibility to wash-off by rain requires them to be reapplied ay least every 2-3 weeks, making them uneconomical and impractical to use. Hand-applied products have sufficient field-life, but the manpower required to apply them at the rate of 200 plastic dispensers per acre makes them impractical to use on the large scale required.

The ideal product is a long-lasting, aerially-applied product with approval for use on organic production sites. Such as product can be made using biodegradable PCL in flake or pellet form as the controlled-release carrier for the LBAM pheromone, provided organic use approval can be obtained. Once the LBAM pheromone has been released from the product, the residual PCL polymer will completely biodegrade to innocuous substances commonly found in food or as end-products of mammalian metabolic processes.

Another major program that could benefit from the approval of PCL for use in organic production is the Gypsy Moth (GM) Slow-The-Spread Program, which has combated GM through the aerial application of a non-toxic GM mating disruptant to 350,000-650,000 acres of eastern US forest annually for the past 15 years. With the high rate of growth of organic production and the smaller-scale organic operations typically found in or near eastern forests, the potential for incidental application of GM mating disruptant over organic production sites is increasing. The availability of a PCL-based product approved for incidental application to organic production would benefit the GM STS Program and organic producers as well.

With the projected trend in global-warming causing expansion of existing or new pest insect infestations, there is likely to be a need for similar non-toxic insect control products with organic use approval for use in similar large area programs that are likely to contain organic production sites.

c) To provide more economical, less labor-intensive, longer-lasting products suitable for use in organic production:

As above, pheromone-based treatment options for organic production are either microencapsulated pheromone sprays or hand-applied plastic dispensers. Microencapsulated sprays must be reapplied frequently to be effective, particularly if rainy weather conditions prevail. Hand-applied products are labor-intensive to apply and contribute to plastic waste build-up in the environment since they typically are not removed after use.

A product made using biodegradable PCL in flake or pellet form as the controlled-release carrier for the required pheromone can provide prolonged field-life combined with ease of application. Such a product can be rapidly blown or sprayed into or onto the crops to be protected. Once the pheromone has been released from the product, the spent flakes or pellets can be washed from the produce and any residual flakes or pellets remaining in the field or orchard will completely biodegrade to innocuous end products.

d) To reduce the accumulation of residual plastic in the environment, especially in organic production sites where hand-applied plastic pheromone dispensers approved for such use are typically not removed at the end of the season as required:

Reduction of residual trash that can accumulate and grow from season to season is becoming a serious problem in farm management. Hand-applied plastic pheromone dispensers, plastic weed control films, and other non-degradable polymers used in organic production tend to accumulate in fields and landfills creating serious problems with plastic waste management with potential deleterious effects to the environment. The use of this biodegradable polymer (PCL) in agricultural applications could help to alleviate these concerns.

The following review indicates the growing concern about non-biodegradable plastics in agriculture:

Biodegradation of Agricultural Plastic Films: A Critical Review (Abstract) Kyrikou, Ioanna; Briassoulis, Demetres, *Journal of Polymers and the Environment,* Vol 15, No. 2, April 2007, pp. 125-150 (attachment 10)

ATTACHMENT

1

Anomalous Release of Hydrophilic Drugs from Poly(ε-caprolactone) Matrices

R. Rosenberg,[†] **W. Devenney,**[†] **S. Siegel,**[*‡] **and N. Dan**[*‡]

Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania 19104, and Stanley Center for Experimental Therapeutics and Division of Neuropsychiatry, Department of Psychiatry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Abstract:

In this paper, we investigate the release of two drugs, nicotine and caffeine, from poly ε-caprolactone (PCL) matrices, as a model for the delivery of highly hydrophilic drugs. Since PCL does not degrade over the period of our experiments (<30 days), drug diffusion through the matrix is expected to be the dominant mechanism of release. Contrary to expectations, we find that the drug diffusion coefficient increases with increasing drug loading, weakly for caffeine and strongly for nicotine. The water content in the PCL matrices (after all of the drug was released) was found to be orders of magnitude higher than the expected value, increasing with increasing drug loading. We suggest that these phenomena arise from the semicrystalline nature of PCL under our experimental conditions, which inhibits matrix collapse when the drug is released, thereby creating voids into which water can diffuse. We apply a quantitative model for these systems that considers counter-diffusion of water *into* the matrix with drug diffusion out of the matrix. The high solubility of both drugs in aqueous solutions leads to drug partitioning into the polymer-encapsulated water, thereby increasing the effective rate of drug diffusion and release. The model is shown to fit the experimental data of both drugs using only one fit parameter.
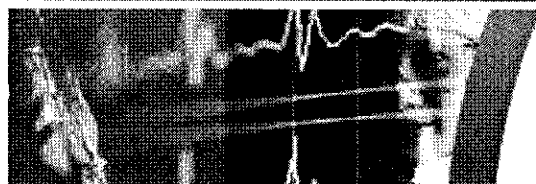
Keywords: Drug delivery; controlled drug release; poly(caprolactone); in vitro test.

ATTACHMENT

2

Components,
Assemblies and Solutions

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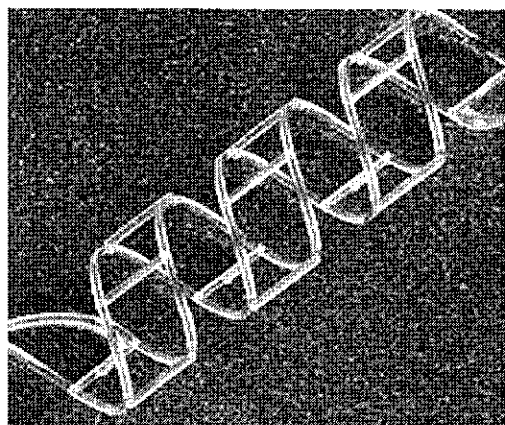
MATERIALS
Synthetic Biodegradable Polymers as Medical Devices
John C. Middleton and Arthur J. Tipton

In the first half of this century, research into materials synthesized from glycolic acid and other α-hydroxy acids was abandoned for further development because the resulting polymers were too unstable for long-term industrial uses. However, this very instability—leading to biodegradation—has proven to be immensely important in medical applications over the last three decades. Polymers prepared from glycolic acid and lactic acid have found a multitude of uses in the medical industry, beginning with the biodegradable sutures first approved in the 1960s. Since that time, diverse products based on lactic and glycolic acid—and on other materials, including poly(dioxanone), poly(trimethylene carbonate) copolymers, and poly (ϵ-caprolactone) homopolymers and copolymers—have been accepted for use as medical devices. In addition to these approved devices, a great deal of research continues on polyanhydrides, polyorthoesters, polyphosphazenes, and other biodegradable polymers.

A biodegradable intravascular stent prototype is molded from a blend of polylactide and trimethylene carbonate. Photo: Cordis Corp. Prototype Molded by Tesco Associates, Inc.

Why would a medical practitioner want a material to degrade? There may be a variety of reasons, but the most basic begins with the physician's simple desire to have a device that can be used as an implant and will not require a second surgical intervention for removal. Besides eliminating the need for a second surgery, the biodegradation may offer other advantages. For example, a fractured bone that has been fixated with a rigid, nonbiodegradable stainless implant has a tendency for refracture upon removal of the implant. Because the stress is borne by the rigid stainless steel, the bone has not been able to carry sufficient load during the healing process. However, an implant prepared from biodegradable polymer can be engineered to degrade at a rate that will slowly transfer load to the healing bone. Another exciting use for which biodegradable polymers offer tremendous potential is as the basis for drug delivery, either as a drug delivery system alone or in conjunction to functioning as a medical device.

Polymer scientists, working closely with those in the device and medical fields, have made tremendous advances over the last 30 years. This article will focus on a number of these developments. We will also review the chemistry of the polymers, including synthesis and degradation, describe how properties can be controlled by proper synthetic controls such as copolymer composition, highlight special requirements for processing and handling, and discuss some of the commercial

dental applications (guided tissue regeneration); cardiovascular applications (stents, grafts); and intestinal applications (anastomosis rings). Most of the commercially available biodegradable devices are polyesters composed of homopolymers or copolymers of glycolide and lactide. There are also devices made from copolymers of trimethylene carbonate and ε-caprolactone, and a suture product made from polydioxanone.

Polyglycolide (PGA). Polyglycolide is the simplest linear aliphatic polyester. PGA was used to develop the first totally synthetic absorbable suture, marketed as Dexon in the 1960s by Davis and Geck, Inc. (Danbury, CT). Glycolide monomer is synthesized from the dimerization of glycolic acid. Ring-opening polymerization yields high-molecular-weight materials, with approximately 1—3% residual monomer present (see Figure 1). PGA is highly crystalline (45—55%), with a high melting point (220—225°C) and a glass-transition temperature of 35—40°C. Because of its high degree of crystallization, it is not soluble in most organic solvents; the exceptions are highly fluorinated organics such as hexafluoroisopropanol. Fibers from PGA exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material. Sutures of PGA lose about 50% of their strength after 2 weeks and 100% at 4 weeks, and are completely absorbed in 4—6 months. Glycolide has been copolymerized with other monomers to reduce the stiffness of the resulting fibers.
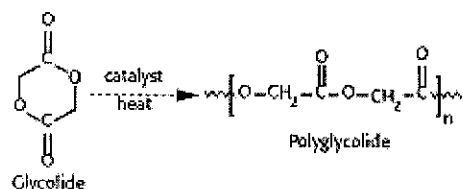

Figure 1. Synthesis of polyglycolide (PGA).

Polylactide (PLA). Lactide is the cyclic dimer of lactic acid that exists as two optical isomers, d and l. l-lactide is the naturally occurring isomer, and dl-lactide is the synthetic blend of d-lactide and l-lactide. The homopolymer of l-lactide (LPLA) is a semicrystalline polymer. These types of materials exhibit high tensile strength and low elongation, and consequently have a high modulus that makes them more suitable for load-bearing applications such as in orthopedic fixation and sutures. Poly(dl-lactide) (DLPLA) is an amorphous polymer exhibiting a random distribution of both isomeric forms of lactic acid, and accordingly is unable to arrange into an organized crystalline structure. This material has lower tensile strength, higher elongation, and a much more rapid degradation time, making it more attractive as a drug delivery system. Poly(l-lactide) is about 37% crystalline, with a melting point of 175—178°C and a glass-transition temperature of 60—65°C. The degradation time of LPLA is much slower than that of DLPLA, requiring more than 2 years to be completely absorbed. Copolymers of l-lactide and dl-lactide have been prepared to disrupt the crystallinity of l-lactide and accelerate the degradation process.

Poly(ε-caprolactone). The ring-opening polymerization of ε-caprolactone yields a semicrystalline polymer with a melting point of 59—64°C and a glass-transition temperature of —60°C (see Figure 2). The polymer has been regarded as tissue compatible and used as a biodegradable suture in Europe. Because the homopolymer has a degradation time on the order of 2 years, copolymers have been synthesized to accelerate the rate of bioabsorption. For example, copolymers of ε-caprolactone with dl-lactide have yielded materials with more-rapid degradation rates. A block copolymer of ε-caprolactone with glycolide, offering reduced stiffness compared with pure PGA, is being sold as a monofilament suture by Ethicon, Inc. (Somerville, NJ), under the trade name Monacryl.
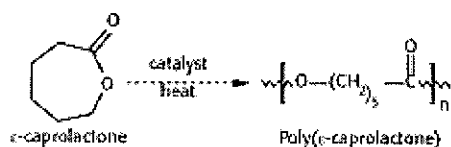

Figure 2. Synthesis of poly(ε-caprolactone).

Poly(dioxanone) (a polyether-ester). The ring-opening polymerization of p-dioxanone (see Figure 3) resulted in the first clinically tested monofilament synthetic suture, known as PDS (marketed by Ethicon). This material has approximately 55% crystallinity, with a glass-transition temperature of —10 to 0°C. The polymer should be processed at the lowest possible temperature to prevent depolymerization back to monomer. Poly(dioxanone) has demonstrated no acute or toxic effects on implantation. The monofilament loses 50% of its initial breaking strength after 3 weeks and is absorbed within 6 months, providing an advantage over Dexon or other products for slow-healing wounds.
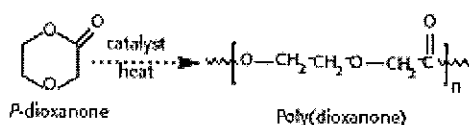

Figure 3. Synthesis of poly(dioxanone).ε-caprolactone).

Poly(lactide-co-glycolide). Using the polyglycolide and poly(l-lactide) properties as a starting point, it is possible to

devices based on these materials.

POLYMER CHEMISTRY

Biodegradable polymers can be either natural or synthetic. In general, synthetic polymers offer greater advantages than natural materials in that they can be tailored to give a wider range of properties and more predictable lot-to-lot uniformity than can materials from natural sources. Synthetic polymers also represent a more reliable source of raw materials, one free from concerns of immunogenicity.

Polymer	Melting Point (°C)	Glass-Transition Temp (°C)	Modulus (Gpa)[a]	Degradation Time (months) [b]
PGA	225—230	35—40	7.0	6 to 12
LPLA	173—178	60—65	2.7	>24
DLPLA	Amorphous	55—60	1.9	12 to 16
PCL	58—63	(—65)— (—60)	0.4	>24
PDO	N/A	(—10)— 0	1.5	6 to 12
PGA-TMC	N/A	N/A	2.4	6 to 12
85/15 DLPLG	Amorphous	50—55	2.0	5 to 6
75/25 DLPLG	Amorphous	50—55	2.0	4 to 5
65/35 DLPLG	Amorphous	45—50	2.0	3 to 4
50/50 DLPLG	Amorphous	45—50	2.0	1 to 2
a Tensile or flexural modulus.				
b Time to complete mass loss. Rate also depends on part geometry.				

Table I. Properties of common biodegradable polymers.

The general criteria for selecting a polymer for use as a biomaterial is to match the mechanical properties and the time of degradation to the needs of the application (see Table I). The ideal polymer for a particular application would be configured so that it:

Has mechanical properties that match the application, remaining sufficiently strong until the surrounding tissue has healed.

Does not invoke an inflammatory or toxic response.

Is metabolized in the body after fulfilling its purpose, leaving no trace.

Is easily processable into the final product form.

Demonstrates acceptable shelf life.

Is easily sterilized.

The factors affecting the mechanical performance of biodegradable polymers are those that are well known to the polymer scientist, and include monomer selection, initiator selection, process conditions, and the presence of additives. These factors in turn influence the polymer's hydrophilicity, crystallinity, melt and glass-transition temperatures, molecular weight, molecular-weight distribution, end groups, sequence distribution (random versus blocky), and presence of residual monomer or additives. In addition, the polymer scientist working with biodegradable materials must evaluate each of these variables for its effect on biodegradation.[1]

Biodegradation has been accomplished by synthesizing polymers that have hydrolytically unstable linkages in the backbone. The most common chemical functional groups with this characteristic are esters, anhydrides, orthoesters, and amides. We will discuss the importance of the properties affecting biodegradation later in the article.

The following section presents an overview of the synthetic biodegradable polymers that are currently being used or investigated for use in wound closure (sutures, staples); orthopedic fixation devices (pins, rods, screws, tacks, ligaments);

copolymerize the two monomers to extend the range of homopolymer properties (see Figure 4). Copolymers of glycolide with both l-lactide and dl-lactide have been developed for both device and drug delivery applications. It is important to note that there is not a linear relationship between the copolymer composition and the mechanical and degradation properties of the materials. For example, a copolymer of 50% glycolide and 50% dl-lactide degrades faster than either homopolymer (see Figure 5). Copolymers of l-lactide with 25—70% glycolide are amorphous due to the disruption of the regularity of the polymer chain by the other monomer. A copolymer of 90% glycolide and 10% l-lactide was developed by Ethicon as an absorbable suture material under the trade name Vicryl. It absorbs within 3—4 months but has a slightly longer strength-retention time.
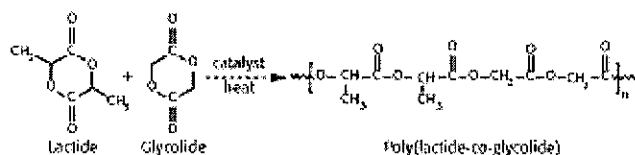

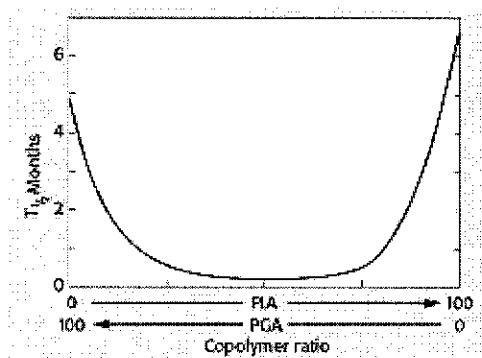*Figure 4. Synthesis of poly(lactide-co-glycolide).ε-caprolactone).*

Figure 5. Half-life of PLA and PGA homopolymers and copolymers implanted in rat tissue. (Figure reproduced courtesy of Journal of Biomedical Materials Research, 11:711, 1977.)

Copolymers of glycolide with trimethylene carbonate (TMC), called polyglyconate (see Figure 6), have been prepared as both sutures (Maxon, by Davis and Geck) and as tacks and screws (Acufex Microsurgical, Inc., Mansfield, MA). Typically, these are prepared as A-B-A block copolymers in a 2:1 glycolide:TMC ratio, with a glycolide-TMC center block (B) and pure glycolide end blocks (A). These materials have better flexibility than pure PGA and are absorbed in approximately 7 months. Glycolide has also been polymerized with TMC and p-dioxanone (Biosyn, by United States Surgical Corp., Norwalk, CT) to form a terpolymer suture that absorbs within 3—4 months and offers reduced stiffness compared with pure PGA fibers.
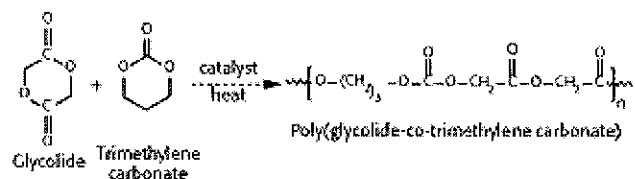

Figure 6. Synthesis of polyglyconate.

Other Polymers under Development. Currently, only devices made from homopolymers or copolymers of glycolide, lactide, caprolactone, p-dioxanone, and trimethylene carbonate have been cleared for marketing by FDA. A number of other polymers, however, are being investigated for use as materials for biodegradable devices.

In addition to their suitability for medical uses, biodegradable polymers make excellent candidates for packaging and other consumer applications. A number of companies are evaluating ways to make low-cost biodegradable polymers. One method is to bioengineer the synthesis of the polymers, using microorganisms to produce energy-storing polyesters. Two examples of these materials—polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV)—are commercially available as copolymers under the trade name Biopol (Monsanto Co., St. Louis) and have been studied for use in medical devices (see Figure 7). The PHB homopolymer is crystalline and brittle, whereas the copolymers of PHB with PHV are less crystalline, more flexible, and easier to process. These polymers typically require the presence of enzymes for biodegradation but can degrade in a range of environments and are under consideration for several biomedical applications.
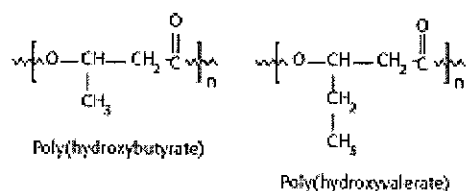

Figure 7. Molecular structure of two bioengineered polyesters that require

specific enzymes for biodegradation.

The use of synthetic poly(amino acids) as polymers for biomedical devices would seem a logical choice, given their wide occurrence in nature. In practice, however, pure insoluble poly(amino acids) have found little utility because of their high crystallinity, which makes them difficult to process and results in relatively slow degradation. The antigenicity of polymers with more than three amino acids in the chain also makes them inappropriate for use in vivo. To circumvent these problems, modified "pseudo" poly(amino acids) have been synthesized by using a tyrosine derivative. Tyrosine-derived polycarbonates, for example, are high-strength materials that may be useful as orthopedic implants. It is also possible to copolymerize poly (amino acids) to modify their properties. The group that has been researched most extensively is the polyesteramides.

A Note on Nomenclature

A polymer is generally named based on the monomer it is synthesized from. For example, ethylene is used to produce poly (ethylene). For both glycolic acid and lactic acid, an intermediate cyclic dimer is prepared and purified, prior to polymerization. These dimers are called glycolide and lactide, respectively. Although most references in the literature refer to polyglycolide or poly(lactide), you will also find references to poly(glycolic acid) and poly(lactic acid). Poly(lactide) exists in two stereo forms, signified by d or l for dexorotary or levorotary, or by dl for the racemic mix.

The search for new candidate polymers for drug delivery may offer potential for medical device applications as well. In drug delivery, the formulation scientist is concerned not only with shelf-life stability of the drug but also with stability after implantation, when the drug may reside in the implant for 1—6 months or more. For drugs that are hydrolytically unstable, a polymer that absorbs water may be contraindicated, and researchers have begun evaluating more hydrophobic polymers that degrade by surface erosion rather than by bulk hydrolytic degradation. Two classes of these polymers are the polyanhydrides and the polyorthoesters.
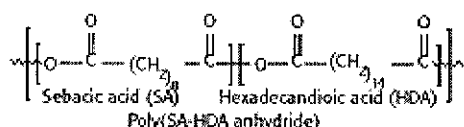

Figure 8. Molecular structure of poly(SA-HDA anhydride).

Polyanhydrides have been synthesized via the dehydration of diacid molecules by melt polycondensation (see Figure 8). Degradation times can be adjusted from days to years according to the degree of hydrophobicity of the monomer selected. The materials degrade primarily by surface erosion and possess excellent in vivo compatibility. So far, they have only been approved for sale as a drug delivery system. The Gliadel product, designed for delivery of the chemotherapeutic agent BCNU in the brain, received regulatory clearance from FDA in 1996 and is being produced by Guilford Pharmaceuticals, Inc. (Baltimore).
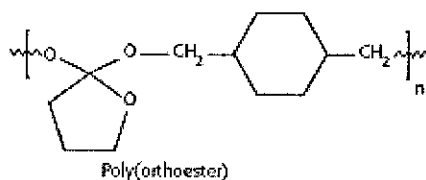

Figure 9. Molecular structure of poly(orthoester).

Polyorthoesters were first investigated in the 1970s by Alza Corp. (Palo Alto, CA) and SRI International (Menlo Park, CA) in a search for new synthetic biodegradable polymers for drug delivery applications (see Figure 9). These materials have gone through several generations of improvements in synthesis, and can now be polymerized at room temperature without forming condensation by-products. Polyorthoesters are hydrophobic, with hydrolytic linkages that are acid-sensitive but stable to base. They degrade by surface erosion, and degradation rates can be controlled by incorporation of acidic or basic excipients.

PACKAGING AND STERILIZATION

Because biodegradable polymers are hydrolytically unstable, the presence of moisture can degrade them in storage, during processing, and after device fabrication. In theory, the solution for hydrolysis instability is simple: eliminate the moisture and thus eliminate the degradation. However, because the materials are naturally hygroscopic, eliminating water and then keeping the polymer free of water are difficult to accomplish. The as-synthesized polymers have relatively low water contents,

since any residual water in the monomer is used up in the polymerization reaction. The polymers are quickly packaged after manufacture—generally double-bagged under an inert atmosphere or vacuum. The bag material may be polymeric or foil, but it must be highly resistant to water permeability. To minimize the effects of any moisture present, the polymers are typically stored in a freezer. Packaged polymers should always be at room temperature when opened to minimize condensation, and should be handled as little as possible at ambient atmospheric conditions. As expected, there is a relationship among biodegradation rate, shelf stability, and polymer properties. For instance, the more hydrophilic glycolide polymers are much more sensitive to hydrolytic degradation than are polymers prepared from the more hydrophobic lactide.

Final packaging consists of placing the suture or device in an airtight, moistureproof container. A desiccant can be added to further reduce the effects of moisture. Sutures, for example, are wrapped around a specially dried paper holder that acts as a desiccant. In some cases, the finished device may be stored at subambient temperature as an added precaution against degradation.

Devices incorporating biodegradable polymers cannot be subjected to autoclaving, and must be sterilized by gamma or E-beam irradiation or by exposure to ethylene oxide (EtO) gas. There are certain disadvantages, however, to both irradiation and EtO sterilization. Irradiation, particularly at doses above 2 Mrd, can induce significant degradation of the polymer chain, resulting in reduced molecular weight as well as influencing final mechanical properties and degradation times. Polyglycolide, poly(lactide), and poly(dioxanone) are especially sensitive to ionizing radiation, and these materials are usually sterilized by EtO for device applications. Because the highly toxic EtO can present a safety hazard, great care must be taken to ensure that all the gas is removed from the device before final packaging. The temperature and humidity conditions should also be considered when submitting devices for sterilization. Temperatures must be kept below the glass-transition temperature of the polymer to prevent the part geometry from changing during sterilization. If necessary, parts can be kept at 0°C or lower during the irradiation process.

PROCESSING

All commercially available biodegradable polymers can be melt processed by conventional means such as injection molding, compression molding, and extrusion. As with packaging, special consideration needs to be given to the exclusion of moisture from the material before melt processing to prevent hydrolytic degradation. Special care must be taken to dry the polymers before processing and to rigorously exclude humidity during processing.

Because most biodegradable polymers have been synthesized by ring-opening polymerization, a thermodynamic equilibrium exists between the forward or polymerization reaction and the reverse reaction that results in monomer formation. Excessively high processing temperatures may result in monomer formation during the molding or extrusion process. The presence of excess monomer can act as a plasticizer, changing the material's mechanical properties, and can catalyze the hydrolysis of the device, thus altering degradation kinetics. Therefore, these materials should be processed at the lowest temperatures possible.

Factors That Accelerate Polymer Degradation

More hydrophilic backbone.

More hydrophilic endgroups.

More reactive hydrolytic groups in the backbone.

Less crystallinity.

More porosity.

Smaller device size.

DEGRADATION

Once implanted, a biodegradable device should maintain its mechanical properties until it is no longer needed and then be absorbed and excreted by the body, leaving no trace. Simple chemical hydrolysis of the hydrolytically unstable backbone is the prevailing mechanism for the polymer's degradation. This occurs in two phases. In the first phase, water penetrates the bulk of the device, preferentially attacking the chemical bonds in the amorphous phase and converting long polymer chains into shorter water-soluble fragments. Because this occurs in the amorphous phase initially, there is a reduction in molecular weight without a loss in physical properties, since the device matrix is still held together by the crystalline regions. The reduction in molecular weight is soon followed by a reduction in physical properties, as water begins to fragment the device (see Figure 10). In the second phase, enzymatic attack and metabolization of the fragments occurs, resulting in a rapid loss

of polymer mass. This type of degradation—when the rate at which water penetrates the device exceeds that at which the polymer is converted into water-soluble materials (resulting in erosion throughout the device)—is called bulk erosion. All of the commercially available synthetic devices and sutures degrade by bulk erosion.
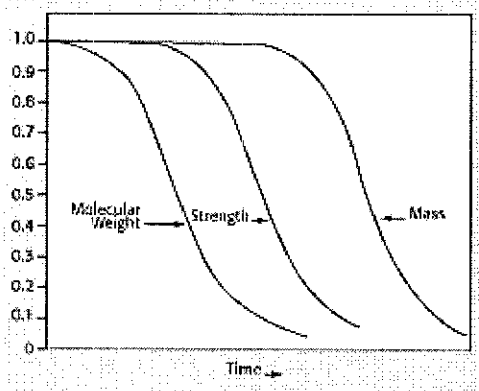

Figure 10. Generic absorption curves showing the sequence of polymer molecular weight, strength, and mass reduction. (Figure reproduced courtesy of Journal of Craniofacial Surgery, (8)2:89, 1997.)

A second type of biodegradation, known as surface erosion, occurs when the rate at which the polymer penetrates the device is slower than the rate of conversion of the polymer into water-soluble materials. Surface erosion results in the device thinning over time while maintaining its bulk integrity. Polyanhydrides and polyorthoesters are examples of materials that undergo this type of erosion—when the polymer is hydrophobic, but the chemical bonds are highly susceptible to hydrolysis. In general, this process is referred to in the literature as bioerosion rather than biodegradation.

The degradation-absorption mechanism is the result of many interrelated factors, including:

The chemical stability of the polymer backbone.

The presence of catalysts, additives, impurities, or plasticizers.

The geometry of the device.

Balancing these factors by tailoring an implant to slowly degrade and transfer stress at the appropriate rate to surrounding tissues as they heal is one of the major challenges facing researchers today.

COMMERCIAL BIODEGRADABLE DEVICES

The total U.S. revenues from commercial products developed from absorbable polymers in 1995 was estimated to be over $300 million, with more than 95% of revenues generated from the sale of bioabsorbable sutures. The other 5% is attributed to orthopedic fixation devices in the forms of pins, rods, and tacks; staples for wound closure; and dental applications.[2] Research into biodegradable systems continues to increase, from the 60 to 70 papers published each year in the late 1970s to the more than 400 each year in the early 1990s. The rate at which bioabsorbable fixation devices are cleared through the FDA 510(k) regulatory process is also increasing, with seven devices cleared for sale in 1995.

What follows is a brief overview of some of the significant commercial applications of biodegradable polymers.

Sutures. While comprising the lion's share of the total medical biodegradables market in 1995, this is a mature area not expected to grow rapidly in the future. About 125 million synthetic bioabsorbable sutures are sold each year in the United States. They are divided into braided and monofilament categories. Braided sutures are typically more pliable than monofilament and exhibit better knot security when the same type of knot is used. Monofilament sutures are more wiry and may require a more secure knot. Their major advantage is that they exhibit less tissue drag, a characteristic that is especially important for cardiovascular, ophthalmic, and neurological surgeries. A recent source in the literature lists eight objective and three subjective parameters for suture selection based on criteria such as tensile strength, strength retention, knot security, tissue drag, infection potential, and ease of tying.[3]

Dental Devices. Biodegradable polymers have found use in two dental applications. Employed as a void filler following tooth extraction, porous polymer particles can be packed into the cavity to aid in quicker healing. As a guided-tissue-regeneration (GTR) membrane, films of biodegradable polymer can be positioned to exclude epithelial migration following periodontal surgery. The exclusion of epithelial cells allows the supporting, slower-growing tissue—including connective and ligament cells—to proliferate. Three examples of these GTR materials are Resolut from W.L. Gore (Flagstaff, AZ), Atrisorb from Atrix Laboratories (Fort Collins, CO), and Vicryl mesh from Ethicon.

Orthopedic Fixation Devices. Orthopedic fixation devices made from synthetic biodegradable polymers have advantages over metal implants in that they transfer stress over time to the damaged area, allowing healing of the tissues, and eliminate

the need for a subsequent operation for implant removal. The currently available materials have not exhibited sufficient stiffness to be used as bone plates for support of long bones, such as the femur. Rather, they have found applications where lower-strength materials are sufficient: for example, as interference screws in the ankle, knee, and hand areas; as tacks and pins for ligament attachment and meniscal repair; as suture anchors; and as rods and pins for fracture fixation. Screws and plates of poly(l-lactide-co-glycolide) for craniomaxillofacial repair have recently been cleared for marketing in the United States under the trade name LactoSorb Craniomaxillofacial Fixation System (Biomet, Inc., Warsaw, IN).

Other Applications. Biodegradable polymers have found other applications that have been commercialized or are under investigation. Anastomosis rings have been developed as an alternative to suturing for intestinal resection. Tissue staples have also replaced sutures in certain procedures. Other applications currently under scrutiny include ligating clips, vascular grafts, stents, and tissue-engineering scaffolds. A list of commercial synthetic biodegradable polymer devices by category is given in Table II.

Application	Trade Name	Composition [a]	Manufacturer
	Dexon	PGA	Davis and Geck
	Maxon	PGA-TMC	Davis and Geck
	Vicryl	PGA-LPLA	Ethicon
Sutures	Monocryl	PGA-PCL	Ethicon
	PDS	PDO	Ethicon
	Polysorb	PGA-LPLA	U.S. Surgical
	Biosyn	PDO-PGA-TMC	U.S. Surgical
	PGA Suture	PGA	Lukens
	Sysorb	DLPLA	Synos
	Endofix	PGA-TMC or LPLA	Acufex
	Arthrex	LPLA	Arthrex
Interference screws	Bioscrew	LPLA	Linvatec
	Phusiline	LPLA-DLPLA	Phusis
	Biologically Quiet	PGA-DLPLA	Instrument Makar
Suture anchor	Bio-Statak	LPLA	Zimmer
	Suretac	PGA-TMC	Acufex
Anastomosis clip	Lactasorb	LPLA	Davis and Geck
Anastomosis ring	Valtrac	PGA	Davis and Geck
Dental	Drilac	DLPLA	THM Biomedical
Angioplastic plug	Angioseal	PGA-DLPLA	AHP
Screw	SmartScrew	LPLA	Bionx
Pins and rods	Biofix	LPLA or PGA	Bionx
	Resor-Pin	LPLA-DLPLA	Geistlich
Tack	SmartTack	LPLA	Bionx
Plates, mesh, screws	LactoSorb	PGA-LPLA	Lorenz
	Antrisorb	DLPLA	Atrix
Guided tissue	Resolut	PGA-DLPLA	W.L. Gore
	Guidor	DLPLA	Procordia

[a] Key to material composition:
DLPLA — poly(dl-lactide)
LPLA — poly(l-lactide)
PGA — polyglycolide
PDO — poly(dioxanone)
PGA-TMC — poly(glycolide-co-trimethylene carbonate)
PGA-LPLA — poly(l-lactide-co-glycolide)

PGA-DLPLA — poly(dl-lactide-co-glycolide)
LPLA-DLPLA — poly(l-lactide-co-dl-lactide)
PDO-PGA-TMC — poly(glycolide-co-trimethylene carbonate-co-dioxanone)

Table II. Some commercial biodegradable medical products.

Biodegradable Polymers in Tissue Engineering

One of the exciting current areas for applications of biodegradable polymers is in tissue engineering. Several companies are investigating using these materials as a matrix for living cells. Important properties in this regard include porosity for cell in-growth, a surface that balances hydrophilicity and hydrophobicity for cellular attachment, mechanical properties that are compatible with those of the tissue, and degradation rate and by-products. The polymer matrix may represent the device itself, or can be a scaffold for cell growth in vitro that is degraded by the growing cells prior to implantation. The device can also be formulated to contain additives or active agents for more rapid tissue growth or compatibility. For example, a bone implant may contain a form of calcium phosphate or a growth factor such as one of the bone morphogenetic proteins.

There are a number of ways of making the three-dimensional matrices required for tissue engineering. These methods include woven or nonwoven preparations from spun fibers, blown films using solvents or propellants, or sintered polymer particles. One of the newest methods is being developed by Therics (Princeton, NJ), which has licensed a system for building three-dimensional devices for use as scaffolds and in drug delivery products. In this system, small spheres of polymer are laid out in thin films. Using technology similar to that found in ink-jet printers, small amounts of solvent are used to fuse particles together. The particles not fused are removed and another layer of particles laid out. This particle placement and fusing is continued for many layers, until the exact three-dimensional structure is obtained. Because each polymer layer is applied in a separate step, different polymers can be used to obtain different properties in the interior and exterior of the device.

CONCLUSION

We have attempted to provide an overview of the medical device uses of biodegradable polymers. While sutures were the first commercial product and still account for the vast majority of all sales, a variety of products are now on the market for an expanding range of applications, with others certain to appear in the next decade.

What is it about these materials that makes them so attractive to the device industry? First, in this conservative field, where devices serve critical, perhaps life-and-death, functions, the industry is slow to accept new materials or new designs. The polymers prepared from these materials, particularly lactide and glycolide, have a long history of safe and effective use. Building on this solid foundation, researchers will continue to evaluate these materials, taking advantage of the wide range of properties that can be obtained in polymers built with relatively few monomer units. We expect that, in the future even more than today, device designers and physicians will have available a wealth of products using biodegradable polymers that will help speed patient recovery and eliminate follow-up surgeries.

ACKOWLEDGMENTS

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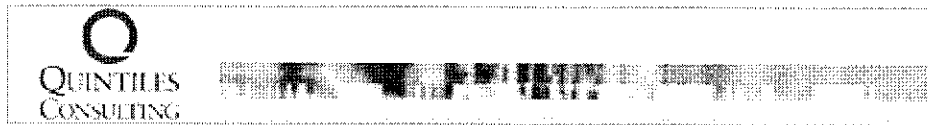
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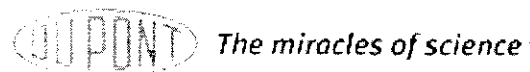
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European Food Contact Approval for VITON® FREEFLOW™ Z200 Process Aids for Food Packaging Films

DuPont at NPE 2006 – South Hall, Booth #2632

Wilmington, DE, June 20, 2006 — DuPont Performance Elastomers has announced that its Viton® FreeFlow™ Z200 fluoroelastomer process aids have been declared compliant with food contact regulations in Europe for use in finished film-type food packaging materials. The processing additive, which uses polycaprolactone (PCL) as the interfacial agent, has been granted a Regulatory Compliance Statement for Food Contact Materials in accordance with European Directive 2002/72/EC, applicable to EU Member States and to Norway and Switzerland.

This is in addition to existing compliance with US FDA Regulations under 21 CFR 177.1520 § (b), Canadian Health Protection Branch (HPB) and with the Japan Hygienic Olefin and Styrene Plastics Association (JHOSPA) under Japanese Food Sanitation Law, granted earlier.

"With the addition of EU compliance, Viton® FreeFlow™ Z200 now has food contact approval effective in the major global markets of the world. This will significantly broaden acceptability of the newest PCL-based process aid, and enable film converters to use the distinctive high temperature stability, olfactory and compatibility advantages of Viton® FreeFlow™ Z200 in food packaging wrap products," said Christopher Fisher, marketing manager – DuPont Performance Elastomers.

In comparison with conventional and polyethylene glycol (PEG) based process aids, Viton® FreeFlow™ Z200 offers better thermal stability at temperatures up to 300°C, minimal olfactory effects, and less interaction with other additives. The process aid can help increase film line yield and eliminate melt-fracture, leading to a film with excellent clarity, limited haze, high gloss, and robust tear and puncture resistance, all of which are highly important in the food packaging industry.

Viton® FreeFlow™ Z200 and its sister product Viton® FreeFlow™ Z100, represented a major breakthrough in process aid technology when they were introduced to the plastics industry in 2002. Both products have become established in many food and non-food contact applications such as trash bags, tape extrusion, wire and cable coatings where process efficiency, good visual appearance, and strength and toughness are required.

About DuPont Performance Elastomers

DuPont Performance Elastomers, a global supplier of specialty elastomers with headquarters in Wilmington, Delaware, USA, is a wholly owned subsidiary of DuPont. The company is an industry leader in chloroelastomers and fluorinated elastomers, serving the automotive, chemical, petrochemical, semiconductor, food and pharmaceutical processing, construction, general rubber and wire and cable industries.

###

Viton® and Viton® FreeFlow™ are registered trademarks or trademarks of DuPont
Performance Elastomers

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June 2006

Click here and save to download a 150dpi JPEG image of the photo.

Caption:
DuPont Performance Elastomers Viton® FreeFlow™ Z200 fluoroelastomer process aid has
received food contact approval in compliance with European Directive 2002/72/EC for use in
finished film-type food packaging materials.

High-resolution images are also available on line at npe.dupont.com

Reader enquiries should be directed to (US) 800-853-5515 or www.dupontelastomers.com

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ATTACHMENT

4

BIODEGRADABLE CAPA® THERMOPLASTICS

Solvay have produced ε-caprolactone and its polymers at our Warrington plant since the mid-1970's. The polymers are made by ring-opening polymerization of ε-caprolactone monomer with alcohol initiators. The products vary in molecular weight from low molecular weight oligomers for use in the polyurethane industry to high molecular weight thermoplastics. These thermoplastics, the CAPA® 6000 series, find wide usage in a range of applications due to the fact that they are readily processed, have wide compatibility with other polymers, are non toxic and biodegradable.

These products are

- **Fully BIODEGRADABLE**
- **Non-Toxic**
- **Low Melting**
- **Semi-Crystalline**
- **Readily Processable**
- **Compatible with a Wide Range of Polymers**

Applications

- **Biodegradable Bottles**
- **Biodegradable Films**
- **Controlled Release of Drugs, Pesticides and Fertilizers**
- **Polymer Processing**
- **Adhesives**
- **Non-Woven Fabrics**
- **Synthetic Wound Dressings**
- **Orthopaedic Casts**

Table 1 Typical Physical Properties of CAPA® Thermoplastics[1]

Property		ASTM Test	CAPA® 6500	CAPA® 6800
Molecular Weight				
	Mn	GPC, THF, 25°C	47500 ± 2000	69000 ± 1500
	Mw	GPC, THF, 25°C	84500 ±1000	120000 ± 2000
	Mz	GPC, THF, 25°C	130000 ± 5000	178500
Polydispersity (Mw/Mn)			1.78	1.74
Melt Flow Index		D 1238		
80°C, 2.16kg, g/10 min			2.36	0.59
80°C, 21.6kg, g/10 min			34.6	9.56
190°C, 2.16kg, g/10 min			28	7.29
Thermal Analysis (DSC)				
Melting Point			60-62	60-62
Heat Of Fusion, ΔHm, J/g			76.9	76.6
Crystallinity, %			56	56
Crystallization Temperature, °C			25.2	27.4
Glass Transition Temperature, Tg ,°C			-60	-60
Tensile Properties				
Yield Stress, σ y, Mpa		D 412-87		
	100mm/min		17.5	16
	500mm/min		17.2	14
Modulus , E. Mpa		D 412-87		
	1mm/min		470	440
	10mm/min		430	500
Draw Stress ,σ d, MPa		D 412-87		
	100mm/min		12.6	11.9
	500mm/min		11.5	11
Draw Ratio , λ d, x		D 412-87		
	100mm/min		>4.2	4
Stress At Break ,σ b, Mpa		D 412-87		
	100mm/min		29) 11	54
Strain At Break, ε b, %				
	100mm/min	D 412-87	>700	920
Flexural Modulus, E , MPa				
	2mm/min	D 790	411	nd
Hardness		D 2240		
Shore A			95	94
Shore D			51	50
Viscosity				
Pa. Sec, 70°C , 10/sec			2890	12650
Pa. Sec, 100°C , 10/sec			1353	5780
Pa. Sec, 150°C , 10/sec			443	1925

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[1] The values quoted here are typical and do not form part of a sales specification.

CAPA® 6500 is a 50000 molecular weight homopolymer which, because of its relatively low viscosity and melting point, has found considerable use in the manufacture of orthopaedic casts, as an adhesive and is particularly suited for making injection molded parts.

CAPA® 6800 is a higher viscosity material having a molecular weight of 80000, and is more suited to the manufacture of films and bottles.

BIODEGRADABILITY DATA

Microbial biodegradation of the CAPA® 6000 series has been tested by PIRA International, the leading independent center for research for the paper, packaging, printing and publishing industries. Two series of tests were carried out - soil burial and mineralization with a municipal sewage sludge culture.

A. Burial tests

Films of CAPA® 6500 (25µm x 200mm x15mm) were buried in soil (moisture content 30%) for 16 days and the physical properties assessed daily. Figures 1 and 2 represent the elongation and tensile strength of the film over this period.
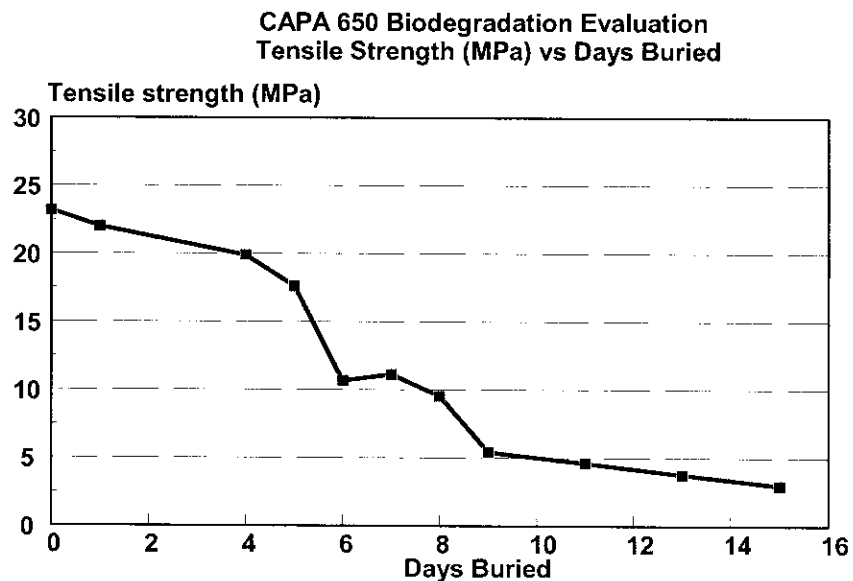
Figure 1

CAPA 650 Biodegradation Evaluation
Tensile Strength (MPa) vs Days Buried

Figure 2

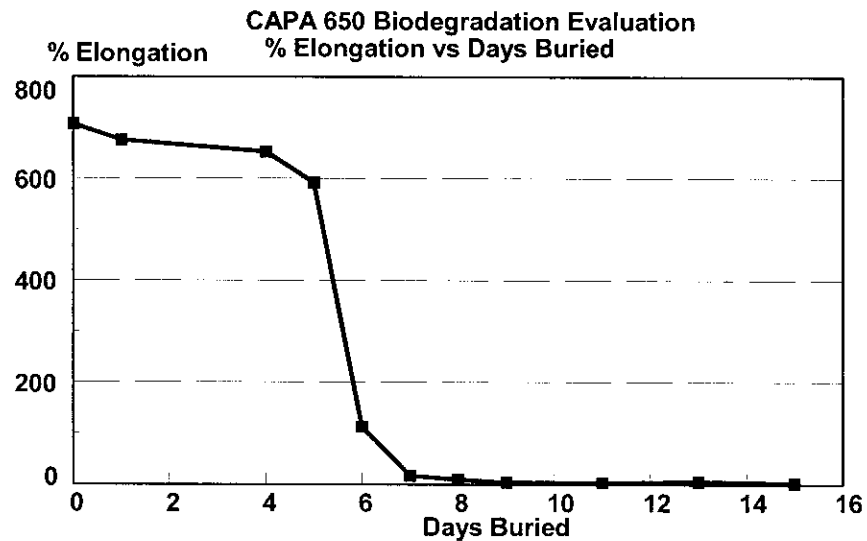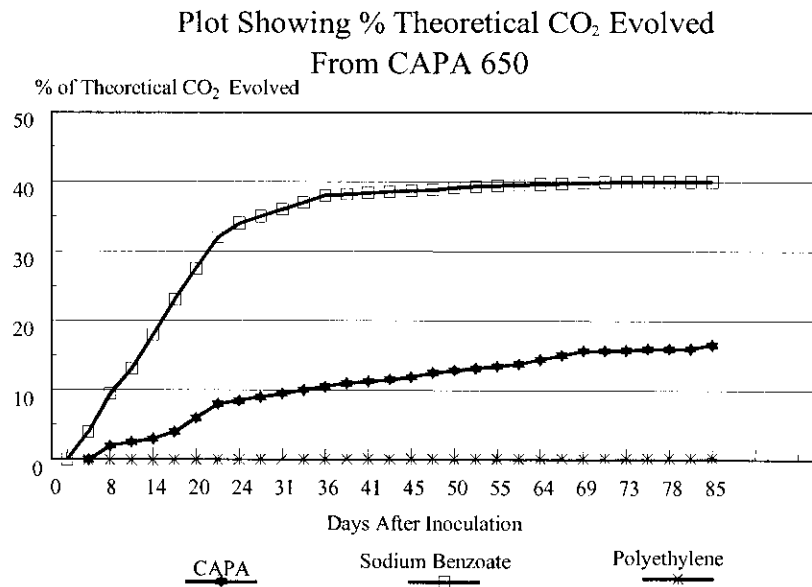CAPA 650 Biodegradation Evaluation
% Elongation vs Days Buried

Figure 1 shows the gradual loss of tensile strength of the samples on soil burial, a more dramatic loss of properties is shown in Figure 2. After seven days burial the elongation at break had dropped from 700% to less than 10%. All of the samples showed considerable biological fouling within five days, and after sixteen days it was impossible to take further tensile measurements as the samples were so heavily degraded.

B. Mineralization studies

A series of test to evaluate the levels of aerobic degradation (ASTM D5209-91) were conducted on CAPA® 6500 in powdered form. Samples were inoculated with activated sewage sludge and degraded by the bacteria present. The CO_2 evolved from this process was monitored over a period of 85 days. Figure 3 depicts the level of CO_2 evolved as a percentage of the theoretical value for CAPA® 6500, polyethylene and sodium benzoate (control).

Figure 3

Plot Showing % Theoretical CO₂ Evolved
From CAPA 650

% of Theoretical CO_2 Evolved

Days After Inoculation

CAPA   Sodium Benzoate   Polyethylene

PROCESSING DATA

Methodology has been developed to produce films and bottles from CAPA® 6500 and 6800. The details of how to do this are given below.

Extrusion (Cast Films and Sheets)	CAPA® 6500	CAPA® 6800
Extruder type	single screw	single screw
Screw Type	two step, compression ratio 2.4 to 4, L/D 20 to 25	
Screw Speed	low	low
Temperature Profile		
feed zone	50°C or less	50°C
compression zone	70°C to 95°C	130°C to 165°C
metering zone	75°C to 105°C	140°C to 150°C
die zone	70°C to 120°C	140°C to 150°C
melt temperature at nozzle	70°C to 120°C	70°C to 120°C
Degassing	not necessary	not necessary
Chill roll	-4°C to 23°C preferably refrigerated	-4°C to 23°C preferably refrigerated
Film or Sheet Thickness	from 35μm to 3.5mm	from 35μm to 1.3mm

Extrusion Blow Molding	CAPA® 6500	CAPA® 6800
Screw Type	L/D 20 compression ratio 2.8	L/D 20 compression ratio 2.8
Screw Speed	low	low
Temperature Profile		
feed zone	60°C at most	60°C at most
compression zone	60°C to 75°C	75°C
metering zone	60°C to 75°C	75°C to 100°C
die zone	62°C to 65°C	75°C to 100°C
mould	4°C to 20°C	4°C to 20°C
Die Design	preferably with a conically convergent mandrel	
Spigot Design	preferably with a conical tip	
Mould	small volumes (up to 100ml)	volumes up to 500ml
	effective and uniform cooling is recommended	
	the use of mechanical injectors is recommended	
Blow Pressure	2 to 2.5 bar	2 to 2.5 bar
Cycle Time	9 to 20 secs	15 to 20 secs

BARRIER PROPERTIES OF CAPA® 6500 FILM

The barrier properties of CAPA® 6500 film have been determined. For water permeability ASTM E96-66 was used, for Carbon Dioxide ASTM D 1434-75 and for Oxygen ASTM D 3985-81 was used. The results are presented graphically below in Figure 4.

Figure 4

Rates of Permeability to Carbon Dioxide and Oxygen gas

Rates of Permeability to water vapour
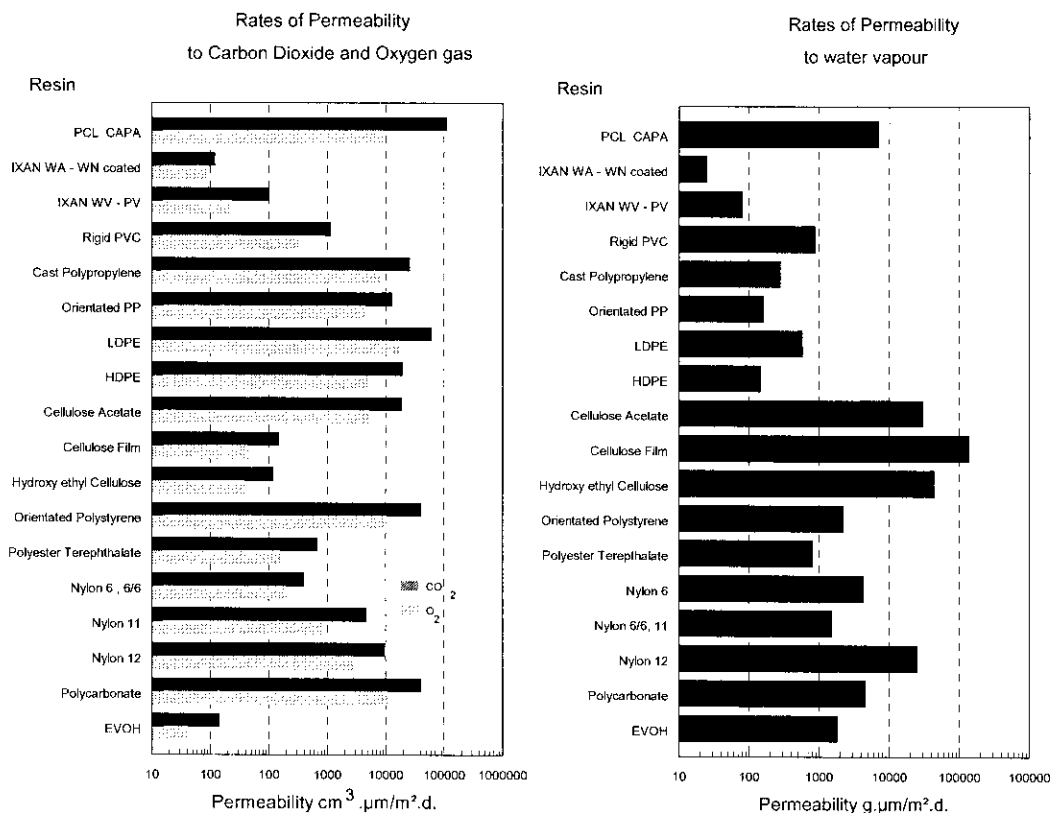
The permeability to oxygen is not unlike medium density polyethylene, but is significantly higher for carbon dioxide and water.

HANDLING AND STORAGE

CAPA® thermoplastics are supplied in quantities of 20-kg paper sacks on pallets of 1000 kg or in bulk quantities in 500-kg "super sacks". CAPA® products should be stored in a dry place away from sources of heat.

For further information please contact:

Solvay Caprolactones
PO Box 27328
3333 Richmond Avenue
Houston, TX 77227

Telephone: 713 525 6500
Telefax: 713 524 9032

www.solvaycaprolactones.com

The information given in this data sheet is given as a general guide and should not be taken to cover all cases. Each customer should ensure that the product concerned is suitable for the specific purpose and the manner in which it is intended to be used. The information given must not be taken in any way to form a specification. This data sheet does not form part of the Conditions of Sale of our products and is of a general nature.

FREEDOM FROM PATENT RESTRICTIONS SHOULD NOT BE ASSUMED.

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ATTACHMENT

5

Journal of Polymers and the Environment

Toxicity screening of biodegradable polymers. II. Evaluation of cell culture test with medium extract

X-Ray Scattering of Soft Matter
Stribeck, Norbert

M. H. Dang[1] ☐, F. Birchler[1] and E. Wintermantel[1]

(1) Chair of Biocompatible Materials Science and Engineering, ETH Zurich, Wagistr. 23, CH-8952 Schlieren, Switzerland

Abstract Cell culture testing with material extracts was applied to toxicity screening of some commercial degradable plastics: a plasticized cellulose acetate, an aliphatic polyester (Bionolle), polyhydroxybutyrate-co-hydroxyvalerate (Biopol), and polycaprolactone (TONE polymer). Cell culture medium with serum was used as extraction medium. Methods for the determination of morphology and viability of cells cultured in the extract were investigated. Phase-contrast light microscopy of cells, enhanced by neutral red staining, provides high-contrast images for qualitative evaluation of cell morphology and lysis. Compared to the determination of protein using the Bradford method and of neutral red uptake, the determination of dehydrogenase activity using 3-[4,5-dimethylthia-zol-2-yl]-2,5-diephenyl-tetrazolium bromide (MTT) is more sensitive and accurate. The relative MTT activity of cells cultured in fresh extracts indicate that TONE polymer (all shapes) and Bionolle (test bars and films) are comparable to materials currently used in the food industry (polyethylene terephthalate, atactic and isotactic polystyrene) with no toxic effects on cells.

Key Words Toxicity screening - biodegradable polymers - cell cultures - test with extract

ATTACHMENT

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CAPA® 6100, 6106S, 6109S, 6250, 6400, 6406, 6430, 6500, 6500C, 6501, 6501S, 6502S, 6503, 6505, 6506, 6506S, 6800, and 6806

Material Safety Data Sheet

CAPA® Polycaprolactones

Chemical: CAPA® Polycaprolactones	NFPA: H=0 F=1 I=0 S=none
	HMIS: H=0 F=1 R=0 PPE= Supplied by user; dependent on conditions

MSDS Number: CAPA 6500-0307
Effective Date: 21 March 2007
Issued by: Solvay Chemicals, Inc. Regulatory Affairs Department

Not valid three years after effective date or after issuance of superseding MSDS, whichever is earlier. French or Spanish translations of this MSDS may be available. Check www.solvaychemicals.us or call Solvay Chemicals, Inc. to verify the latest version or translation availability.

Material Safety Data Sheets contain country-specific regulatory information. Therefore, the MSDS's provided are for use only by customers of Solvay Chemicals, Inc. in North America. If you are located in a country other than Canada, Mexico or the United States, please contact the Solvay Group company in your country for MSDS information applicable to your location.

1. Company and Product Identification

1.1 Product Name: CAPA® 6100, 6106S, 6109S, 6250, 6400 (fka 640), 6406 (fka 646), 6430, 6500 (fka 650), 6500C (fka 651), 6501, 6501S, 6502S, 6503, 6505 (fka 655), 6506 (fka 656), 6506S, 6800 (fka 680), and 6806 (fka 686).

Chemical Name: 2-Oxepanone, homopolymer

Synonyms: epsilon-Caprolactone polyester with 1,4-butanediol
epsilon-Caprolactone polymer with 1,4-butanediol

Chemical Formula: $(C_6H_{10}O_2)x$

Molecular Weight: CAPA® 6100, 6106S, 6109S: 10000
CAPA® 6250: 25000
CAPA® 6400 (640), 6406 (646): 37000
CAPA® 6500 (650), 6500C (651), 6501, 6501S, 6502S, 6503, 6505 (655), 6506 (656), 6506S: 50000
CAPA® 6800 (680), 6806 (686): 80000
CAPA® 6430: 43000

CAS Number: 24980-41-4

EINECS Number: Not Applicable.

1.2 Recommended Uses: Used in hot melt adhesives, polymer processing aids, dispersion medium, and orthopedic applications.

1.3 Supplier: Solvay Chemicals, Inc.
PO BOX 27328 Houston, TX 77227-7328
3333 Richmond Ave. Houston, Texas 77098

**SOLVAY
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CAPA® 6100, 6106S, 6109S, 6250, 6400, 6406, 6430, 6500, 6500C, 6501, 6501S, 6502S, 6503, 6505, 6506, 6506S, 6800, and 6806

Material Safety Data Sheet

(vertical left margin) CAPA® Polycaprolactones

1.4 Emergency Telephone Numbers

Emergencies (USA): 1-800-424-9300 (CHEMTREC®)
Transportation Emergencies (INTERNATIONAL/MARITIME): 1-703-527-3887 (CHEMTREC®)
Transportation Emergencies (CANADA): 1-613-996-6666 (CANUTEC)
Transportation Emergencies (MEXICO-SETIQ): 01-800-00-214-00 (MEX. REPUBLIC)
525-559-1588 (Mexico City and metro area)

2. Composition/Information on Ingredients

INGREDIENTS	FORMULA	WT. PERCENT	CAS #
2-Oxepanone homopolymer	$(C_6H_{10}O_2)x$	> 99	24980-41-4

3. Hazards Identification

Emergency Overview: Under normal use conditions, this material is considered to present minimal human health and environmental hazards.

3.1 Route of Entry: Inhalation: Yes Skin: Yes Ingestion: Yes

3.2 Potential Effects of exposure:

Inhalation: Dust particles may require cleaning of nasal passages.

Eyes: Mechanical irritation from particulates generated by product.

Skin contact: Decomposition gases may be irritating to the skin.

Ingestion: Minimal hazard expected in normal industrial use.

Carcinogenicity: See section 11.3.

4. First-Aid Measures

General Recommendations: No specific treatment is necessary.

4.1 Inhalation:
- Clear nasal passages of dust and particulates.
- If exposed to excessive levels of decomposition products, remove to fresh air and get medical attention if cough or other symptoms develop.

Eyes:
- Hold eyelids apart and flush eyes with plenty of water for at least 15 minutes.
- Get medical attention if symptoms develop.

Skin:
- Remove contaminated clothing.
- Wash skin with soap and water. Get medical attention if symptoms develop.
- Molten polymer can burn skin.

Ingestion: If subject is completely conscious, rinse mouth and administer fresh water.

4.2 Medical Treatment/Notes to Physician: None.

CAPA® 6100, 6106S, 6109S, 6250, 6400, 6406, 6430, 6500, 6500C, 6501, 6501S, 6502S, 6503, 6505, 6506, 6506S, 6800, and 6806

Material Safety Data Sheet

5. Fire-Fighting Measures

5.1 Flash point:
- CAPA® 6100, 6106S, 6109S, 6250, 6400 (640), 6406 (646), 6430, 6500 (650), 6500C (651), 6501, 6501S, 6502S, 65003 6505 (655), 6506 (656), 6506S: 527°F (275°C).
- CAPA® 6800 (680) and 6806 (686): No data.

5.2 Auto-ignition Temperature: No data.

5.3 Flammability Limits: Combustible.

5.4 Unusual Fire and Explosion Hazards: Dust explosion possible.

5.5 Common Extinguishing Methods:
- Powder.
- Foam, AFFF.
- CO_2.
- Water, water spray.

Inappropriate extinguishing means: No restriction.

5.6 Fire Fighting Procedures
Specific hazards: Formation of dangerous gas/vapors in case of decomposition (see Section 10). Possible buildup of electrical charges which could cause a fire by electrical discharge.

Protective measures in case of intervention:
- Evacuate all non-essential personnel.
- Intervention only by capable personnel who are trained and aware of the hazards of the product.
- Wear self-contained breathing apparatus when in close proximity or in confined spaces.

Other precautions:
- If safe to do so, remove exposed containers, or cool with large quantities of water.
- As with any fire, clean and ventilate room before reentry.

6. Accidental Release Measures

6.1 Precautions:
- Observe the protective measures given in Section 8.
- Spilled material may cause slipping hazard.

6.2 Cleanup methods:
Solid:
- Collect the product with suitable means avoiding dust formation.
- Place material into a closed, labeled container compatible with the product.
- Place the container in a safe and isolated place.
- For disposal methods, refer to Section 13.

Molten Solid:
- If possible dam large quantities of molten solid with sand or earth and allow to solidify.
- Place into a closed, labeled container compatible with the product.
- Place the container in a safe and isolated place.
- For disposal methods, refer to Section 13.
- Clean the spill area with large quantities of water.

6.3 Precautions for protection of the environment:
- Avoid discharges into the environment (sewers, rivers, soils, etc.) and take any measure required by applicable federal, state and local laws.
- Immediately notify the appropriate authorities in case of significant discharge or if required by applicable federal, state or local laws.

7. Handling and Storage

7.1 Handling:
- Use electrically conductive materials for piping circuits and equipment.
- Avoid heating product above decomposition temperature (see Section 9).

7.2 Storage:
- Keep in the original packaging, closed.
- Store in dry area.
- Keep away from ignition and heat sources.

7.3 Specific Uses: See Section 1.2.

7.4 Other precautions:
- Use grounded equipment.
- No open flames or sparks. No smoking.
- Prevent electrostatic discharge.
- Avoid dust and formation of dust clouds.
- Warn personnel of the dangers of the product.
- Follow protective measures given in Section 9.

7.5 Packaging:
- Paper bags.
- Polypropylene sacks.

8. Exposure Controls/Personal Protection

This material does not have established exposure limits.

8.1 Exposure Limit Values

Authorized limit Values	OSHA PEL
PNOC (Particulates not otherwise classified)	15 mg/m³ - total dust 5 mg/m³ - resp. frac.

8.2 Exposure Controls:

8.2.1 Occupational Exposure Controls:

8.2.1.1 Ventilation: Provide local ventilation suitable for the emission risk (see Section 9).

8.2.1.2 Respiratory protection: Use appropriate respiratory protection in case of dust or dust formation.

8.2.1.3 Hand protection: Where contact is likely, wear chemical-resistant gloves (PVC).

8.2.1.4 Eye protection:
- Wear safety glasses with side shields.
- Wear chemical splash goggles and face shield, if risk of splashing.

8.2.1.5 Skin protection:
- Where contact is likely, wear chemical-resistant gloves, a chemical suit and boots.
- Recommended materials are PVC, neoprene or rubber.
- Wear appropriate thermal protection when handling hot material.
- Wear chemical protective clothing in dusty areas.

8.3 Other precautions:
- Provide a shower and eyewash station.
- Consult your industrial hygienist or safety manager for the selection of personal protective equipment suitable for the working conditions.

9. Physical and Chemical Properties

9.1 Appearance:
- CAPA® 6100, 6400 (640), 6430, 6500 (650), 6500C (651), 6800 (680): pellets.
- CAPA® 6106S, 6109S, 6406 (646), 6501, 6501S, 6502S, 6503, 6505 (655), 6506 (656), 6506S, 6806 (686): powder.
- CAPA® 6100, 6250: solid.

Color: White.

Odor: Odorless.

9.2 Important Health, Safety and Environmental information:
pH: Not applicable.

Change of state:
Melting point: 136-140°F (58-60°C).
Boiling point: Not determined.
Decomposition Temperature: 392°F (200°C).

Flash Point:
- CAPA® 6100, 6106S, 6109S, 6250, 6400 (640), 6406 (646), 6430, 6500 (650), 6501, 6501S, 6502S, 6500C (651), 6505 (655), 6506 (656), 6506S: 527°F (275°C).
- CAPA® 6800 (680) and 6806 (686): No data.

Flammability: Non-flammable.

Explosive Properties: Dust explosion possible.

Oxidizing Properties: Non-oxidizer.

Vapor Pressure: No data.

Relative Density:
Specific gravity (H_2O=1): • CAPA® 6100, 6106S, 6109S, 6250, 6400 (640), 6406 (646), 6430, 6500 (650), 6500C (651), 6501, 6501S, 6502S, 6503, 6505 (655), 6506 (656), 6506S: 1.10 @ melting point.
         • CAPA® 6800 (680), 6806 (686): No data.

Solubility:
Water: Insoluble in water.
Fat: Not Applicable.
Soluble in aromatic solvents and chlorinated hydrocarbons.

Partition coefficient: P (n-octanol/water): Not determined.

Viscosity:
- CAPA® 6100, 6106S, 6109S: 9300 mPa·s @ 212°F (100°C).
- CAPA® 6400 (640), 6406 (646): 315000 mPa·s @ 212°F (100°C).
- CAPA® 6250, 6500 (650), 6500C (651), 6501, 6501S, 6502S, 6505 (655), 6506 (656), 6506S: 1.5 million mPa·s @ 212°F (100°C).
- CAPA® 6800 (680), 6806 (686): 8 million mPa·s @ 212°F (100°C).
- CAPA® 6430: 1000 mPa·s @ 212°F (100°C).
- CAPA® 6501, 6503: 80 mPa·s @ 212°F (100°C).

Vapor Density (air=1): Not determined.

Evaporation Rate: Not Applicable.

9.3 Other Information: None.

10. Stability and Reactivity

Stability:
- Stable under normal conditions of use (see Section 7).
- Moisture.
- Excessive temperatures.

10.2 Materials and substances to avoid:
- Acids.
- Alkalis.

10.3 Hazardous decomposition products:
- Carbon monoxide and carbon dioxide when involved in a fire.
- Particulates of carbon.
- Caprolactone / monomer.

10.4 Hazardous Polymerization: Will not occur.

10.5 Other information: None.

CAPA® 6100, 6106S, 6109S, 6250, 6400, 6406, 6430, 6500, 6500C, 6501, 6501S, 6502S, 6503, 6505, 6506, 6506S, 6800, and 6806

Material Safety Data Sheet

11. Toxicological Information

11.1 Acute toxicity:
Inhalation: No data.

Oral: No data.

Dermal: No data.

Irritation: No data.

Sensitization: No data.

Comments: None.

11.2 Chronic toxicity: No data.

11.3 Carcinogenic Designation: Not listed.

12. Ecological Information

12.1 Acute ecotoxicity: No data.

12.2 Chronic ecotoxicity: No data.

12.3 Mobility: No data.

12.4 Degradation: No data.
Abiotic: No data.

Biotic: No data.

12.5 Potential for bioaccumulation: No data.

12.6 Other adverse effects/Comments: Ingestion of pellets by wildlife and fish may cause satiation (fullness) or bowel constriction. Consult the Society of the Plastics Industry's Clean Sweep Program to assure minimal impact to the environment.

13. Disposal Considerations

13.1 Waste treatment: CAPA® 6100, 6106S, 6502S, 6109S, 6250, 6400 (640), 6406 (646), 6430, 6500 (650), 6500C (651), 6501, 6501S, 6502S, 6503, 6505 (655), 6506 (656), 6506S, 6800 (680), and 6806 (686) are not considered hazardous waste under Federal Hazardous Waste Regulations (40 CFR 261). Please be advised, however, that federal laws may change and that state and local requirements for waste disposal may be more restrictive or otherwise different from federal regulations. Consult current federal, state and local regulations regarding the proper disposal of this material and its emptied containers.

13.2 Packaging treatment: Consult current federal, state and local regulations regarding the proper disposal of emptied containers.

13.3 RCRA Hazardous Waste: Not listed.

Left margin vertical text: **CAPA® Polycaprolactones**

14. Transport Information

Mode	DOT	IMDG	IATA
UN Number	Not a regulated hazardous material	Not a regulated hazardous material	Not a regulated hazardous material
Other	It is recommended that ERG Guide # 111 be used for all non-DOT-regulated material.		

15. Regulatory Information

National Regulations (US)

TSCA Inventory 8(b): Yes.

SARA Title III Sec. 302/303 Extremely Hazardous Substances (40 CFR 355): No.

SARA Title III Sec. 311/312 (40 CFR 370): No.

SARA Title III Sec. 313 Toxic Chemical Emissions Reporting (40 CFR 372): No.

CERCLA Hazardous Substance (40 CFR Part 302)
Listed: No.
Unlisted Substance: No.

State Component Listing:
State Comment: None identified.

National Regulations (Canada)

Canadian DSL Registration: Yes # 11183.

WHMIS Classification: Not a controlled product.

This product has been classified in accordance with the hazard criteria of the **Controlled Products Regulations,** and the MSDS contains all the information required by the **Controlled Products Regulations.**

16. Other Information

16.1 **Ratings:**
NFPA (NATIONAL FIRE PROTECTION ASSOCIATION)
Health = 0   Flammability = 1   Instability = 0   Special = None

HMIS (HAZARDOUS MATERIAL INFORMATION SYSTEM)
Health = 0   Fire = 1   Reactivity = 0   PPE = Supplied by User; dependent on local conditions

16.2 **Other Information:**
The previous information is based upon our current knowledge and experience of our product and is not exhaustive. It applies to the product as defined by the specifications. In case of combinations or mixtures, one must confirm that no new hazards are likely to exist. In any case, the user is not exempt from observing all legal, administrative and regulatory procedures relating to the product, personal hygiene, and integrity of the work environment. (Unless noted to the contrary, the technical information applies only to pure product).

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In all instances, it is the responsibility of the medical device or pharmaceutical manufacturer to determine that the Solvay Chemicals product is safe, lawful and technically suitable for the intended use. SOLVAY CHEMICALS MAKES NO WARRANTIES, EXPRESS OR IMPLIED, CONCERNING THE SUITABILITY OF ANY SOLVAY CHEMICALS PRODUCT FOR USE IN MEDICAL APPLICATIONS.

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16.3 Reason for revision:
Supersedes edition: Solvay Chemicals, Inc. MSDS# CAPA-6500-0805 dated 08/20/05
Purpose of revision: Add CAPA® 6502S.

ATTACHMENT

7

Polycaprolactone

Authors: J. E. Gough [a]; P. Christian [b]

Affiliations: [a] School of Materials, University of Manchester, Manchester, Greater Manchester, U.K.

[b] School of Chemistry, University of Manchester, Manchester, Greater Manchester, U.K.

Abstract

Polycaprolactone (PCL) is an aliphatic polyester and was initially investigated for use as a biodegradable packaging material after the realization of its degradability by microorganisms. PCL is also degraded by hydrolysis in physiological conditions and has therefore received a great deal of attention for use as an implantable material.

PCL is now one of several degradable polymers approved for use in the human body as drug delivery devices, adhesion barriers, sutures, and staples and is being extensively investigated as a biomaterial for tissue repair and regeneration. Degradable polymers have different degradation rates and are commonly investigated as blends as a method to tailor the degradation rate. The focus of this article is the recent use of PCL as a biomaterial.

Keywords: Degradable; Polyester; Drug delivery; Tissue engineering; Bone; Cartilage; Skin; Regeneration

ATTACHMENT

8

Preparation and Biodegradation of Starch/Polycaprolactone Films

Authors: Yavuz H.[1]; Babaç C.[2]

Abstract:

Starch granules were modified with trisodium trimetaphosphate (TSTP) and characterized by P^{31}-NMR, FTIR and DSC. Seventy-micron films were prepared from modified starch and polycaprolactone blends by solvent casting technique. Three different types of films—PCL (100% polycaprolactone), MOD-ST/PCL (50% modified starch and 50% polycaprolactone blend) and NONMOD-ST/PCL (50% nonmodified starch and 50% polycaprolactone blends)—were prepared, and their thermal, mechanical, and morphologic properties were investigated to show the increased performance of PCL with the addition of starch and also the effect of modification. It was observed that with the addition of starch the Young's modulus of polycaprolactone was increased and became less ductile, whereas tensile strength and elongation at break values decreased. Biodegradation of these films was inspected under different aerobic environments with the presence of *Pseudomonas putida*, activated sludge, and compost. It was observed that whereas *P. putida* had almost no effect on degradation during 90 days, with the presence of activated sludge, considerable deformation of films was observed even in the first 7 days of degradation. In a compost environment, degradation was even faster, and all polymer films were broken into pieces within first 7 days of degradation and no film remained after 15 days.

Keywords: Starch; polycaprolactone; modification; degradation; activated sludge; *Pseudomonas putida*; compost

Language: English

Document Type: Research article

Affiliations: 1: Hacettepe University, Engineering Faculty, Chemical Engineering Department, 06532 Beytepe, Ankara, Turkey. hyavuz@hacettepe.edu.tr **2:** Hacettepe University, Engineering Faculty, Chemical Engineering Department, 06532 Beytepe, Ankara, Turkey

Links for this article

- *http://www.ingentaconnect.com/klu/jooe/2003/00000011/00000003/00469330*
- http://openurl.ingenta.com/content?genre=article&issn=1566-2543&volume=11&issue=3&spage=107&epage=113

ATTACHMENT

9

ELSEVIER

Material Properties

Biopolymers: overview of several properties and consequences on their applications

K. Van de Velde *, P. Kiekens

Department of Textiles, Ghent University, Technologiepark 9, B-9052 Zwijnaarde, Belgium

Abstract

Recently, interest in composite manufacturing has shifted towards the use of natural fibres as reinforcement because of their environmental benefits. The use of a biodegradable matrix is worth considering since this would result in a completely biodegradable composite.

In order to assess the most suitable matrix polymer, one must know the properties of the available polymers. Since data tend to be widely scattered over many sources and are very scarce compared to the conventional polymers, it is the purpose of this article to give an overview of the most relevant properties of a range of biodegradable polymers. An overview such as the one given here may provide a useful guide in establishing the best compromise between conflicting property demands. Data are presented mostly as ranges (in tables) as well as in graphs for quick comparison reasons. One specific application (thermoplastic pultrusion with flax as reinforcement) is also studied. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biopolymers

1. Introduction

Before discussing the different properties of a series of biodegradable polymers [1–25], it may be interesting to elaborate on their current applications.

Many of these applications can be found in the medical field and can be roughly divided into three categories: drug delivery systems, wound closure and healing products, and surgical implant devices [9]. Drug delivery inside the human body can be quite easily controlled with the use of biodegradable capsules [9,31]. In wound healing, resorbable non-wovens for the replacement of human tissue [27], as well as simple sutures, staples, clips or meshes are available [9,28–30]. Related to these

applications, also the use as bioresorbable scaffolds for tissue engineering [22] is worth mentioning.

Other applications are numerous. Many of the biodegradable polymers have good film forming properties, making them suitable for applications in high performance applications as well as in traditional commodity uses [13]. Some applications include food containers, soil retention sheeting, agriculture film, waste bags [16] and the use as packaging material in general [31]. When used as non-wovens, these biopolymers can also be used in agriculture, filtration, hygiene and protective clothing [26].

This list of possible applications is by no means complete. In fact, the number of possible applications is almost infinite. It has also to be remarked that many of the applications involve the fibre form of the biopolymer. Since this paper considers the use as matrix material in a composite, fibre properties are not relevant. However, a few fibre properties will also be discussed.

The quantity of available data is rather limited compared to the data that can be found on conventional poly-

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mers. Therefore a restriction is made in the number of listed properties and studied polymers. More detailed but fragmented data can be found in the consulted literature [1–49]. Many of the data given here varied according to the source [1–25] consulted. Part of this variance is due to differences in standards used. However, most of the differences are thought to be due to differences in polymer types: degree of polymerisation, type and concentration of additives, etc. Besides the overall property ranges, individual data points are also given (in graphs) which gives a better understanding of the mean reported properties.

Composites are commonly based on traditional reinforcement fibres, such as glass fibres. However, natural fibres can also be used as reinforcement. One of the most cited natural fibres for this purpose is flax. This case will be more intensively studied in this paper, but in fact any other case study can be based on the reported properties.

Fig. 1. Structural formulas of some biopolymers [19,25,26,32].

2. Studied materials and properties

There are numerous biodegradable polymers. However, four basic polymers have been chosen, as well as two copolymers and two optically active polymer forms. This selection was based on the quantity of available data for all the reported biopolymers. For convenience reasons, from now on, these polymers will be denoted by their abbreviations:

PLA: Polylactic acid or polylactide.
L-PLA: Poly-L-lactic acid or poly-L-lactide.
DL-PLA: Poly-DL-lactic acid or poly-DL-lactide.
PGA: Polyglycolic acid or polyglycolide.
DL-PLA/PGA 50/50: copolymer of 50% DL-PLA and 50% PGA (molar percentages).
DL-PLA/PGA 75/25: copolymer of 75% DL-PLA and 25% PGA (molar percentages).
PCL: Poly-ε-caprolactone.
PHB: Polyhydroxybutyrate.

The structural formulas of the four basic polymers are given in Fig. 1. All these polymers are polyesters. Furthermore, PLA contains an asymmetrical carbon atom in its structural unit that enables it to become optically active. In this way, it is possible to obtain the isotactic L-PLA and D-PLA polymers. Consequently, DL-PLA is a syndiotactically alternating D,L-copolymer or a copolymer having L-and D-units. However, the exact nature of this D,L-copolymer is never explicitly stated in the literature. Mostly, even no D- or L-designation can be found. The latter findings have been gathered under 'PLA' and are thought to be mostly non-syndiotactic DL-PLA.

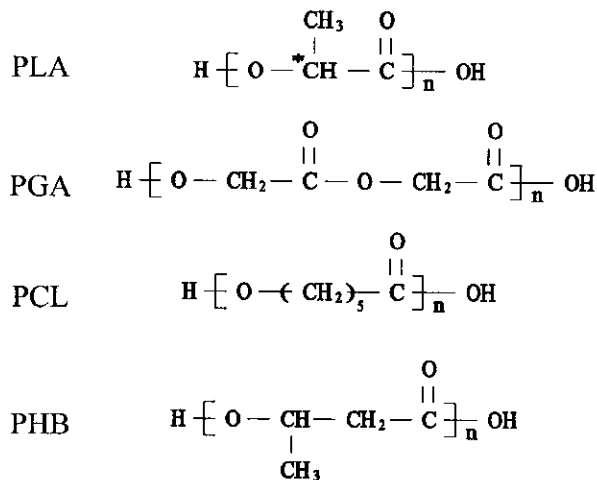Both polylactide and polylactic acid (or polyglycolide

and polyglycolic acid) are terms that are used. PLA (and PGA) can be made from the original acid as well as from the cyclic lactide (or glycolide). These last products can be obtained by intermolecular splitting of water from the acids. The lactides are, furthermore, still optically active as can be seen in Fig. 2. Also visible in this figure is the fact that also a meso-lactide, which is optically not active, can be formed [3].

The following properties are more intensively studied:

- Polymer density (ρ, in g/cm^3).
- Tensile properties: tensile strength (σ, in MPa), tensile modulus (E, in GPa) and ultimate strain (ϵ, in %).
- Specific tensile properties are obtained by dividing the original properties by the polymer density, leading to: specific tensile strength (σ^*, in Nm/g) and specific tensile modulus (E^*, in kNm/g).
- Characteristic temperatures: glass transition temperature (T_g, in °C) and melt point (T_m, in °C).

Less documented cases on other properties and biopolymers could also be found in the literature. These data were too fragmentary to be included in the tables and graphs. However, attention will also be drawn to these properties if considered important enough.

Further details on these properties will be given later. Mostly, no reference to the used standard could be found. The standards quoted for the determination of certain properties are therefore not always the only possible ones used.
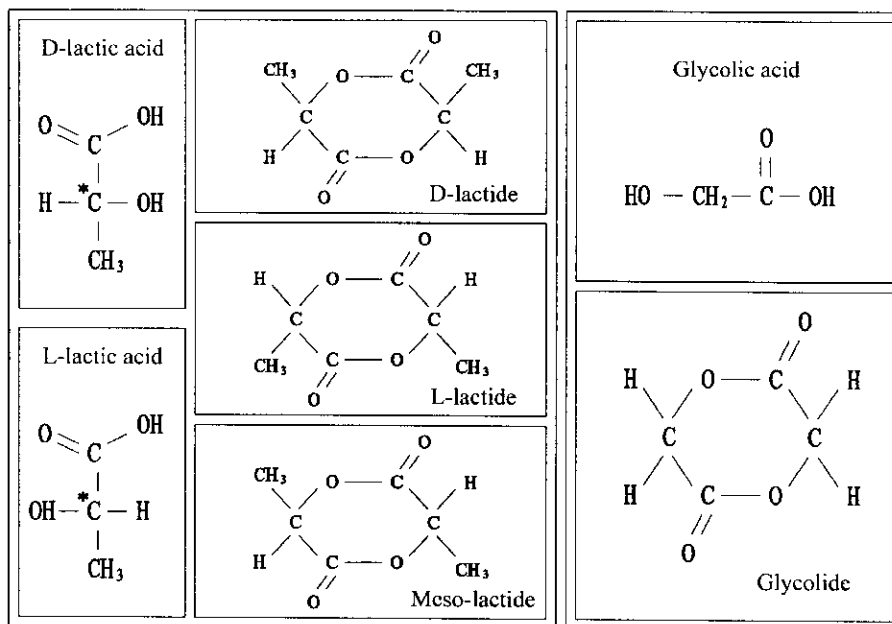
Fig. 2. Structural formulas of some monomers for the production of PLA and PGA [3,16].

3. Properties

3.1. Physical properties

The density of a series of biopolymers is given in Table 1 and Fig. 4. Reported values are mostly based on standards such as ASTM D792. Density can be a very important design parameter since elevated density values imply high transportation costs (e.g. light car parts reduce energy consumption). Implementation of the material also becomes much easier and less hazardous when lighter. Density is often used for the calculation of 'specific properties', i.e. dividing mechanical properties by the appropriate density. These specific properties consequently give a better notion of the intrinsic strength of the construction one wants to build. This will be explained later in Section 3.3.

In the case of flax reinforcement, (DL)-PLA, PCL and PHB seem to be the best choices since it is the purpose to produce a composite as light as possible. Apart from the values given in Table 1 and Fig. 4, the density data — 1.02 g/cm³ — found on PHO (polyhydroxyoctanoate) may also seem interesting [13]. However, calculation of the specific mechanical properties might result in different conclusions.

Aiming for a low density can also be a reason for selecting flax as composite reinforcement: its density of 1.45 g/cm³ is significantly lower than that of the more conventional glass fibre reinforcement (2.54 g/cm³).

Fragmented data on several other useful properties could be found: crimp [5,20], melt flow indices [1–

5,12,17,22,33,34,39,40], impact properties [2,3,5,12,17,32], hardness [12,14,17], vapour transmission characteristics (mainly for film applications) [1,4,13,18,35–37], compostabilities [1,2,33–37], coefficients of friction [1], surface energies [1] and contact angles with water [38]. Since data on these and other properties were so fragmentary, they were nearly impossible to evaluate.

A very important property is the water content or water uptake of the biopolymer resin. Only values for PLA resins are known [4,38] and they are situated near 0.5%. In fact the main PLA manufacturer (Cargill Dow) explicitly specifies that water should be removed from the resin — by drying — up to a level below 250 ppm, in order to make good processing of the pellets possible. All the biopolymers studied here are rather hydrophilic polyesters and so it is believed that moderate water uptake takes place when these polymers are exposed to water. Especially in composites, water absorption should be considered a disadvantage. Migration of water through the polymer can lead to a disturbance of the fibre/polymer interface, reducing the overall strength of the composite. In the case of flax reinforcement this could be even more dramatic since flax tends to absorb rather large amounts of water when exposed to it. The resulting swelling could lead to severe loss in composite strength. It might therefore be necessary to modify the flax in order to lower its water uptake significantly. The similarity between matrix and fibre polarities, on the other hand, might prove to enhance adhesion.

Compared to conventional polypropylene (PP) that

Table 1
Physical properties of various biopolymers [1–25]

Properties	Limits	Type of biopolymer							
		PLA	L-PLA	DL-PLA	PGA	DL-PLA/PGA 50/50	DL-PLA/PGA 75/25	PCL	PHB
ρ (g/cm^3)	Upper	1.21	1.24	1.25	1.50	1.30	1.3	1.11	1.18
	Lower	1.25	1.30	1.27	1.707	1.40		1.146	1.262
σ (MPa)	Upper	21	15.5	27.6	60	41.4	41.4	20.7	40
	Lower	60	150	50	99.7	55.2	55.2	42	
E (GPa)	Upper	0.35	2.7	1	6	1	1.38	0.21	3.5
	Lower	3.5	4.14	3.45	7	4.34	4.13	0.44	4
ϵ (%)	Upper	2.5	3	2	1.5	2	2.5	300	5
	Lower	6	10	10	20	10	10	1000	8
σ^* (Nm/g)	Upper	16.8	40.0	22.1	40.0	30.9	31.8	18.6	32.0
	Lower	48.0	66.8	39.4	>45.1	41.2	42.5	36.7	33.9
E^* (kNm/g)	Upper	0.28	2.23	0.80	4.00	0.77	1.06	0.19	2.80
	Lower	2.80	3.85	2.36	4.51	2.14	2.12	0.38	2.97
T_g (°C)	Upper	45	55	50	35	40	50	−60	5
	Lower	60	65	60	45	50	55	−65	15
T_m (°C)	Upper	150	170	am.	220	am.	am.	58	168
	Lower	162	200		233			65	182

am.: amorphous and thus no melt point.

was in a previous paper [50] selected as the most convenient conventional thermoplastic matrix, the densities found here are rather high.

Another important property is the degradation time [4,9,14,19]. With respect to disposal policy, this degradation time should be as short as possible. Corrosion resistance, on the other hand, might decrease too heavily when the polymer has an extremely short degradation time. Depending upon the source and the test procedure, these times range from several months (for the PLA/PGA copolymers) to over 2 years (for L-PLA). PGA and (DL)-PLA degrade after roughly 1 year. No data on PHB could be found. Based on these limited data, one can already conclude that the PGA/PLA copolymers seem to degrade too quickly to consider them for use in high performance composites.

3.2. Mechanical properties

Only tensile properties (ASTM D882, ASTM D638) are given in Table 1 and Fig. 3. These properties include: tensile strength (σ, in MPa), tensile modulus (E, in GPa), and ultimate tensile strain (ϵ, in %). No flexural properties are given here since data on these properties [3–5,18,41] was too limited to use in a comparison. Flexural and tensile properties are mostly correlated anyway and

the tendencies found here, are probably the same as found when comparing flexural properties.

Tensile properties are clearly best for the densest reported polymers, especially for PGA. PCL, on the other hand, seems to be the weakest polymer with a remarkable high strain at failure. It has to be remarked that molecular mass can play a very important role in the obtained mechanical properties. Varying the molecular mass from 50,000, over 150,000 to 200,000 will yield tensile strengths for L-PLA [3] of 15.5, 80 and 150 MPa, respectively.

When used as a matrix in a unidirectional composite, however, these mechanical polymer properties are not very important since the reinforcing (flax) fibre provides most of the composite strength [50]. For example, when a composite with a strength of 400 MPa and modulus of 23 GPa is required, one can calculate the volume percentage (v_f) that is needed, using a rule of mixtures. If a strength of 750 MPa and a modulus of 45 GPa is taken for the reinforcement (typical for flax), this results in the volume percentages given in Table 2. Typical polymer properties that are also needed for the calculation are also given in Table 2. Again using the rule of mixtures, the composite density can be obtained as well (Table 2; flax density is set at 1.45 g/cm^3). Apparently the presence of PGA leads to the heaviest types of composites (with
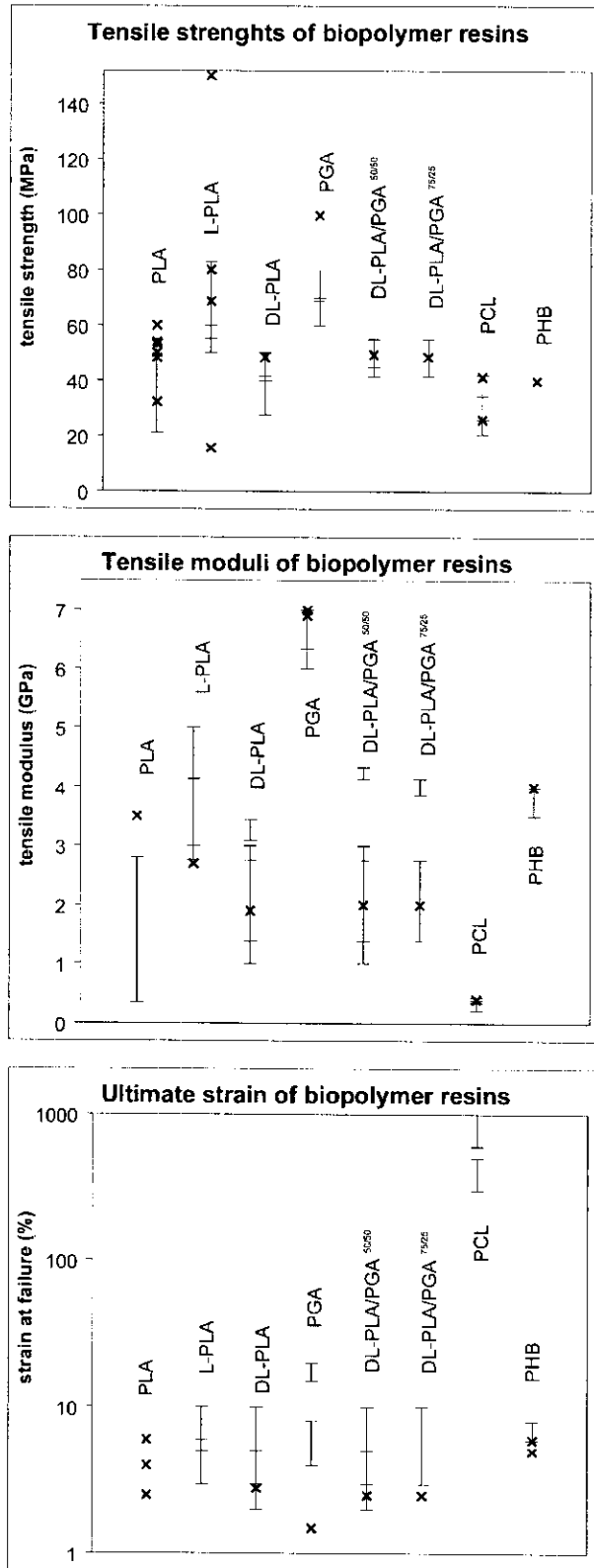
Fig. 3. Tensile properties of various biopolymers [2–5,7,9,12–19].

equal mechanical properties). PLA and PCL seem to lead to the lightest composites, with a relatively high v_f needed. High v_f values may be desirable since this would result in less use of expensive polymer (as far as good wetting of the fibre is still achievable). Even a biopolymer as weak as PHO (polyhydroxyoctanoate) with $\sigma=9$ MPa and $E=8$ MPa [13] would be suitable as a matrix, since the v_f needed is hardly any higher (51–53%) than the ones given in Table 2. The resulting composite density would be even lower (1.24–1.25 g/cm^3) than the one for PCL/flax. It seems that the weaker the matrix polymer gets, the lighter the resulting composite will be, while the composite mechanical properties seem hardly affected at all.

In order to a have a broader view on the effect of matrix type on the expected composite properties, one can also look at Figs. 6 and 7. These figures show the expected composite properties — expressed as specific properties — as a function of the reinforcement level. By using specific properties, the difference in density is also taken into account. Again PLA and PCL (also PHB) seem to be the best candidates for composite matrix use. This is most clear in the detailed parts of the figures, which are chosen to be the most likely v_f interval. It is also clear that increasing use of PGA progressively leads to composites with worse specific mechanical properties.

Up till now — based on the densities and mechanical properties — preference for the selected application (pultrusion with flax as reinforcement) is given to PLA and PCL, or any light biopolymers in general.

3.3. Specific mechanical properties

In Fig. 4 one can find the specific tensile strength and tensile modulus ranges for the different biopolymers. These values were obtained by dividing the original mechanical properties by the density. If either density or the mechanical property was not available within the same reference, no specific data were calculated. This restriction was necessary since it is likely that the polymers' density is related to its mechanical properties.

If one would like to use the biopolymers as structural element without using reinforcement, specific properties become important as they determine the dimensions necessary for a certain mechanical strength or stiffness.

Contrary to the usefulness as composite matrix, in this case, PGA and L-PLA seem the best choices, whilst PCL and also PHO (polyhydroxyoctanoate, $\sigma^*=8.8$ MPa and $E^*=7.8$ MPa) are clearly the worst ones.

3.4. Characteristic temperatures

Characteristic temperatures of a polymer can be determined in several ways, but DSC (differential scanning calorimetry) is the most cited one.

The flexibility of amorphous polymers is reduced

Table 2

Composition and density of flax fibre based composites with σ=400 MPa and E=23 GPa

Biopolymer type	Typical polymer properties			Composite (σ=400 MPa and E=23 GPa) properties			
	σ (MPa)	E (GPa)	ρ (g/cm³)	Based on desired σ		Based on desired modulus	
				v_f (%)	ρ (g/cm³)	v_f (%)	ρ (g/cm³)
PLA	50	2.5	1.24	50.0	1.35	48.2	1.34
L-PLA	75	3.0	1.26	48.1	1.35	47.6	1.35
DL-PLA	45	2.5	1.26	50.4	1.36	48.2	1.35
PGA	75	6.5	1.61	48.1	1.53	42.9	1.54
DL-PLA/PGA 50/50	50	2.5	1.35	50.0	1.40	48.2	1.40
DL-PLA/PGA 75/25	50	2.5	1.30	50.0	1.38	48.2	1.37
PCL	30	0.35	1.13	51.4	1.29	50.7	1.29
PHB	40	4.0	1.24	50.7	1.35	46.3	1.34

Typical flax properties: σ=750 MPa and E=45 GPa.

drastically when they are cooled below a characteristic transition temperature called the glass transition temperature (T_g). At temperatures below T_g, there is no segmental motion and any dimensional changes in the polymer are the result of temporary distortions of the primary valence bonds. Amorphous plastics — such as all the DL-PLA containing ones — perform best below T_g, but elastomers must be used above the brittle point [42]. The glass transition temperature (given in Table 1 and Fig. 5) can be very important when studying mechanical properties. These properties are always obtained in standard conditions (comparable to room temperature), but one should know that they may decrease at higher temperatures and that the glass transition temperature may be a limit above which mechanical properties may degrade drastically.

In the specific case of a flax reinforced plastic, the application temperature of the product should remain relatively low (e.g. maximum 100°C) because of the possible degradation of flax when exposed to elevated temperatures for prolonged time (Figs. 6 and 7). All the studied biopolymers have already surpassed their T_g at this temperature but this is not necessarily a problem since the major part of the composite strength (unidirectionally reinforced composite) is determined by its fibres. However, all DL-PLA containing biopolymers can probably be rejected for use in composites since — besides their low T_g (40–60°C) — they are amorphous. PGA and PHB have a T_g near to regular ambient temperatures. Further study of the mechanical properties above these temperatures should be done prior to using these polymers as composite matrix in applications above regular ambient temperatures. The same can be said about PHV (polyhydroxyvalerate) with a T_g of 5°C [43] and Biopol (PHB/PHV copolymer with 5–12% PHV) with a T_g of 18–22°C [32]. The other studied

biopolymers (PCL, L-PLA and PLA) would probably do better since their glass transition temperatures are distinctly different from normal ambient temperatures. On this basis also PHO (polyhydroxyoctanoate) would be acceptable for use as matrix material since its T_g is −35°C [13].

The melting point (T_m, also given in Table 1 and Fig. 5) is a more important parameter. Above it, whole polymer chain mobility occurs and the mechanical properties are virtually reduced to zero. Together with the melt points one should also look at the process temperatures. These are by definition significantly higher than the melt points because at these higher temperatures viscosity is reduced drastically in order to improve processability. These temperatures are not given in Table 1 since only data on PLA, ranging from 190 to 250°C [1,2,5,20,33–37], could be found. Generally the processing temperatures are 20–100°C higher than the melt points [50]. This range mainly depends upon the use of additives that can prevent thermal degradation of the polymer at elevated temperatures. A low process temperature (and melt point), on the other hand, may be advantageous when considering the energy cost of the production process.

In the specific studied case, temperatures already have to be kept relatively low in order to prevent the degradation of the flax. And since the purpose is to produce an environmentally friendly product, low energy consumption is to be considered as an extra advantage. Studying Fig. 5 leads to the conclusion that PGA and PCL are not suited for use in combination with flax. PGA would require process temperatures — possibly higher than 250°C — that would lead to thermal degradation of the flax, while PCL has such a low melt point that application of the composite should be limited to temperatures below 58°C. This is also the case for PHO (polyhydroxyoctanoate) with a melt point of 61°C [13]
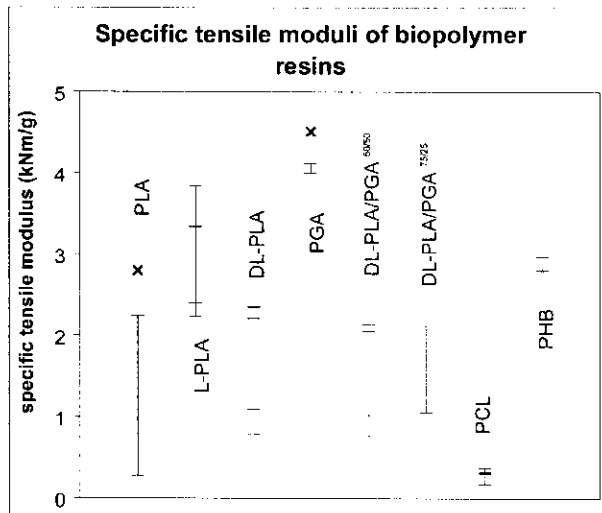
Densities of biopolymer resins

Glass transition temperatures of biopolymer resins

Specific tensile strenghts of biopolymer resins

Melt point of biopolymer resins

Fig. 5.   Thermal properties of various biopolymers [1,3,4,6,8–13,15–25].
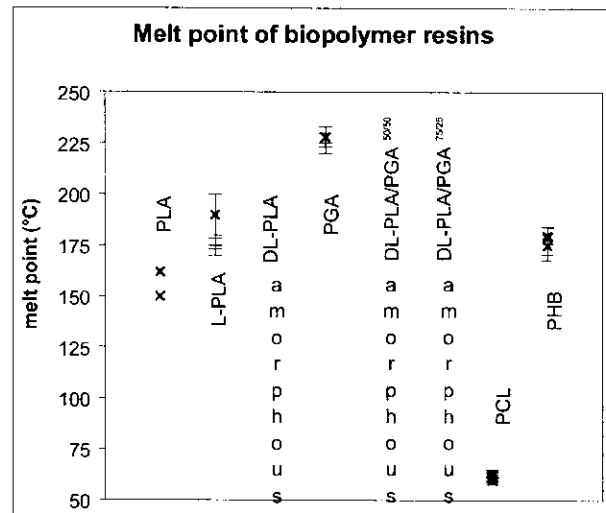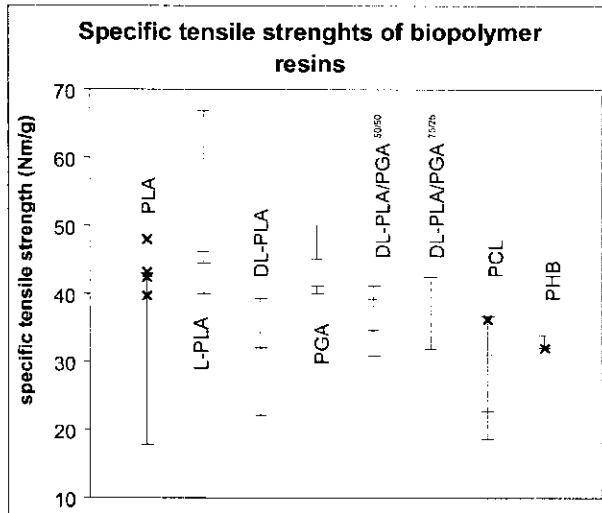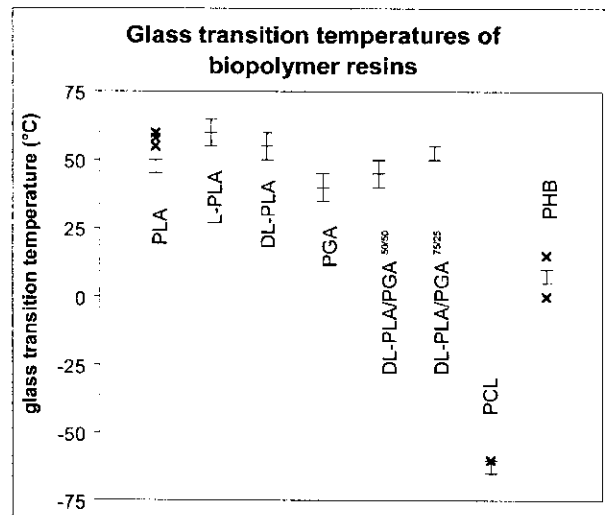
Specific tensile moduli of biopolymer resins
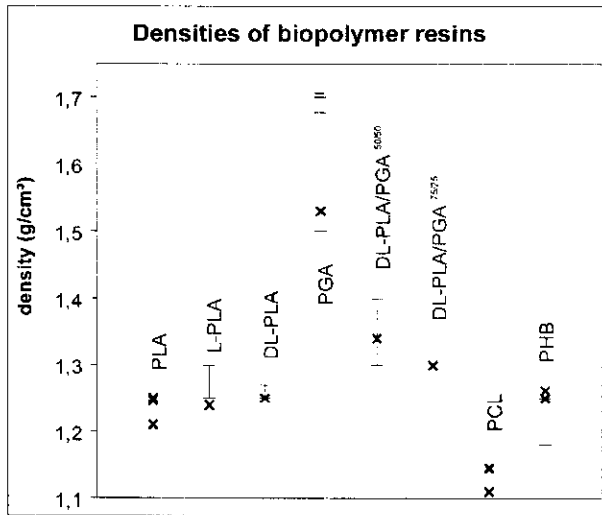
Fig. 4.   Densities and specific tensile properties of various biopolymers [1–13,15].

and, to a lesser extent, for PHV (polyhydroxyvalerate) with a melt point of 105–108°C [3]. L-PLA, PLA and PHB have all ideal melt points since they are high enough for sufficient thermal stability of the composite as well as low enough to limit flax degradation and energy costs. The same can be said for Biopol (PHB/PHV copolymer with 5–12% PHV) with a melt range from 144 to 170°C [3,32].

Only crystalline polymers have a melting point. Furthermore, crystalline regions in the polymer tend to improve the adhesion with a reinforcing fibre. Percentages of crystallinity found in literature range from 25% for PHO to 80% for PHB [3,13,18,19,44]. All other listed crystalline polymers have comparable percentages of crystallinity (37–55%). Based on crystallinity, preference for use in composites should be given to PHB.
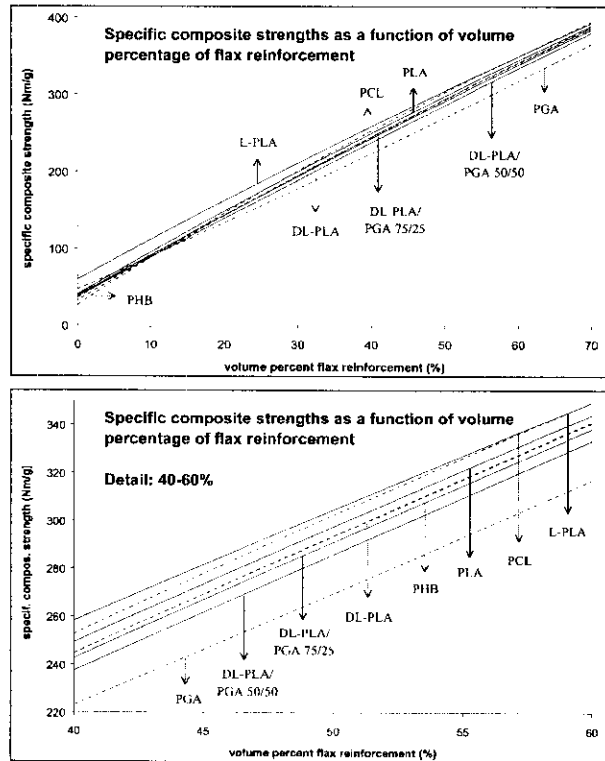
Fig. 6.   Specific composite strengths as a function of volume percentage of flax reinforcement.
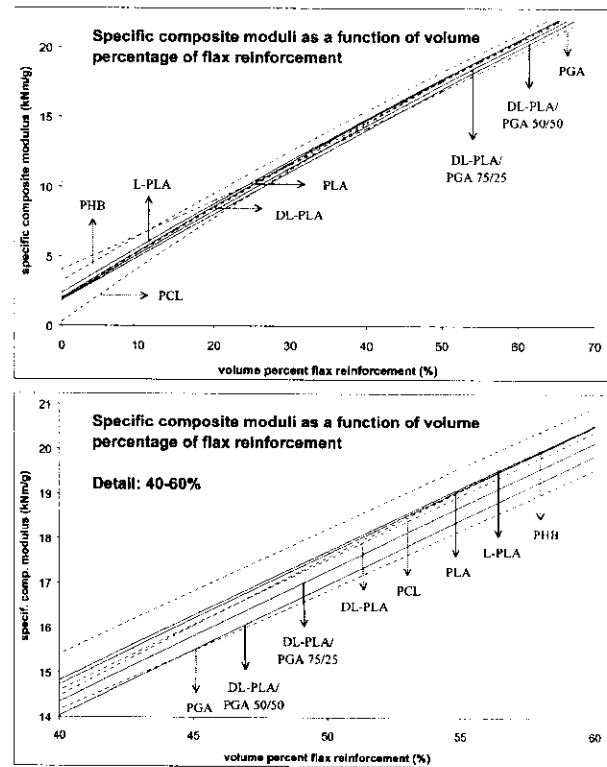

Fig. 7.   Specific composite moduli as a function of volume percentage of flax reinforcement.

3.5. Fibre mechanical properties

Sometimes, mechanical properties of polymer fibres can be found. As an example, tenacity (tensile strength, in MPa) and tensile modulus (in GPa), together with the production methods of some biopolymers are given in Table 3. It should be clear that these values cannot be used for design calculations unless the fibres are kept in their original form. The fibres display such high mechanical properties because of the high degree of orientation of the polymer chains in the fibre. The influence of the polymer type apparently is of secondary importance and only becomes important when the material is melted again.

4. Conclusions

It has been the purpose of this paper to search for the most suitable thermoplastic biopolymer matrix for a flax fibre reinforced composite. Density and temperature related properties seemed to be the limiting criteria for the choice of a suitable polymer. As has been pointed out, the mechanical strength of the biopolymer is not very important for this particular application.

PGA is easily eliminated as a candidate for composite

Table 3
Biopolymer fibre properties [28–30,33,34,45–49]

Biopolymer type	Fibre production method	σ (MPa)	E (GPa)
PLA	conventional melt spinning	313·642	5.6
L-PLA	melt spinning + hot drawing	500–870	9.2
L-PLA	solvent spinning + hot drawing	1000–1200	12 15
DL-PLA	dry spinning or melt spinning + hot drawing	190–1000	(data not available)
PHB	high-speed melt spinning + hot drawing	330	7.7

matrix use as its density and melt point are too high in order to be energy saving. Also, high processing temperatures would cause flax degradation. PCL on the other hand may be light enough but its melt temperature is too low in order to be used in a composite exposed to slightly elevated temperatures. The DL-PLA/PGA copolymers seem to be too easily degraded, which could be an indication of low corrosion resistance, and furthermore they are amorphous which would lead to bad adhesion with the reinforcing fibre. In fact, any studied polymer based on DL-PLA is amorphous and glass transition temperatures are too low to ensure resistance to slightly elevated temperatures. Some other, not well-documented biopolymers can also be eliminated for use as matrix in flax fibre reinforced composites. For instance PHO may lead to light composites but its melt temperature is too low (as is the case for PHV).

PLA (and L-PLA) seem to score well on all the discussed properties: polymer and composite densities are low; degradation behaviour, mechanical properties and glass transition temperatures are acceptable and their melt points are almost ideal in order to produce flax fibre reinforced composites. Preference should be given to PLA rather than to L-PLA since the latter is likely to be more expensive and PLA is already commercially available.

The use of PHB or PHB based copolymers such as Biopol may also be possible in this studied case. Density and melt point are optimal for these polymers but the low glass transition temperature may be a problem.

Since all studied biopolymers are likely to be sensitive to water, it is probably also necessary to modify the flax in order to render it less sensitive to water.

In general, the properties that are reported here may help to decide on choosing the right biopolymer for many given problems. As already mentioned, one best first selects some limiting properties and then further selects the polymer with the best overall properties.

Acknowledgement

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
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Biodegradation of Agricultural Plastic Films: A Critical Review

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Abstract:

The growing use of plastics in agriculture has enabled farmers to increase their crop production. One major drawback of most polymers used in agriculture is the problem with their disposal, following their useful life-time. Non-degradable polymers, being resistive to degradation (depending on the polymer, additives, conditions etc) tend to accumulate as plastic waste, creating a serious problem of plastic waste management. In cases such plastic waste ends-up in landfills or it is buried in soil, questions are raised about their possible effects on the environment, whether they biodegrade at all, and if they do, what is the rate of (bio?)degradation and what effect the products of (bio?)degradation have on the environment, including the effects of the additives used. Possible degradation of agricultural plastic waste should not result in contamination of the soil and pollution of the environment (including aesthetic pollution or problems with the agricultural products safety). Ideally, a degradable polymer should be fully biodegradable leaving no harmful substances in the environment. Most experts and acceptable standards define a fully biodegradable polymer as a polymer that is completely converted by microorganisms to carbon dioxide, water, mineral and biomass, with no negative environmental impact or ecotoxicity. However, part of the ongoing debate concerns the question of what is an acceptable period of time for the biodegradation to occur and how this is measured. Many polymers that are claimed to be `biodegradable' are in fact `bioerodable', `hydrobiodegradable', `photodegradable', controlled degradable or just partially biodegradable. This review paper attempts to delineate the definition of degradability of polymers used in agriculture. Emphasis is placed on the controversial issues regarding biodegradability of some of these polymers.

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