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BIODEGRADABLE PLASTICS BASED ON CELLULOSE ACETATE

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ABSTRACT

It is generally known that secondary cellulose acetate (with 53 to 56% acetyl groups) is suitable for thermoplastic processing. With appropriate plasticizers a plastic material is obtained which excels in transparency and pleasant texture, and it is therefore often used for tool handles, combs, spectacle frames, and the like. In principle, cellulose acetate with such a degree of substitution is biodegradable, although degradation proceeds extremely slowly. However, when common plasticizers are substituted by specific esters and other low molecular components (at least 30% by weight), the "plastic material" has the same thermoplastic properties but will decompose in soil or water within just a few years. For example, a cellulose acetate cup buried in sewage sludge lost more than 70% of its original weight within about 18 months. In an aqueous environment (Sturm's test), the decomposition amounted to more than 60%. Under appropriate composting conditions or conditions of anaerobic fermentation, the degradation process is likely to be even faster. However, the material can also be recycled or incinerated without residue. This new kind of biodegradable plastics can be processed on conventional injection molding machines or on extruders adapted to their specific processing properties. They can be turned into granular materials, strips and films, and into injection molded and extrusion blow-molded shapes. The material properties are comparable to those of the known cellulose ester-based plastics. Films and thin-walled hollow bodies are highly transparent. The mechanical properties compare well with those of conventional packaging materials. The thermal resistance is somewhat

lower, but the permeability to steam and oxygen is relatively high compared to that of standard plastics. The material is resistant to oils and fats and, for a short while, even to weak acids and alkalies.

INTRODUCTION

The reorientation concerning waste prevention and minimization has led to the development of new packing materials and techniques. Politicians, industrialists, and the general public are now advocating the total prevention, or at least the reduction, of packaging waste and the reutilization of packing materials. Like other recycling plastics, the new biologically degrading materials are in fact reutilized because they are composted and returned to natural cycles.

Table 1 shows the three most important completely biodegradable plastics currently available in Europe [1]. With a total of 500,000 tons per year (tpy), the substitution potential of packing materials in the food (250,000 tpy) and nonfood (250,000 tpy) sectors is fairly great [1]. In view of this demand, the German government, for example, supported research and development concerning renewable raw materials with roughly 88 million DM in 1992 [2]. A major portion of this budget was spent on the development of new packing materials [3–7].

Waste disposal is one of the most important aspects in connection with biodegradable plastics. Like standard plastics, many of the "bioplastics" can be recycled; at the end of their life cycle, however, they cannot only be incinerated, deposited in landfills, or subjected to pyrolysis, but can also be disposed of by biological means. Although some technical problems still remain to be solved, the new plastics can in principle be degraded either by large-scale composting or by industrial anaerobic fermentation. Most of them will also decompose in natural water bodies or biological sewage treatment plants.

These new plastics are usually based on natural raw materials such as starch and cellulose. German industry, for example, processed about 155,000 tons of chemical conversion pulp in 1988 [5]. It is known from the relevant literature that

TABLE 1. Biodegradable Plastics (1992)

Trade name	Manufacturer	Annual capacity (tons) (in part estimated)	Annual production (tons) (in part estimated)	Uses
Biopol	ICI	300	50	Shaped parts, films + sheets, medical carrier materials
Mater Bi	Novamont	>5000	>500	Shaped parts, films + sheets
Biocéta	Tubize Plastics	>1000	100	Shaped parts, films + sheets

some cellulose derivatives are decomposed by fungi and bacteria, but that this biological process takes significantly longer than the decomposition of the cellulose itself. By means of appropriate additives, the degrading time of the cellulose-based plastics that are described here has been drastically shortened; in fact, it is comparable to that of such slowly degrading cellulose as oak leaves.

CELLULOSE ACETATE PREPARATION

As cellulose acetate makes up the major part of the new kind of biodegradable plastic, it is suitable to describe very briefly the preparation of this polymer produced from wood or cotton linters.

Thermoplastic cellulose acetate must be prepared from high-grade cellulose. This cellulose is obtained either from specific fast growing trees that are cultivated on plantations or from cotton linters. The plant materials are converted into kraft pulp by sulfate digestion. New, sulfurless methods, such as the organocell process, might also be used. Methylene chloride-acetic acid processing turns the cellulose into cellulose acetate which, in pulverized form, then serves as the basic polymer component of the new "plastic" material.

FABRICATION OF THE BIODEGRADABLE PLASTIC

The powdered cellulose acetate is mixed with liquid additives at a ratio of about 2/3:1/3. The additives are specific low-molecular weight and oligomeric compounds which, when taken alone, biodegrade relatively fast. These additives are also nontoxic. A high-speed mixer with a special agitator is used to mix the components thoroughly. The fine-grained homogeneous powder that results is granulated in a standard extruder.

Important processing parameters are a 20–30 D screw-type mixer, a temperature between 160 and 190°C, and predrying of the material for about 2 hours at around 70°C.

Given adequate processing conditions, a circular pelletizer will produce transparent and lustrous cylindrical granules. Any inhomogeneities in the extruded material, or insufficiently molten particles, will show up as white spots in the granules. The granular material can then be subjected to thermoplastic processing; for example, injection molding, extrusion blow molding, sheet and profile extrusion, or film blowing.

The plastic granules must be kept absolutely dry during intermediate storage.

PROCESSING

By using a single-screw or a twin-screw extruder, the granular material can be processed into strands, sheets, and films.

After a certain retention time, the material will form a homogeneous melt with only relatively little mechanical energy having to be expended. The melt will solidify and form a highly transparent mass when exposed to a minor tensile force.

It can be blow-extruded into hollow bodies or films with appropriately adjusted blow heads. Injection molding is also possible with the usual machinery and without any specific preparations. The body walls and sheets or films will be slightly turbid when somewhat thicker, possibly because the polymer molecules are oriented in a certain direction.

Material scraps can be completely recycled after having been carefully sorted. Up to 20% recyclings can be admixed to newly prepared material for many uses.

PROPERTIES

Some properties are presented in Table 2.

At temperatures above 200°C, the material begins to decompose gradually. It is combustible but generates no toxic decomposition products when incinerated.

The short-time and medium-time resistance against water, weak acids, lyes, oils, and gasoline is good, but it may absorb a certain volume of water and it is permeable to water vapor and alcohol. The material tends to shrink when exposed to heat for an extended time; it remains flexible at temperatures below −20°C.

Bottles and similar vessels have a slight smell of vinegar inside.

BIODEGRADATION TESTS

Aerobic and anaerobic degradation tests were performed to demonstrate the biodegradability of the material. In particular, Sturm's test was used to determine the degradation rate quantitatively. For this test a material sample is comminuted and put into an aqueous bioactive medium that is aerated without carbon dioxide. The carbon dioxide that forms during the degradation is taken up in barium hydroxide which is then back-titrated. The carbon dioxide content that is identified serves as the basis from which to derive the carbon content of the degraded substance. Based on the original material quantity, a scale can be established extending from zero to 100% degradation (Fig. 1)

TABLE 2. Property Profile of the New Cellulose-Based Plastics

Density	1.27 g/cm^3	DIN 53479
Shore hardness D	70–75	
MFI (210°C/2.16 kg)	6–8 g/10 min	DIN 53735
Deflection temperature:		
At 0.46 MPa	>70°C	DIN 53461
At 1.82 MPa	>55°C	DIN 53461
Tensile strength at break	40 MPa	DIN 53455
Percentage elongation at break	15%	DIN 53455
Modulus in tension	>1200 MPa	DIN 53457
Flexural strength	40 MPa	DIN 53452
Modulus in flexure	>1000 MPa	DIN 53457
Impact strength, notched	>4 kJ/m^2	DIN 53453

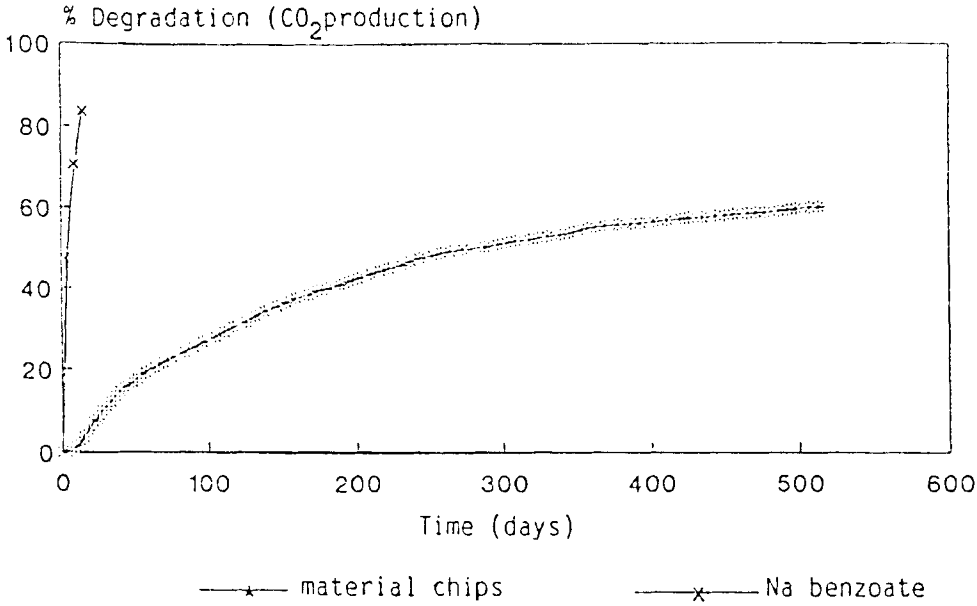

FIG. 1. Biodegradation in an aqueous medium (Sturm's test).

To measure the degradation rate under anaerobic conditions, a small cup (i.e., a commemorative handle holder) was embedded in wet bioactive sewage sludge. The loss of material was then determined at relatively large intervals by cleaning and weighting the sample (Fig. 2).

Scanning electron micrographs (Figs. 3 and 4) clearly show the microbial attack on a plastic film that was originally transparent, and the structural change of the said film. (Both micrographs have the same resolution.)

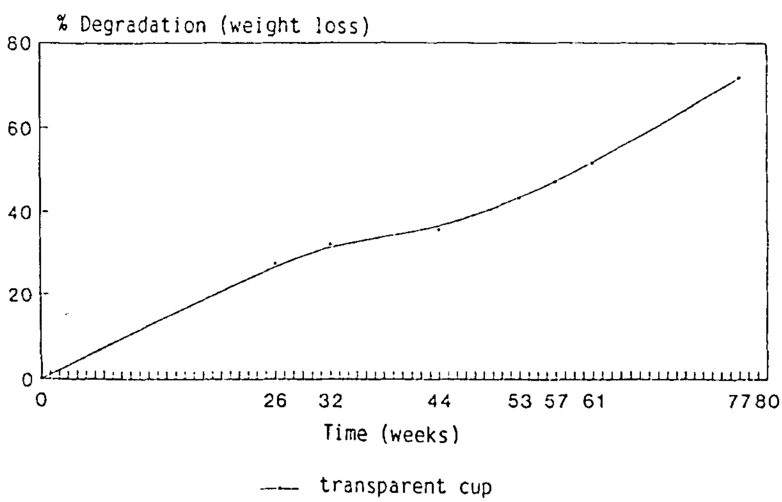

FIG. 2. Biodegradation in soil/sewage sludge.

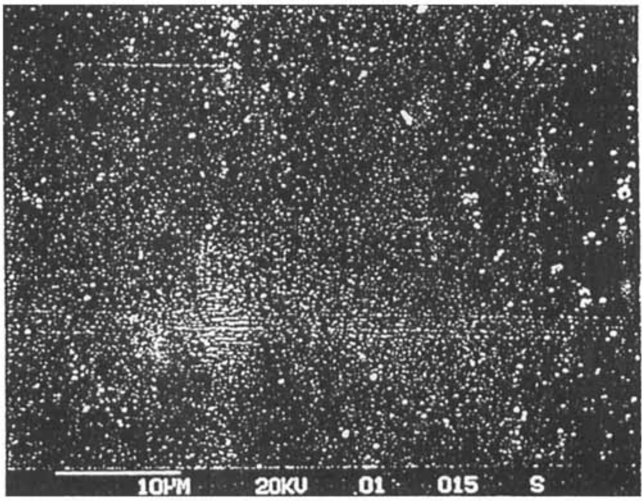

FIG. 3. Scanning electron micrograph of the untreated film.

APPLICATIONS

The main field of application of the new plastic material is packaging. It can be formed into sheets and films, blister packages, hollow bodies (boxes), bottles, and cans. However, as the material is somewhat permeable to water and alcohol, it cannot easily be used for bottles for these liquids, but it is rather more suitable

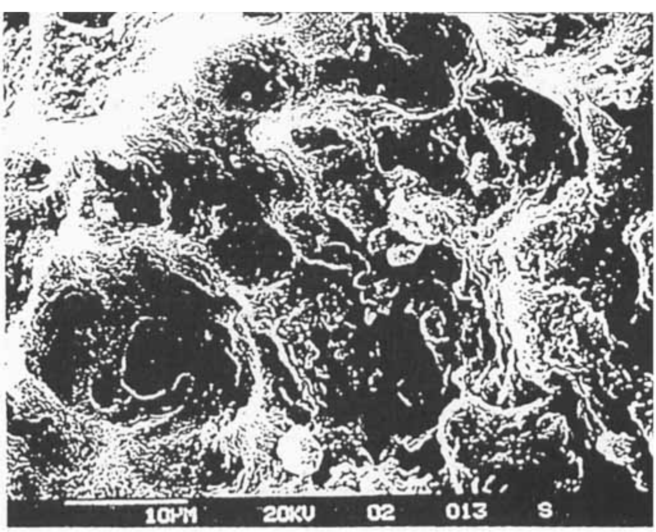

FIG. 4. Scanning electron micrograph of a biodegrading film.

for dry packaging. It is not yet approved for packing food and pharmaceutical products.

The material is resistant to biodegradation for several years when kept in a normal ambient environment. Thick-walled containers will remain unchanged in a natural humid environment for at least 6 months without showing any signs of microbial attack.

With the exception of its permeability to water and alcohol, the material properties, and hence the possible uses, are similar to those of the usual plastic packing materials. Adhesive joining, for example with paper, printing, and sealing, are also possible.

The transparency and the luster of the new plastic are even better than those of many other mass-produced plastics, and the material is soft and pleasant to touch.

DISPOSAL

The new material has been developed with a view to biological disposal. In fact, it degrades in soil and water within several years.

Ideally, however, it should be collected with other biodegradable wastes such as paper and plant residues for subsequent composting or fermentation. This will require collection and disposal routes at the communal level.

The new plastic can also be recycled, but it should be noted that even minor portions of other plastics, such as polyolefins and polyvinyl chloride, will be disadvantageous.

The material can be incinerated without residues. No toxic decomposition products will result, provided enough air is fed into the waste incinerator.

Depending on the landfill structure and other conditions, the material degrades more slowly in landfills than when composted or fermented.

CONCLUSIONS

This new, cellulose acetate-based biodegradable plastic is a promising alternative to many of the known mass-produced plastic materials. Compared with other biodegradable materials, it is relatively resistant and, in the form of sheets, films, or shaped bodies, its properties are hardly different from those of "classical" plastics.

However, the material properties can be further improved. For example, the composting rate might be increased, the smell of the material reduced, its thermal stability enhanced, and at the same time its heat shrinkage and permeability to water vapor might also be reduced. It goes without saying that these improvements cannot be made simultaneously, but the properties of the material can be optimized for different uses.

As regards waste disposal, appropriate logistic systems are still lacking for any kind of biodegradable material. In view of the growing demand and increasingly widespread use of such materials, solutions should be sought fairly soon.

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