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BIODEGRADABLE BLENDS OF CELLULOSE ACETATE AND STARCH: PRODUCTION AND PROPERTIES

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ABSTRACT

Blends of cellulose acetate (2.5 degree of substitution) and starch were melt processed and evaluated for mechanical properties, biodegradability during composting, and marine and soil toxicity. Formulations containing, on a weight basis, 57% cellulose acetate (CA), 25% corn starch (St) and 19% propylene glycol (PG) had mechanical properties similar to polystyrene. Increasing plasticizer or starch content lowered tensile strength. Simulated municipal composting of cellulose acetate alone showed losses of 2–3 and 90% dry weight after 30 and 90 days, respectively. CA/St/PG blends in both soil burial and composting experiments indicate that propylene glycol and starch are degraded first. Extended incubations are required to detect losses from cellulose acetate. Marine toxicity tests using polychaete worms and mussels showed no toxicity of cellulose acetate or starch. High doses had an adverse effect due to oxygen depletion in the marine water due to rapid biodegradation of the polymers. Preliminary plant toxicity tests of the CA/St blends showed no negative impact on growth and yield for sweet corn, butternut squash, and plum tomatoes. The results indicate that CA/St blends have acceptable properties for injection-molded applications and are biodegradable and nontoxic.

INTRODUCTION

Concerns over entrapment and ingestion hazards associated with persistent plastics in the environment have spurred research in developing materials which can function like plastics during storage and use, yet are broken down into nontoxic by-products if disposed in the environment. Many approaches have been taken to commercially produce either biodegradable or photodegradable plastics [1]. One approach involves the incorporation of starch into blends with synthetically produced polymers which are made to be susceptible to biological, chemical, or UV breakdown. Alternatively, fermentation has been used to convert sugars or waste biomass into polyesters such as polyhydroxybutyrate/valerate or lactic acid for polylactic acid production which have been shown to be biodegradable and/or hydrolyzable. Limitations in producing and commercializing these biodegradable formulations are production costs, which can be 2–10 times higher than commodity plastics such as polystyrene or polyethylene, and lack of biodegradation and toxicity test standards for intended disposal environments.

Cellulose acetate is a commodity plastic produced from cotton linters or wood pulp and used as textile fibers, injection-molded items, and coatings. Its performance characteristics and biodegradability have been linked to the degree of substitution (DS). Studies conducted in simulated aerobic sludge [2] and composting [3, 4] have shown that cellulose acetate with a DS of 3 was not biodegradable, while at 2.5 DS the polymer was slowly degraded and at DS <2.2 was readily biodegraded. Since the cost of cellulose acetate is approximately three times higher than that of polystyrene, blending with inexpensive plasticizers or fillers is desirable to lower product cost without severely compromising mechanical properties. In this paper we discuss the effects of blending starch and propylene glycol with cellulose acetate on mechanical properties and biodegradability. Marine and soil toxicity testing of cellulose acetate and starch is also presented since marine disposal and composting are potential disposal routes for these materials.

Materials Preparation

Cellulose acetate/starcl
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Michigan) or rice starch (C
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was first suspended in the prc
of starch and cellulose acetat

The powdered mixture v
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Physical Testing

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Capillary Rheometry.
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Scanning Electron Microsc

Cellulose acetate 398-30
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Biodegradation Testing

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glycol with cellulose acetate
e and soil toxicity testing of
ine disposal and composting

EXPERIMENTAL

Materials Preparation

Cellulose acetate/starch blends were mixed, extruded, and pelletized as previously described [5]. Cellulose acetate with a DS of 2.5 (CA 398-30, Eastman Chemical, Kingsport, Tennessee) was mixed with a variety of corn starches, Argo brand (Best Foods, Englewood Cliffs, New Jersey), Melogel (National Starch and Chemical Co., Bridgewater, New Jersey), and Crisp-Tex and Amalean I (American Maize Products Co., Hammond, Indiana), or potato (Difco Laboratories, Detroit, Michigan) or rice starch (California Products, San Diego, California) and food grade propylene glycol (Dow Chemical Corp., Midland, Michigan) in a Henschel brand high intensity mixer (Purnell International, Houston, Texas) at 3000 rpm for several minutes. Calcium carbonate (Omyacarb UF, Omya Products, Lucerne Valley, California) was added to some samples to neutralize residual acid. The $CaCO_3$ was first suspended in the propylene glycol at low mixing speed prior to the addition of starch and cellulose acetate.

The powdered mixture was fed into a 42-mm diameter twin screw extruder (C. W. Brabender Instruments, Inc., Hackensack, New Jersey) equipped with a four hold (3.2 mm) strand die. The screw speed was 60 rpm and the temperature profile was as follows: zone 1, 120°C; zone 2, 150°C; zone 3, 160°C; and zone 4 (die), 170°C. The strands were then pelletized and the pellets heated at 185°C and molded into 38 mm long × 3.2 mm thick dogbone tensile bars in a labtop scale injection molder (Custom Scientific Instruments, Cedar Knolls, New Jersey).

Physical Testing

Mechanical Properties. Tensile strength and modulus of the dogbone samples were determined using a Model 4204 tensile strength tester (Instron Inc., Canton, Massachusetts) using a crosshead speed of 1.3 mm/min.

Capillary Rheometry. High impact polystyrene (Dow Chemical Corp., Midland, Michigan) and the blend of cellulose acetate 398-30 (57% wt/wt), cornstarch (25% wt/wt), and propylene glycol (18% wt/wt) pellets were analyzed in a capillary rheometer (Instron Inc., Canton, Massachusetts) at shear rates between 20 and 2000 (1/s) at temperatures between 170 and 225°C.

Scanning Electron Microscopy

Cellulose acetate 398-30, starches, and cellulose acetate/starch blend morphologies were examined using a S-900 Field Emission Gun SEM (Hitachi Instruments, Mountain View, California). Samples were coated with 50 Å tungsten and viewed under low voltage (1 keV).

Biodegradation Testing

Composting Studies. Cellulose acetate (398-30, 2.5 DS) films and cellulose acetate/starch blend dogbones were exposed in simulated municipal solid waste composting reactors as described previously [6]. The compost mixture had the following composition: 3500 g dehydrated alfalfa meal, 1300 g cottonseed meal, 1400 g poplar sawdust, 1000 g fresh cow manure, 1500 g black garden soil, 2500 g finely shredded newspaper, 480 g $CaCO_3$, 40 g $NaHCO_3$, and 13 L water, which resulted in a C:N ratio of 30:1. After blending in a Hobart Mixer to obtain a 3–4 mm particle size, the mixture was placed in a 276 mm (o.d.) by 432 mm length stainless steel cylinder with screens on the ends and airtight seals for aeration or gas sampling. The natural microorganisms found in the compost ingredients served as the inoculum. Samples were incubated for 15 to 90 days, and weight loss was determined after washing and drying the samples to a constant weight.

Soil Burial. The laboratory soil burial system consisted of 1 part commercial sand to 1 part topsoil to 1 part composted cow manure (1881 Select brand, Earth Grow Inc., Lebanon, Connecticut) containing 30% by weight moisture [7]. Cellulose acetate/starch dogbones were placed in the soil mixture and incubated at 30°C. Samples were periodically removed after 14 to 112 days, washed, dried to constant weight, and the percent weight loss and weight loss/surface area determined.

Toxicity Testing

Marine Mussel Toxicity. Mytilus edulis were grown in large mesocosms (1.8 m diameter × 5.5 m height tanks) which were filled with marine water containing natural populations of organisms from Narragansett Bay, Rhode Island, to which 10 mg/L starch or cellulose acetate was added. After exposure for 3 weeks in sample and control tanks, growth of the mussels was measured, and mussel meat and fecal material were analyzed for differences in stable isotope values [8].

Benthic Core Toxicity. Benthic cores containing natural populations from Narragansett Bay were collected and supplemented with 10 and 50 mg/L starch and cellulose acetate. The number of viable species, mostly polychaete worms, were enumerated in the control and test cores before and after a 1-month incubation.

Plant Toxicity Testing. Cellulose acetate (57% wt/wt)/starch (25% wt/wt)/propylene glycol (19% wt/wt) pellets were powdered in a disk mill until a particle size of approximately 300 μm was produced. A 1% (wt/wt) loading of the powdered blend was then added to potting soil and placed in greenhouse pots. Twenty pots, each containing four seeds, were used for both control and test experiments. Sweet corn, butternut squash, and plum tomatoes were used as test plants in the study. When the control plants reached maturation, all of the plants were harvested and measured for plant length and fruit weight. The percent change in size/weight compared to the control was then determined.

RESULTS AND DISCUSSION

Physical Properties

Initially, cellulose acetate was blended with propylene glycol alone to determine the plasticizer range required to produce injection-molded items which have high strength without being too brittle. Figure 1 shows the tensile strength at break and Young's modulus for injection-molded dogbones made from powdered samples or pellets produced from the powders by twin screw extrusion. Strength and modu-

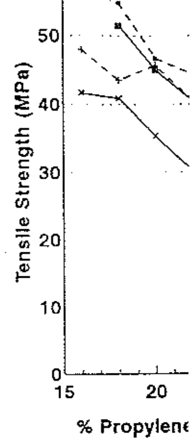

FIG. 1. Mechanical pro
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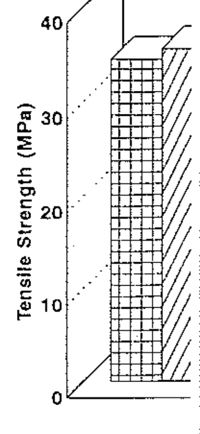

FIG. 2. Effect of starch

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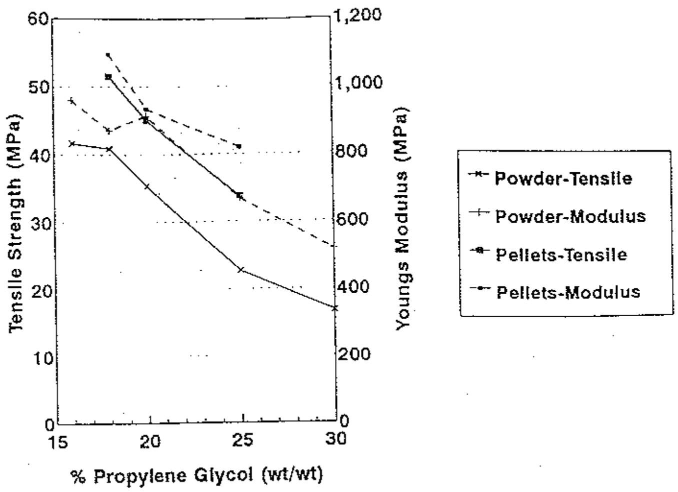

FIG. 1. Mechanical properties of cellulose acetate/propylene glycol tensile bars produced from powders and extruded pellets ($N = 5$).

lus increase with decreasing plasticizer content, and a 16–20% propylene glycol range results in better properties. Tensile strength values show the differences between the powdered and pelletized samples at different plasticizer contents more consistently than the modulus.

The effect of starch type on the tensile strength of injection-molded dogbones with 57% cellulose acetate and 19% propylene glycol is shown in Fig. 2. Corn starch performed better in the blends than potato or rice starch. Among the corn starches, the Melogel and Argo brands, which contain 30:70 amylose:amylopectin, performed similarly. The two blends containing 50:50 amylose:amylopectin brands,

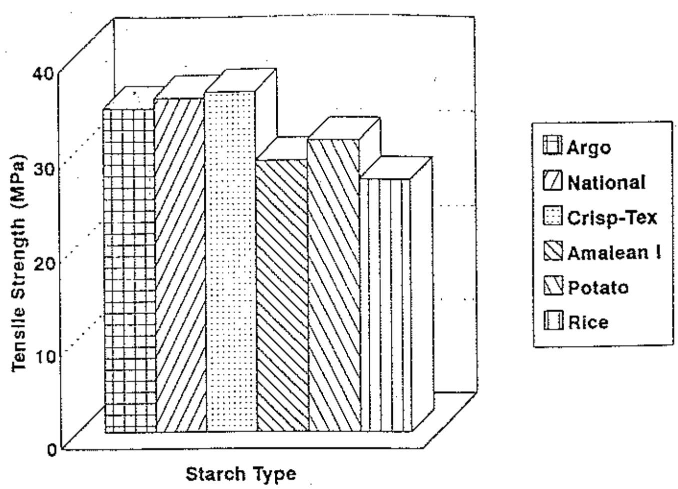

FIG. 2. Effect of starch type on tensile properties ($N = 5$).

TABLE 1. Effect of $CaCO_3$ on Mechanical Properties of Cellulose Acetate/Argo Starch/Propylene Glycol (60:20:17 wt/wt) Blends

Formulation	Tensile strength (MPa)	Young's modulus (MPa)
Polystyrene	22.1	905
CA/St	35.6	924
CA/St 2.5% $CaCO_3$	40.4	1060
CA/St 5% $CaCO_3$	36.2	974

Crisp-Tex and Amalean I, had very different strength properties which could be attributed to differences in compatibility with cellulose acetate. Crisp-Tex has a low degree of acetylation whereas Amalean I is derivatized with a low DS of propylene oxide.

Pellets produced from cellulose acetate, starch, and propylene glycol had an acidic smell and taste. Therefore, calcium carbonate ($CaCO_3$) was added to the blend in an attempt to neutralize residual acetic acid released during extrusion. Table 1 shows that addition of 2.5 and 5.0% $CaCO_3$ improves mechanical properties and also eliminated the taste and odor problems. The dogbones molded from CA/St/PG/$CaCO_3$ blends had better tensile strength and modulus than polystyrene (Table 1). However, in performance tests with utensils molded from this blend, the impact resistance was not as high as for polystyrene (data not shown).

Capillary rheometry studies were performed to compare flow, at different temperatures and shear rates, of the CA/St blends to high impact polystyrene to facilitate production of injection-molded utensils. The results presented in Fig. 3. indicate that the viscosity curve for the CA/St blend is similar to polystyrene. These results guided the successful production of prototype utensils during the first trial run.

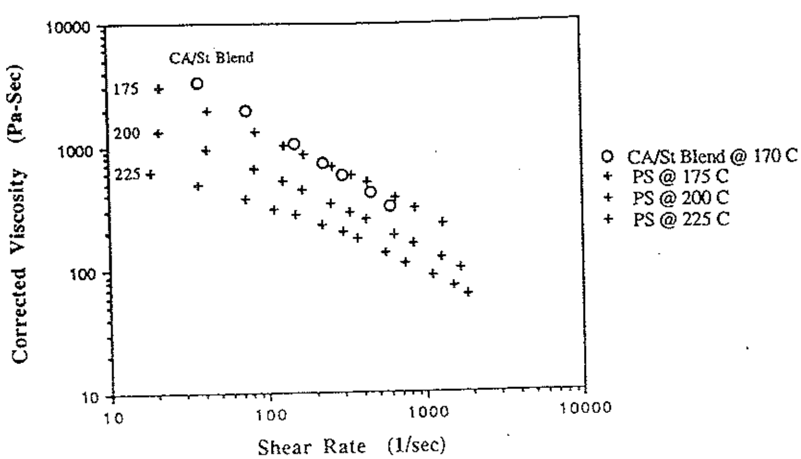

FIG. 3. Comparison of the rheology of cellulose acetate/Argo starch blends with polystyrene.

Scanning Electron Microscopy

Electron micrographs of cor
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Biodegradation Testing

Figure 5 shows the weight l
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Toxicity

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Mussel Toxicity. Filter f
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Benthic Core Toxicity.
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Scanning Electron Microscopy

Electron micrographs of corn and potato starch before and after blending and extrusion with cellulose acetate are presented in Fig. 4. The corn starch granules appear to be unbroken within the cellulose acetate matrix; however, the potato starch granules look partially disrupted. There is evidence of void formation between the starch granules and cellulose acetate in some areas, and some coating of CA on the granules.

Biodegradation Testing

Figure 5 shows the weight loss/surface area data for CA/St blends in compost and soil burial exposures and cellulose acetate alone in composting. The cellulose acetate film lost 50 $\mu m/mm^2$ surface area (>90% total weight) during the 90-day test period. The blends (in tensile bars) in soil and compost studies lost approximately 20% of their total weight (approximately 230 to 270 $\mu g/mm^2$), which is probably indicative of leaching or degradation of the propylene glycol and partial leaching or biodegradation of the starch. We would expect the organisms present in compost or soil to attack the most readily degradable substrates first.

Toxicity

Polymers can be transformed into metabolites that have greater toxicity due to the action of microorganisms. While it is not expected that biodegradable polymers will form toxic by-products, testing should be done to verify their benign nature.

Mussel Toxicity. Filter feeders such as mussels are sensitive to pollutants in the marine environment. Stable carbon isotope ratio of the mussel biomass and fecal material, if different from the ratio in cellulose acetate and starch, can be used to determine if these materials are ingested and metabolized by the mussel, ingested but excreted without being metabolized, or not ingested. When related to changes in growth, reproduction, or mortality, this technique can help to pinpoint the mode of toxicity. It has been successfully used in tracing the toxicological fate of sewage sludge in sediments and estuarine ecosystems upon ingestion by phytoplankton and benthic organisms [8]. Large mesocosms, which are filled with marine water and sediment containing natural fish larvae populations, have been used to mimic an ecosystem response to exposure to starch-containing biodegradable plastics [9]. The results from these experiments showed that larval fish growth rate was reduced because they ingested the starch blend but could not digest it. In the experiment with mussels, growth was not inhibited by the presence of starch or cellulose acetate in the mesocosms. Table 2 indicates that starch was ingested based on the change in the fecal stable carbon isotope value, but neither starch nor cellulose acetate was incorporated into mussel biomass.

Benthic Core Toxicity. Figure 6 shows the effects of addition of starch or cellulose acetate to sediment cores containing benthic organisms, primarily polychaete worms. The number of viable species recovered was reduced at dose levels of

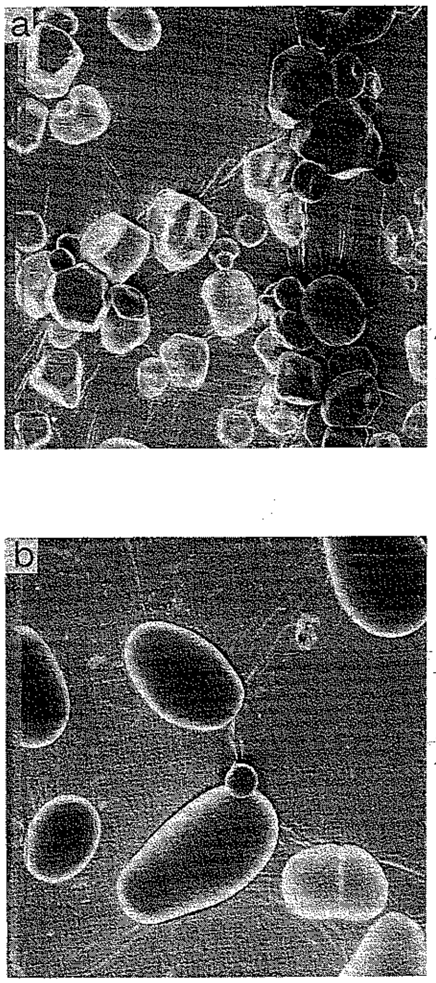

FIG. 4. Scanning electron micrographs of (a) corn starch granules, (b) potato starch granules, (c) cellulose acetate/corn starch pellets, and (d) cellulose acetate/potato starch pellets (1000 ×).

TABLE 2. Stable Carbon Isotope ($^{12}C/^{13}C$) Ratios of Mussel Meat and Feces after Exposure to Starch and Cellulose Acetate 398-30

Sample	Carbon isotope, initial	Carbon isotope in meat, 3 weeks	Carbon isotope in feces, 3 weeks
Mussel control	−19.2	−19.0	−14.1
CA-398-30	−31.7	−18.8	No data
Starch	−10.1	−18.9	−11.5

FIG. 4

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Plant Toxicity Testing.
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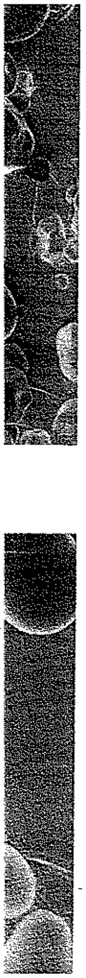

tarch granules, (b) potato starch
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ıtope veeks	Carbon isotope in feces, 3 weeks
)	−14.1
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)	−11.5

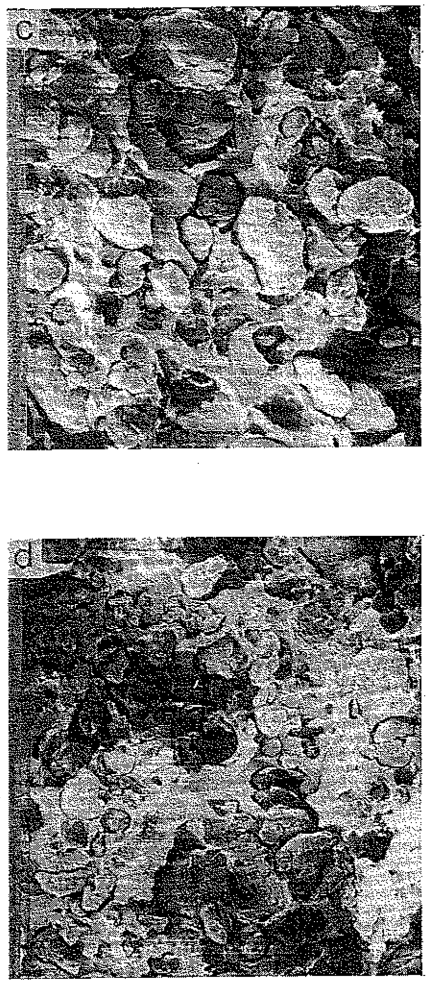

FIG. 4 (continued).

50 mg/L, particularly with the starch-treated cores. The appearance and smell of hydrogen sulfide in these cores indicates that the problem is a secondary one, the reduction in oxygen, and not direct toxicity of the rapidly biodegraded starch.

Plant Toxicity Testing. The primary route being considered for disposal of biodegradable materials is composting. An important consideration for this disposal route is verification that there is no plant toxicity from the compost containing the biodegradable polymers, formulation additives, or their breakdown products. The effect of addition of CA/St blends on the growth and fruit production of corn, squash, and tomatoes when directly applied in the potting soil was evaluated (Table 3). The blend slightly improves the growth and yield of these vegetables.

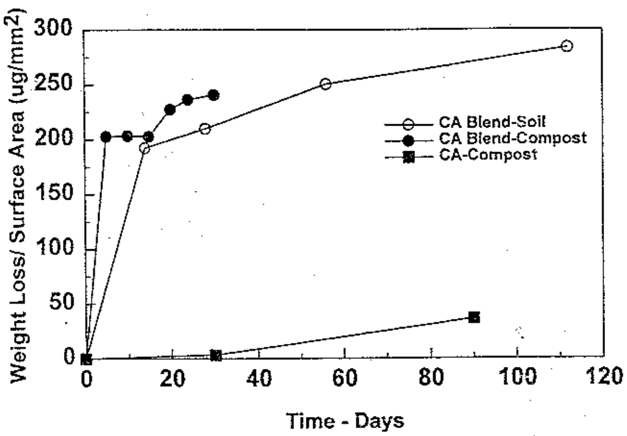

FIG. 5. Weight loss/surface area of cellulose acetate (2.5 DS) in compost and cellulose acetate/corn starch/propylene glycol blends in compost and soil.

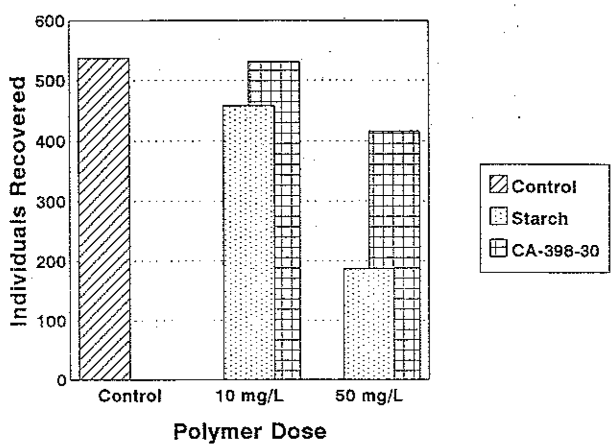

FIG. 6. Effect of starch and cellulose acetate on the mortality of benthic organisms.

TABLE 3. The Effect of CA/St Blend on Plant Growth and Yield

Plant	Plant length (% control)	Yield weight (% control)
Corn	105	105
Squash	110	115
Tomato	110	115

Cellulose acetate/starcl styrene and have similar mec well as plasticizer content i with a DS of 2.5 was shown starch and propylene glycol : blend. Marine and plant tox disposed of in the marine env

We wish to thank Be processing, Paul Dell for co for taking the SEM photogr ducting the soil biodegradati

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CONCLUSIONS

Cellulose acetate/starch blends were produced which process similarly to polystyrene and have similar mechanical properties. The type and amount of starch as well as plasticizer content influenced mechanical performance. Cellulose acetate with a DS of 2.5 was shown to be slowly biodegraded in compost, and addition of starch and propylene glycol seems to delay the utilization of the CA portion of the blend. Marine and plant toxicity tests indicate that these blends should be safe if disposed of in the marine environment or through composting.

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