ENGINEERING THE CONTAINER -- Panel Discussion

Ninth of Nine Papers

BIODEGRADABLE CONTAINERS:- DEGRADATION RATES AND FABRICATION TECHNIQUES1/

Robert A. Clendinning2/, Steven Cohen3/, James E. Potts4/

Abstract.--This paper describes the development of biodegradable plastic containers suitable for growing and transplanting trees in various regions of North America, based on a new plastic developed by Union Carbide Corporation called polycaprolactone. Factors affecting the biodegradation rate and performance of such containers are discussed, such as additives in the plastic and container design and fabrication.

INTRODUCTION

The biodegradability of organic materials such as paper, plastics and chemicals is defined as the susceptibility of the material to being attacked and assimilated by microorganisms such as fungi and bacteria. Although most polymers are affected by outdoor exposure to some extent, it has been observed that synthetic plastics are generally rather resistant to microbiological degradation. This conclusion was reinforced in a recent study by Union Carbide conducted for the Environmental Protection Agency (Potts, et al 1972). It was pointed out in that study that aliphatic polyesters in general are susceptible to microbiological attack. The purpose of the present paper is to concentrate on one commercially available aliphatic polyester, polycaprolactone, and show its potential utility as a biodegradable container for seedling growth and transplantation.

SOIL BURIAL METHODOLOGY

All of the work reported in this paper was done indoors in red clay flower pots. The soil used was a mixture of equal parts (by volume) of New Jersey top soil, peat moss, and builders sand. The mixing was accomplished in a gallon V-type blender. The flower pots, containing the soil and the samples, were kept in stainless steel trays in a cabinet. The soil was kept constantly wet with water. The laboratory temperature was generally around 22 °C.

The samples were compression molded plaques, 1" by 3" by 40 mils thick except for the small PCL containers and the samples used to demonstrate the effect of thickness on degradation rate. A nylon filament was attached through a small hole near one end of the sample so that the entire sample could be buried and subsequently located. Numbers attached to the nylon monofilament enabled each sample to have its own identity and thus weight loss could be determined. Excess oil was removed from the sample by gentle washing with water and the samples were dried overnight in a vacuum oven prior to weighing.

DEGRADATION OF POLYCAPROLACTONE

Polycaprolactone (PCL) is a crystalline, thermoplastic polyester prepared by the ring opening polymerization of epsilon-caprolactone. The repeating unit of PCL consi3ts of a straight chain of five methylene units and an ester unit.

$$-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-$$

PCL has a crystalline melting point of 60 °C. It has been fabricated by many conventional plastics fabrication processes such as injection molding, compression molding and sheet extrusion.

1/Paper presented at North American Containerized Forest Tree Seedling Symposium Denver Colorado, August 26-29, 1974.

2/R· A. Clendinning, Project Scientist, Union Carbide Corp. 1 River Rd. Bound Brook, NJ

3/S. Cohen, Project Science, Union Carbide 1 River Rd. Bound Brook, N. J.

4/J. E. Potts, Sr. Research Scientist, Union Carbide Corp. 1 River Rd. Bound Brook, N. J.

Soil burial studies on small injection molded containers showed the weight loss data given in Table 1.

TABLE 1

MONTHS OF BURIAL	% WEIGHT LOSS
0	0
2	12
4	29
6	48
12	95

Pictures of these containers are shown in figure 1.

FIGURE 1 PCL CONTAINERS,
SOIL BURIED FOR 0,2,4,6,12 MONTHS

Scanning electron micrographs of the surface reveal the extent of the attack. Figure 2 is a photo of the surface magnified about 1000 times before any soil burial degradation. The streaks and straight lines are simply replicas of the surface of the mold in which the container was made. Figure 3 shows the surface of a sample, at the same magnification that has been soil buried for two months. The deep pitting, channeling and cavernous appearance resulting from the degradation process is readily apparent.

Since the degradation is a surface phenomenon the sample thickness or surface to volume ratio is very important in determining the rate of weight loss and the rate at which penetration of the container wall can be expected. Accordingly a study of the degradation rate vs. thickness was done for PCL. The results are shown in Figure 4.

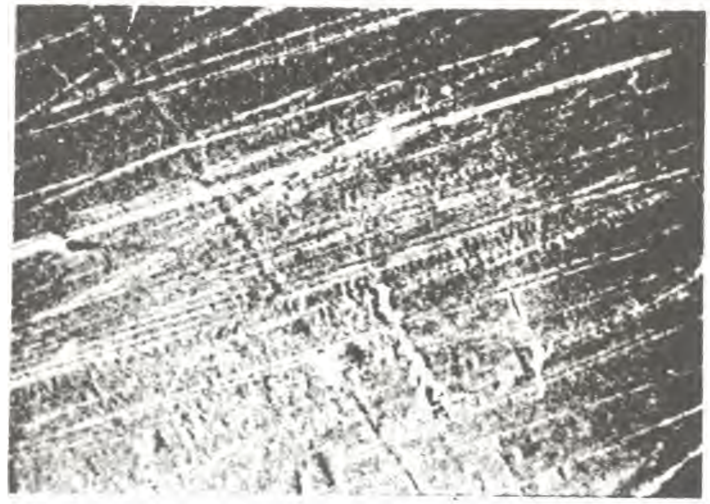


FIGURE 2 SCANNING ELECTRON MICROGRAPH
BEFORE SOIL BURIAL (1000X)

FIGURE 3 SCANNING ELECTRON MICROGRAPH
AFTER 2 MONTHS SOIL BURIAL (1000X)

The percent weight loss is plotted againnL cne thickness in mils with each sample thickness being measured for weight loss once a month for six months. It can be seen from the graph that the weight loss decreased as the thickness increased. The 20 mil sample appears to be out of line in that greater weight loss was expected.

ALTERATION OF DEGRADATION RATE

Polycaprolactone 700 as a biodegradable thermoplastic alone is limited in use by two factors. The first is dependence of degradation

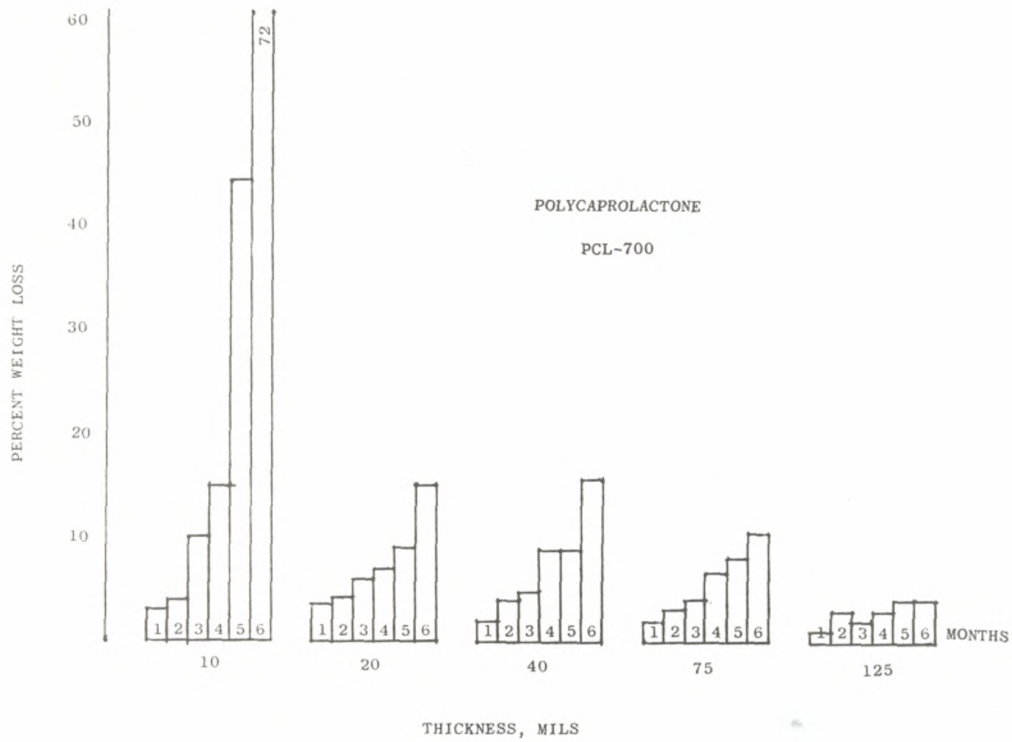


FIGURE 4

rate on thickness and the second is processibility. For the pure homopolymer the technique available to control degradation is modification of containers/specimen geometry, especially the thickness as outlined above. Processing the homopolymer is also difficult due to its low melting point, high tack, and low melt strength. Early in this program it became apparent that one method of altering the above factors was to dilute the PCL-700 homopolymer with various additives. Numerous ad ditive/ filler systems were explored in the early work which formed the basis for Several UCC patent applications and permitted the development of some generalizations about the effect of certain additives on physical properties, fabricability and degradation rate.

Additive systems can be broadly classified into two major categories:

Polymeric
Non polymeric

Polymeric additives usually decrease the degradation rate through a masking effect in that they make the PCL-700 homopolymer less available for attack by the microorganisms. This effect is shown dramatically in Table 2.

TABLE 2

BIODEGRADABILITY OF POLYCAPROLACTONE ALLOYS

SAMPLE	% WEIGHT LOSS, MONTHS				
	0	2	4	6	12
PCL	0	12	29	48	95
PCL-PE 50-50 1/	0	6	10	12	17
PCL-PST 50-50 1/	0	2	5	9	13

1/ PE = Polyethylene, PST = Polystyrene

Polymer additives improve the processability of the basic PCL material because they reduce tack and increase melt viscosity to the point where the polymer-PCL alloy can be handed more like a conventional commodity thermoplastic resin like polyethylene. When water soluble polymers are used as additives the degradation rate of the alloy system (weight loss/ unit time) can be increased above that of the PCL-700 homopolymer.

The second additive category, nonpolymeric, is essentially made up of fillers. These can be further subdivided into:

Biologically inert
Biologically active

The former simply fall out of the polymer matrix as the "thermoplastic glue" is consumed by the microorganisms. The latter sub group contribute to the growth of the soil microbes and can be used to substantially alter and control the rate of degradation.

The use of fillers results in changes in physical properties such as tensile strength and stiffness. The ultimate test of a part produced from a filled PCL alloy is its performance in the specific end use application. Consequently we have relied on this input more so than absolute values obtained in small scale physical tests.

Examples of the effect of polymeric additives and fillers is shown in Table 3 which illustrates both the types of mechanical properties one can get and the range of weight losses that can be observed. PCL (compound A) is a relatively slow degrading system. The remainder of the compounds represent PCL formulations containing varying amounts and kinds of polymeric and non-polymeric additives. Compound C for example has about the same degradation rate as A but is a much stiffer product as measured by its higher secant modulus. Other compounds intermediate in stiffness show degradation rates which range from about 50% in six months to disintegration in one month. Disintegration means that sufficient sample could not be found to make a meaningful measurement of weight.

It should be mentioned that one cannot simply select from Table 3 the degradation rate that is desired and proceed to make the container from that compound. The fabrication technique plays an important role in the compound selection and therefore, it is necessary to optimize alloy formulation in terms of end product properties, fabrication performance and degradation rate.

In addition to varying the ingredients in a compound in order to alter the degradation rate it is also possible to alter the rate by varying the sample thickness in the same manner as that shown in Figure 4 for PCL. A study of this type for some of the compounds in Table 3 is shown in Figure 5-7. Here the weight loss is plotted as a function of sample thickness and burial time. As with PCL in Figure 4, the thinner samples are seen to experience higher rates of weight loss since the attack of the microorganisms is a surface phenomenon and the surface exposure per unit volume is greater for the thinner samples.

On a practical basis this enables one, for example, to move from a faster formulation to a slower formulation and keep the same degradation rate by going to a thinner-walled container. This is illustrated in Figure 8 where a 75 mil sample of compound H is compared to 10 and 20 mil samples of compound C. Thus one would predict that a container with a wall thickness of about 15 mils made from compound C would have about the same degradation rate as the same container with a wall thickness of 75 mils made from compound H.

APPLICATIONS FOR BIODEGRADABLE PLANTING CONTAINERS

Three areas have been defined which would merit use of biodegradable planting con-

TABLE 3

PHYSICAL PROPERTIES AND WEIGHT LOSS FOR PCL FORMULATION

COMPOUND	MODULUS psi K=1000	IZOD IMPACT 1/	TENSILE 2/ IMPACT	WEIGHT LOSS % MONTHS OF SOIL BURIAL 1	2	3	4	5	6
A (PCL)	50K	0.83	100	--	7	9	12	--	16
B	89K	0.5	11	--	33	--	47	74	D 3/
C	230K	0.3	6	8	11	--	14	--	16
D	133K	0.38	8	11	25	30	37	--	50
E	124K	0.49	6	D 3/					
F	172K	0.41	4	22	47	63	D 3/		
G	180K	0.18	2	35	38	42			
H	130K	0.62	8	10	16	57	47	46	

1/ Ft. Lbs./In.
2/ Ft. Lbs./In.^{3}
3/ D Sample Disintegrated

tainers. They include:

1. seedling containers
   a. Pacific Northwest
   b. Southern Pine Forest
   c. Great Plains

2. bedding flats/containers

3. ornamental containers
   a. roses
   b. evergreens

In order to meet the differing end product performance requirements for each of the above areas - raw material and fabrication parameters must be optimized with respect to:

1. mechanical properties
2. degradation performance
3. design flexibility
4. unit cost

During the early stages of the biodegradable alloy development many fabrication techniques were reviewed to assess suitability for conversion of the polycaprolactone alloys into useful end products. Since PCL-700 and its alloys are thermoplastic resins the major fabrication techniques explored were:

1. injection molding
2. blow molding
3. extrusion
4. thermoforming

CRITERIA FOR FABRICATION OF PCL ALLOYS

The key element in the successful fabrication of any thermoplastic resin is defining the optimal melt temperature level for each specific fabrication process and polymer. Melt temperature for a particular polyolefin resin may vary by as much as 225°F depending on whether the material is extruded or injection molded.

As shown in Table 4 flow tests conducted between 140°C and 230°C indicate that PCL-700 is substantially less viscous than typical polyethylene/polypropylene resins. However, the melt viscosity of alloys produced using PCL-700 can be controlled in order to aid fabrication process.

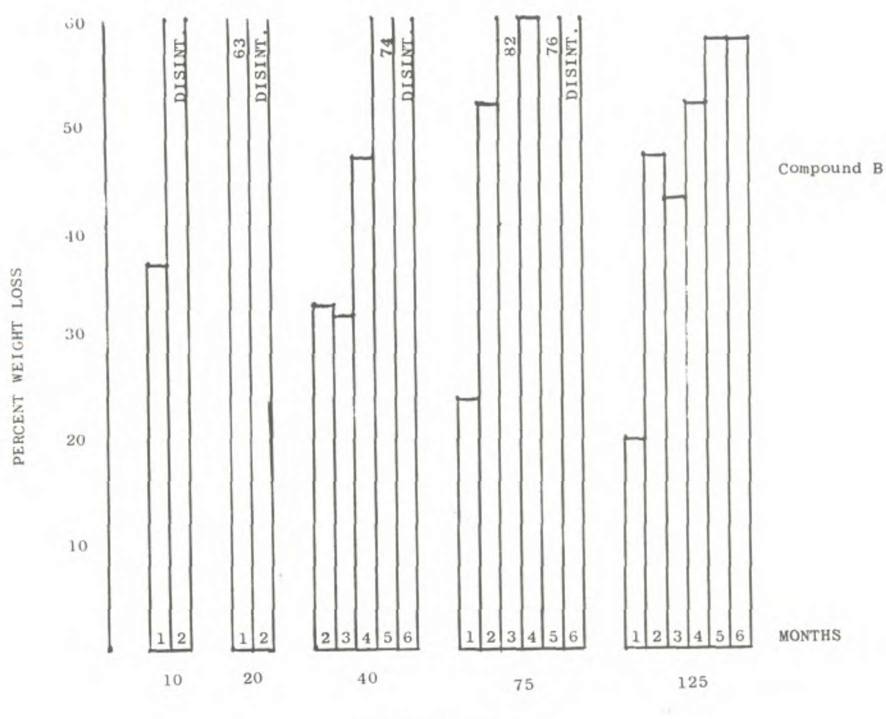


FIGURE 5

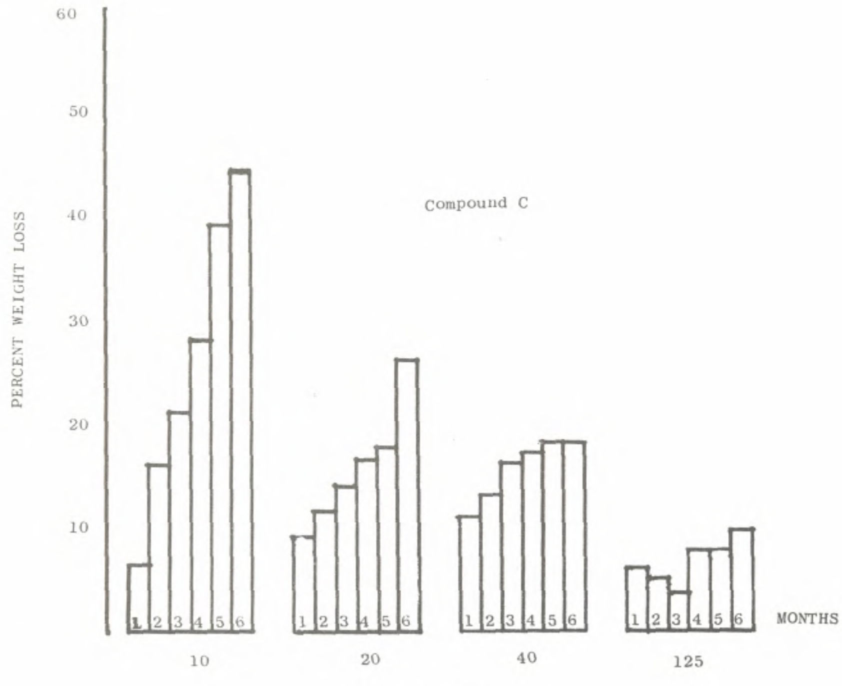


FIGURE 6

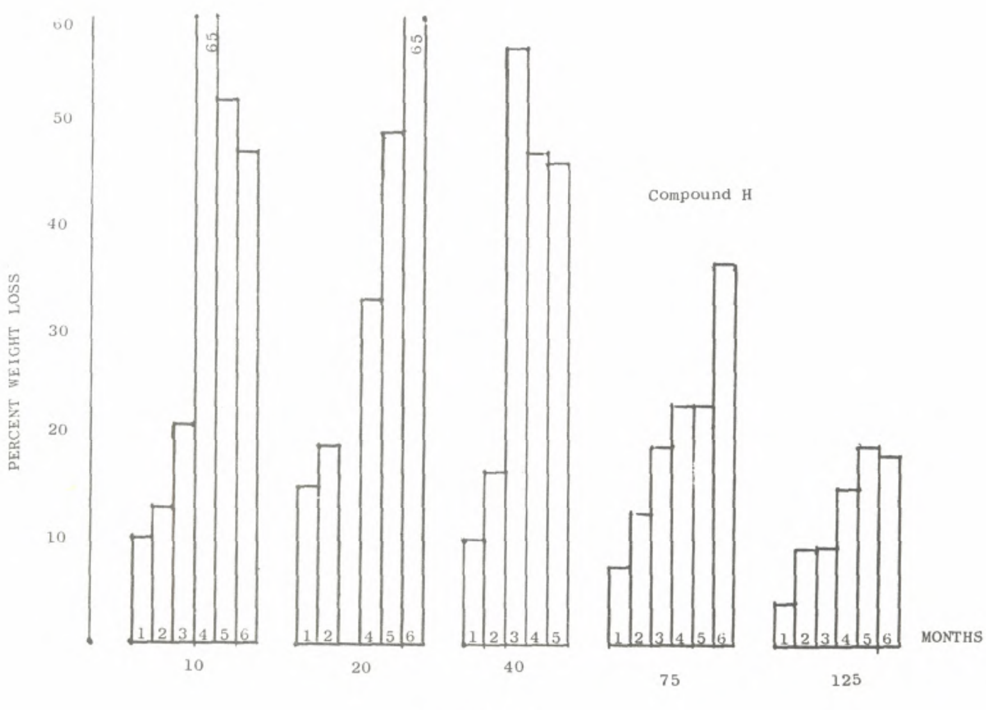


FIGURE 7

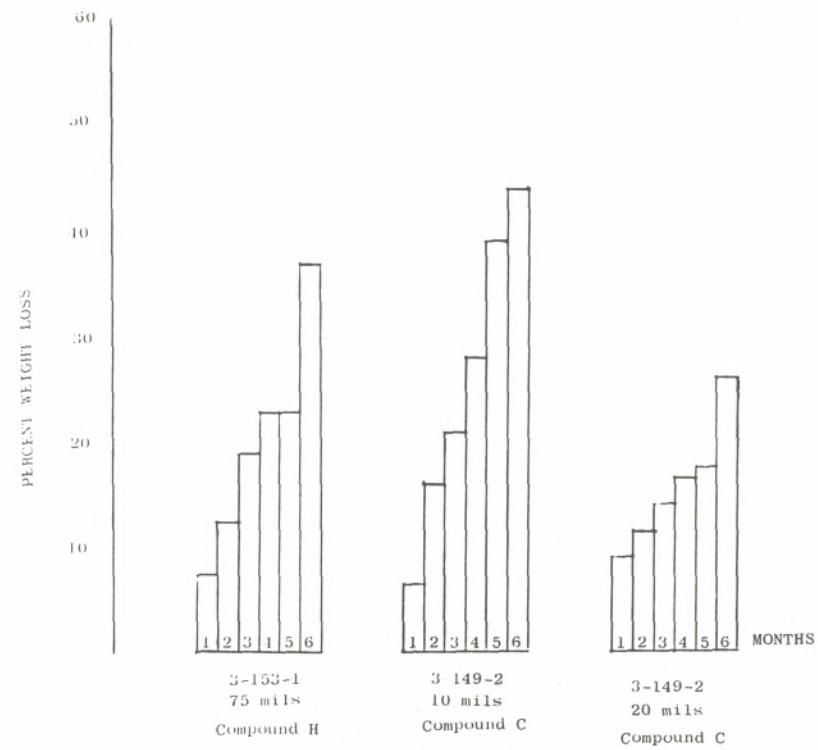


FIGURE 8

TABLE 4

FLOW PROPERTIES OF VARIOUS POLYMERS

PRODUCT	MELT TEMPERATURE, °C	MELT FLOW, GRAMS/10 MINUTES PISTON LOAD 44 psi.	100 psi.	220 psi.
Polycaprolactone PCL-700	190	34	82	164
	140	12	32	96
8 Melt Index - High Density Polyethylene Homopolymer	190	8	26	90
3.8 Melt Flow Polypropylene Homopolymer	230	3.7	19	88
Polycaprolactone Alloy	190	13	48	160

Table 5 summarizes the recommended melt temperature for various PCL alloys and fabrication processes.

Figures 9 to 14 display various end products fabricated from these PCL alloys.

The seedling containers shown in Figure 9 are injection molded from a polycaprolactone alloy. Here the final container, designed for use in the Pacific Northwest, must provide sufficient mechanical strength to permit soil implantation using a hand operated "gun". In addition, the biodegradable bullet must possess

TABLE 5

FABRICATION CONDITIONS FOR PCL FORMULATIONS

	INJ. MOLD.	EXTRUSION	THERMOFORMING	BLOW MOLD.
PCL-700	230°F	180°F	175°F	- -
Alloy C	300	340	250	250-275°F
Alloy B	300	- -	240	- -

FIGURE 9 - WALTERS PLANTING BULLETS

FIGURE 11 - LIGHT WEIGHT THERMOFORMED CONTAINERS

FIGURE 10 - PLANTING CONTAINERS FOR ORNAMENTALS AND BEDDING PLANTS

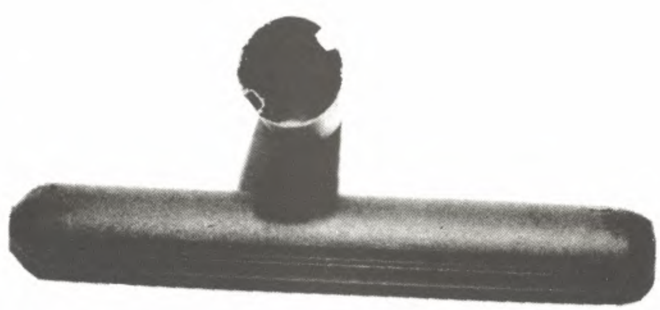


FIGURE 12 - CIRCULAR RIBBED CONTAINER FOR TREE PLANTING

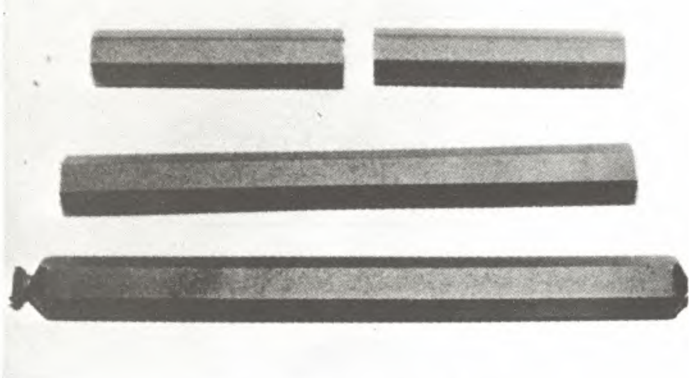


FIGURE 13 - HEXAGONAL CONTAINERS FOR TREE PLANTING SHOWING LENGTH VARIABILITY

FIGURE 14 - HEXAGONAL CONTAINERS FOR TREE PLANTING (5")

this attractive impact strength after a nursery period of about one year.

CONTAINER DESIGN

This portion of the text is related to the development of thin walled - biodegradable-thermoplastic planting containers developed for use in the U.S.F.S. Southern Pine Forest Experimental Container Program. Project guidelines followed during the development effort included:

1. Thin walled - rigid
2. Integrity suitable for 6-10 week nursery period
3. Degradability controlled for So. Pine Forest Environment
4. Applicable for mechanized planting systems
5. Broad spectrum of possible fabricators.

A polycaprolactone filled alloy was chosen for this container ba3ed on good processibility, high rigidity and suitable degradability. Table 6 presents the summary of weight loss as a function of specimen thickness and exposure time. Here we see the specimens of about 20 mils lose less than 1 0% of their weight after 4-8 weeks - thus assuring sufficient integrity for nursery planting and mechanized handling. In order to achieve suitable levels of production with the above wall thickness blow molding was chosen as the fabrication process.

In addition to the capability of providing light weight hollow containers, blow molding unit investment is attractively low yet provides significant design flexibility. Custom fabricators are also available on a contract basis for small and intermediate volumes.

Two designs were developed as shown in Figure 15 based on assessments of the U.S.F.S. needs for the southern pine region. Engineering details are provided in Table 6 which includes the laboratory weight loss data on three inch containers. During the early stages of this program, the optimal container length was not fully defined. Consequently, "infinite length" tubes were initially produced (Figures 13 and 15) so that various lengths could be evaluated. One indication of process versatility was demonstrated by the relative ease by which an internal stiffening was added to the initial circular design. Currently, the hexagonal tube is favored since: 1) soil is not "lost" between containers during filling, because of better packing, 2) internal ribs are not necessary since the 60° angle is sufficient to minimize root spiraling, and 3) rigidity is provided.

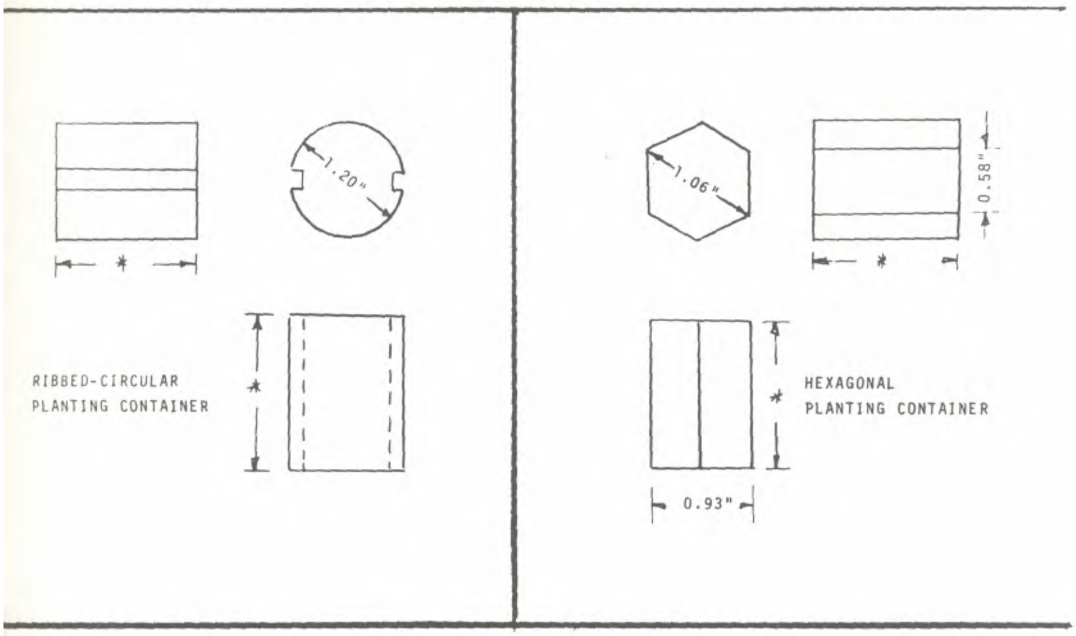
CHOOSING THE FABRICATION TECHNIQUE

When considering the economics of any fabricated object such as a container costs can be broken down into four major items. These include: (a) raw material cost, (b) fabrication variable costs, (c) fabrication period (fixed) costs, (d) fabricators return on investment or profit.

In the present instance blow molding

FIGURE 15

BLOW MOLDED - THIN WALLED BIODEGRADABLE PLANTING CONTAINERS



* Planting tubes can be cut to any desired length up to 8"

TABLE 6

ENGINEERING DETAILS

BIODEGRADABLE BLOW MOLDED PLANTING CONTAINERS

	CIRCULAR	HEXAGONAL
I D	1.2"	0.93" (1.06")
Wall Thickness	0.020"	0.016"
Weight/Inch	1.2 Gram	< 1 Gram
Overall Length Tube 1/	8 1/2"	12 1/2"
5" Container Weight	6.0	4.5
Weight Loss %		
1 Month	7.6	6
2 Month	11	7
3 Month	14	9
4 Month	22	9

1/ Smaller containers are cut from initial tube - 2-6" containers can be produced from hex tube.

appears ideal for the fabrication of biodegradable thin walled planting containers due to: (a) its high degree of flexibility for unique part design (b) modest cost for molds (c) compatibility with Polycaprolactone Alloys (d) low fabrication cost per unit (e) attractive investment and availability of broad spectrum of blow molders.

FIELD DATA

Circular and hexagonal thin-walled containers have been tested in our indoor soil burial laboratory with the results shown above in Table 6. In addition these containers have been evaluated at the U. S. Forestry Service Laboratory in Pineville, La. Figures 16 and 17 show seedling growth in these containers after the nursery period, indicating that container integrity is maintained throughout this period. That degradation has started is shown in Figure 17 where a rootlet has penetrated the container wall. About 9000 of the hexagonal containers have been out planted in various southern forests this past spring.

FIGURE 16 - PINE SEEDLING IN HEXAGONAL CONTAINERS

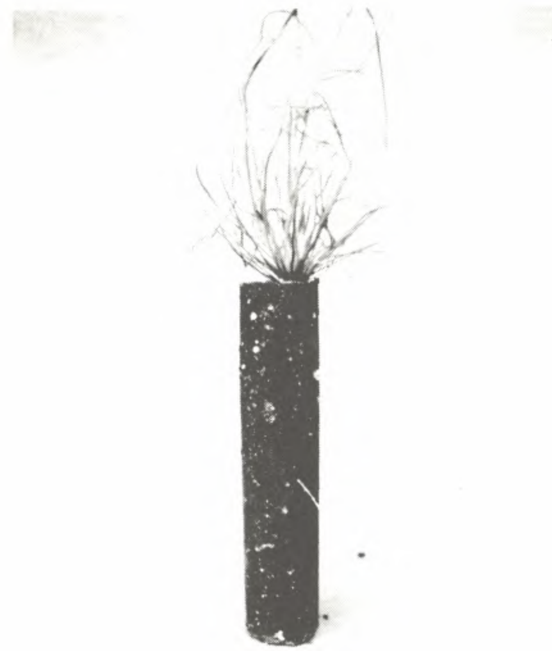


FIGURE 17 - PINE SEEDLING IN CIRCULAR CONTAINER SHOWING ROOTLET PENETRATION OF CONTAINER WALL

LITERATURE CITATION

Potts, J. E., Clendinning, R. A., Ackart, W. B. (1972) An Investigation of the Biodegradability of Packaging Plastics. U. S. Environmental Protection Agency Report EPA-R2-72-046.

Question: What are the projected costs for PCL containers in large quantities?

Clendinning: I don't have any good information on that. PCL itself is available commercially, but we currently make up formulations in experimental quantities only.

Question: How are the flow rates in cold (50^{o}) molds? How about wall thickness versus distance?

Clendinning: The distance of flow will be a function of the formulation. The more PCL in it, the further it is going to flow. For straight PCL you may need to chill the cooling water for best results with injection molding.

END OF PANEL DISCUSSION