November 15, 1993

LCMR WORK [illegible]GRAM 1991 (Short Version; for more detailed information, please refer to the Detailed Version which was submitted separately to the LCMR on November 15, 1993)

I. Cellulose Rayons for Packaging-Waste 18

Program Manager: Fu-Hsian Chang
Center for Environmental Studies
Bemidji State University
Bemidji MN 56601-2699
(218) 755-4104

A. M.L. 91 Ch 254 Art. 1, Sec. 14 Subd: 13 (g)
Appropriation: $150,000.00
Balance: $ 94.02

Cellulose Rayons for Packaging: This appropriation is to the Commissioner of Administration for a grant to Bemidji State University, Center for Environmental Studies, to research and develop cellulose rayons.

B. Compatible Data Language: Not applicable.

C. Match Requirement: Not applicable.

D. Appropriate patents will be filed to protect any discoveries and pursued according to the patent and royalty language set by the LCMR in subd. 20 of SC9400-1.

II. Narrative

A. Statement of the problem: The goal is to develop cellulose-based polymers, attractive to large manufacturers to switch from petrochemicals based plastics to a safer and more recyclable materials. The raw material will be Minnesota grown cellulose, thus potentially creating a demand for Minnesota products. The questions to be answered are: (i) What forms of cellulose give optimum recyclability plus feasibility and performance in making package material? (ii) Can these cellulose based packaging materials attract large scale manufacture, compatible with package engineering, production and performance? (iii) Can cellulose products produced in Minnesota compete with current large scale imports of petrochemicals resins based packaging, by virtue of recyclability and disposability plus performance by cellulosics? (iv) Can multimarket outlets be developed for cellulosic rayon waste product, either as material, compost or heat? Can this enable more investment in recovery facilities to be considered and less paper simply being disposed of to landfill?

B. Importance

Waste reduction and reuse of materials is a top priority of many municipalities. Plastics pose a disposal problem, regardless of whether they are incinerated or landfilled. Alternative products which can reduce the problems created by plastics are needed. This project will compare plastic to cellulosics, which is a cellulose derived material that can be converted to a thermoplastic material and used in packaging. Other cellulose derived materials have been developed previously, including cellophane, food additives, and 'plastic wood.' Recyclability of other cellulose based products offers encouragement that cellulosics can also be recycled efficiently. Derived celluloses are completely bu[illegible]ble at reasonable temperatures. They are also biodegradab[illegible]t at different rates depending [illegible] how they are substituted and made into packages. Thus [illegible]tuting cellulosics for plastics would reduce Minnesota's dependence on petroleum products, and reduce the amount of environmentally harmful waste generated.

C. Extent of the problem.

The problem is multiheaded. It can be outlined best by listing the questions that bear.

(i) Can Minnesota produce cellulosic packaging materials, in competition with current petrochemicals (plastics) based materials?
(ii) What happens if petroleum gets more expensive?
(iii) Can cellulosic packaging be recycled?
(iv) How much energy will it take to recycle cellulosics? Also, what are the central energy costs of petrochemicals plastics recycling?
(v) Can cellulosics and rayons be made to fit process engineering requirements (thermoplasticity tensile strength, film forming, body forming properties)?
(vi) If solvents have to be used for recycling, can nontoxic, completely recoverable solvents serve?
(vii) If burning (energy recovery) is carried out, what is the energy value of derivatized celluloses-cellulosics such as rayons?
(viii) May regenerated cellulose have a role in packaging?
(ix) Can Minnesota expect to become an exporter rather than importer of packaging raw materials?

III. Objectives

A. Develop cellulosics with desirable physical properties, including recyclability.

A1. Narrative

This objective will review other work on cellulosics, develop new cellulosic compounds, and test the compounds for water absorbability and recyclability. Several process engineering characteristics need to be addressed to determine workable combinations for manufacturing, including tensile strength, extrudability (formability), shear modulus, thermoplasticity, and hot flow indexes such as melt viscosity. Recycling requirements as defined by the OWM also need to be met by the new compounds.

A2. Procedures

I. Already available commercial rayons will be analyzed, including HWM and LWM (high/low wet modulus) cellulosics, and thermoplastic cellulosics which are esterified with C4-C8 fatty acids. Cellulosics which lend themselves to non-viscose manufacturing processes will be reviewed, as these are considered to be more ecologically sound as well as more efficiently manufactured than older viscose and cuprammonium cellulosics.

II. New compounds will be derived in our laboratories. Compounds that are likely the best compromise between cost, ease of fabrication, and biodegradability will be the principal factors that determine our choice of cellulosics for packaging development. The two main kinds of derivatives we have been making are cellulose propionates and butyrates (esters), and cellulose esthers. Compounds to be developed include acetylated, propylated and butylated cellulosics which confer properties suitable for package fabrication, function, and recyclability. Reaction media include the anhydrides of the derivatization compounds (acetyl propyl, butyl anhydrides), which drive the derivatization reactions by contributing as substitutes as well as removing water as the reactions proceed. Catalysts for driving derivatization are those which are easily leachable and

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destroyed by small amounts of alkali after isolation of the polymeric products, such as methyl methane sulfonic [illegible] and homologous series. Derivatization with aromatics i[illegible] first priority because they ten[illegible] somewhat more toxic if incinerated than are all-alkyl derivatives.

Cellulose ethers shall be made by ethyl chloride and ethylene oxide reaction with cellulose. These derivatives are 'self plasticized' cellulose, having water adsorption capacities of ca 5-10% of their weight as water, depending on humidity (water tension) and the degree of ether substitution. Alkyl ethers of cellulose will be formed via propylene oxide derivatization at low to intermediate propylene oxide concentrations, 1 to 3%. Variation of propylene oxide concentration during derivatization gives control over the degree of substitution, the mechanical and thermal properties of such etherated cellulosics, and their water penetrability or uptake.

The degree of substitution on cellulose derivatives will be measured by formulation and by periodate oxidation uptake. The course of periodate oxidation is gotten from measuring oxidant consumption via analyzing simply for periodate left after incubation of standard periodate and the sample.

All derivatizing agents and any solvents used to handle them in prospective manufacturing processes are picked to be largely (probably completely) recoverable. In case there is any difficulty in this regard, derivatizing agents and solvents also are available which are completely biodegradable and nontoxic when diluted.

A.3. <u>Budget</u>	<u>LCMR Funds</u>	<u>Matching Funds</u>
a. Amount Budgeted:	$ 50,000.00	-0-
b. Balance:	$ 31.00	-0-

A. 4. <u>Timeline for Products/Tasks</u>

	Nov 91	May 92	Nov 92	May 93	Nov 93
i. Laboratory survey of rayons	X------------	--X			
ii. Synthesis and Derivatization of thermoplastic celluloses	X------------	------------	------------	--X	
iii. Relations of mechanical strength and packaging parameters to recyclability of both commercial and modified cellulose materials	X------------	------------	------------	------------	X
iv. Water absorbability and penetration of packaging celluloses		X------------	------------	------------	X
V. Coordination with actual manufacturing needs				X------------	X

A. 5. <u>Status</u> :

Due to the delay in funding allocation, this project was not initiated until the beginning of November, 1991.

I. Over more than 200 literature references on cellulose rayons and cellulose esters have been reviewed. They indicate that development of a wide variety of the new, stronger and more durable rayon fibers have resulted in significant broadening of the range of viscose composition employed commercially. Raw materials used for the manufacturing of rayons and cellulose, sodium

hydroxide, carbon [illegible]fide, modifiers and water and the most practical source [illegible]ulose is wood. Cellulose [illegible]plastics have long been used for the extrusion of film an[illegible]ting and for the injection molding of parts. Cellulose esters are thermoplastic and are adaptable to compression molding, injection molding, extrusion and solution casting. There was paucity information on manufacturing process of cellulose rayons or cellulose esters for packaging uses. Almost all of the packaging materials cited in the references are petroleum by-product base, such as fluorocarbon, ionomer, acrylonitrile, nylon, polycarbonate, polyester, polyethylene, polympropylene and polyvinyl chloride etc. The only most popular packaging material that is made from cellulose is cellophane. It was produced by DuPont in 1924. In the manufacturing process of cellophane, viscose was produced, then cast, onto a large roll operating in a sulfuric acid bath.

In response to 70 letters requesting product samples from cellulosic rayon/esters manufacturers, only four rolls of cellophane packaging products were obtained (through purchasing) from Flexel, Inc. Atlanta, Georgia. The rest of the companies either did not respond to our request or sent us a letter explaining that they did not manufacture any packaging materials. Eastman Chemical Company made some tenite cellulosic plastics of acetate, butyrate and propionate but none of them is for packaging use. Typical uses of tenite cellulosics are tool handles, optical applications - ophthalmic frames and face shields, toothbrushes and hairbrushes, cosmetics and personal care items, tubing and pipe, medical devices, automotive steering wheels and trim, appliance parts, toys and sporting goods, writing instruments, sheeting and furniture profiles. Of the four cellophane that we purchased from Flexel, Inc. they are all uncoated and/or unsized regenerated cellulose film. Major applications of these products are cellophane tape, roll leaf and release sheet applications.

II. Some types of cellulosic material have been derived in our labs. Aspen hard wood sawdust, ground hybrid poplar and waste paper towel were used as the raw materials. The most promising material is cellulose acetate propionate grafted methyl acrylate and blended with copolymer (MA/CAP-BC). It was made from poplar, sawdust or paper towel by multiple polymerization process. Favorable characteristics of the material are heat stable, low water absorption capacity and low gas (carbon dioxide and amonia) diffusion rate. The primary shortcoming of the material is it's high cost. It is the most expensive cellulosic among the three products we manufacture in our lab. Other products we made in the lab are cellulose acetate (CA); cellulose acetate propionate (CAP)); cellulose acetate butyrate (CAB); and cellulose acetate propionate blended with homopolymer (CAP-BH). CA is the least expensive product but it is easily hydrolyzed. CAP is intermediate in cost but it is the weakest in terms of physical strength.

III. Mechanical strength of the materials ranged from the strongest MA/CAP-BC to the weakest CAP. Tensile strength of these products is stronger and more recyclable than the petroleum derived plastics. It is our objective to improve the mechanical strength of these products and to reduce water and gas permeabilities.

IV. Water absorption capacity of the cellulosic material is significantly less than that of cellophane. This implies that manufacturers will find these materials more attractive than cellophane and more suitable for packaging material uses.

V. In order to improve mechanical strength (tensile strength) of cellulosic products we are undertaking the following approaches:

1. Modify the pretreatment process of raw materials to optimize degree of hydrolysis.
2. Increase molecular weight by adding alkyl group to the polymer or improve conditions for polymerization.
3. Use graft and crosslink technique in manufacturing processes.
4. Synthesize new copolymer or homopolymer as blending agent.

VI. Clarity and flexibility of film formation have been improved after graf olymerization. The conditions afting and esterification are similar to those for previous fication, except that nitrogen was filled in the grafting system. The percent grafting, the efficiency of grafting, and total conversion were calculated. Paper towel yielded highest efficiency of grafting among three kinds raw material because its lignin content is the lowest. The percent of homopolymer was seen to decrease with decreasing lignin content. The reduction of polymerization rate of cellulose was the main reason for higher grafting rates. Increases in the surface area of cellulosic samples have been shown to increase grafting rates as well as grafting yields.

VII. Water Vapor Transmission Rate (WVTR)

The permeability of films prepared by solvent casting may be influenced by many factors, including polymer hydrophobicity, solvent composition and plasticizer content and may be modified by changing the structure of the polymer. The permeability coefficient is dependent on the physiochemical characteristics of the polymer and is influenced by the type of substituent used to make the cellulose polymer. A change in the permeability coefficient would alter the water vapor transmission rate constant. When the WVTR constants were averaged over the relative humidities (RH) the following rank order of substituent types was observed: CAB<CAP<CA<CAP/MA < Cellophane. A decreasing order of WVTR (CAP>CAB>CA) was observed at low RH condition.

Comparision of results of WVTR of cellulosics or cellophane suggests that the WVTR of cellophane is higher than cellulosics at higher RH. It appears that cellophane is more sensitive to moisture than cellulosics.

VIII. Permeability of some cellulosic films to gases was about 0.1 to 0.25 of that of cellophane except cellulose acetate propionate product made from sawdust which do not show significant difference among three cellulosic films. The permeability of NH_3 is about 50% more than the of CO_2.

IX. Clarity of cellulosics films derived from three kinds of raw material are all as good as that of cellophane and have little difference among raw material used. Clarity of films is not affected by grafting.

X. Color of cellulosic solution increased with increasing temperature, the increasing order of heat stability of cellulosics is CAP<CA<CAB, and was charred or decomposed over 190°C. However, solutions can maintain good clarity at 160°C for most cellulosics

XI. Permeabilities of cellulosic packaging in relation to film forming properties

In order for packaging to form films (to be useful as recycled materials in packaging) they need to have physical properties in the following ranges. Tenacity; 1, 2 - 3.2 gm/denier; Elongation, 20-30% dry and about 20-40% wet. Derivatized cellulosics and rayon-like materials which fall in this range also may adsorb, and be permeable to some extent toward water, low M.W. flavor-taste components. Accordingly relatively uniform cellulosics were evaluated (regenerated cellulose), also regrinds from recycle cellulosic packaging, for their permeabilities to ethyl acetate, acetic acid, and ammonium ion. These were analyzed for by gas chromatography, and by colorigenic reaction using dichloroisocyanurate for ammonium.

Film recasting was carried out by partial dissolving of regrind cellulosics in a pressure tube at autoclave temperatures, then cold-wire redrawing out the film from the melt. This technique does not produce a film of the desired thickness in each draw. However, by reasonably careful attention to conditions, experimenttion, one can produce several square centimeters of films in 2-10 mils thickness, uniform to ±20% relative to overall thickness. The films can be squeezed to make them thinner, by heating metal plates and inserting them quickly in the jaws (insulated) of a vise, with the plastic material in between the plates. The latter kind of technique is more recent. Most of our data pertains to cold wire draw materials.

The thiaz take values refer to films of 5-8 mil thickness (5 to 8 th lths inch). The permeabilities are cm^3 (STP) x cm/cm^2 of film area x sec x Pascal pressure.

The technique is sensitive and accurate. Cellulose contents of the materials in the table, range from 62-90% by weight. These cellulose contents are useful in case these cellulosics are to be diodegraded. They roughly predict long-term biological oxygen demand, the B.O.D. Also they should predict, contingent on further determinations, approximately how much nonbiodegradable, or slowly biodegradable, material remains to be handled by any other disposal process. We should expect this latter (non-readily degradable) material, are plasticizer-organic compounds used in original manufacture, which should be recycled if possible, or otherwise reused. Increasingly it looks likely that some of these materials, instead of recycling aimed at packaging, could advantageously be used for recycling their carbon. That is, to make adsorbent and catalytic carbons. This is explained in the next section, based partly of discussion with Donald Eaton at 3M Company, and some of our own work.

A. 6 Benefits: A successful development of cellulosic packaging material will help combat the disposal problem of plastics at the landfill site by recycling, reuse and composting. It will produce completely nontoxic packaging and salable technology.

B. Recycling

The project shall include R and D for cellulosics: Aim at getting central physical data for selecting energy efficient means and paths, in re-use and recycling cellulosics.

B1. Narrative

Several possible paths for recycling cellulosics are apparent. These are either single operations, or combinations, or grinding, low temperature fracture, solvent extraction, melting, reprecipitation, hydrolysis, critical point gas (CO_2) extraction. Choice of these depends on the cellulosic material at hand, also on what the resource recovery use actually shall be. Recycled cellulosics headed for re-use as packaging materials, reblending with other recycled products, would be recycled in a different way than cellulosics which might be hydrolyzed and partly fermented if fermentation is possible.

We shall carry out three areas of work that we view as probably most practical at this point to carry out, useful in most recycling paths. Namely, determination of regrinding energetics, reprecipitation and melting energetics, combustion energies.

There are several technical factors which hinder plastics recycling: the production of thermosetting plastics requires the setting into permanent shape of the resin by the application of heat and pressure. These plastics are thus by their nature impossible to recycle as a material, though they do offer limited potential for by-product generation; thermoplastics are frequently mixed with plastics based on different resins or with completely different materials during the course of fabrication and conversion. As different thermoplastic polymers are incompatible they must be separated before they can be used for re-processing.

Effective recovery technology declines rapidly as the virgin resin moves towards the end-use item. The more mixed, the dirtier, the wetter and the less consistent the scrap, the cruder and less consistent are the products that can be made from it and the greater the cost of converting it.

All processes, including recycling, have a 'cost', meaning energy costs. It is logical to find what those energy requirements actually are. That is, minimal energy requirements. Although incineration or burning of cellulosics is not recycling them as polymeric materials, burning can produce process heat. Process heat shall be needed in almost any recycling strategy. Therefore the combustion energy content of cellulosics (oxygen bomb combustion) is wanted in order to determine what fraction of packaging material might be used to supply adequate process heat to drive the rest of [illegible]ocess. Or, to drive recycling processes for other materi[illegible]. other plastics.

B2. Procedures

I. Two kinds of calorimeters shall be used to make the energetics measurements. For burning energies values, we need a bomb combustion (oxygen bomb) calorimeter. There exists one such calorimeter at the Center for Environmental Studies, Bemidji State University and another unit at the U of M - St. Paul campus.

II. A path for recycling of cellulosics is likely to involve extraction of them out of packaging particulates. They likely will be re-incorporated again in packaging, probably via light crosslinking of recovered cellulosics to rebuild their polymeric nature. We shall carry out such extraction with environmentally compatible solvents. These extractions shall be carried out at intermediate temperature, from ca. 20° less than the boiling point of the solvents, up to the boiling point. After extraction, temperatures are kept at the boiling point, pressure is relieved, solvent is distilled off and recovered (condensed). The energy costs are primarily the heat of evaporation of whichever solvent is chosen, less whatever heat can be obtained by recycling heat from the condenser to raise temperatures of incoming material ("cogeneration").

III. Extraction of cellulosics out of mixed materials such as cellulosics agglomerated with other plastics will be studied. This should accrue if the second plastic is made more porous, less aggregated, or in effect attains a lower melting or softening point as cellulosic is removed.

B. 3 Budget

		LCMR Funds	Matching Funds
a.	Amount Budgeted:	$ 50,000.00	-0-
b.	Balance	$ 40.00	-0-

B. 4. Timeline for Products/Tasks

Nov 91 May 92 Nov 92 May 93 Oct 93

i. Determination of regrinding energetics x---------------------------------- x

ii. Determination of reprecipitation and melting energetics x--x

iii. Determination of combustion energetics x--------------------------------x

iv. Extraction of cellulosics with environmentally compatible solvent x---------------------------------x

v. Extraction of cellulosics out of mixed materials x---x

vi. Final Report x

B. 5. Status:

This research element was not initiated until the beginning of November, 1991, due to the delay of funding allocation.

I. The 'energy value' of a large variety of cellulosics involved in packaging are intended to be measured. Dr. Chang has acquired several of these from companies who manufacture and sell diverse cellulosics. These cellulosics shall be partly solubilized or regenerated using nontoxic solvents.

Heats of combustion of pure cellulose are close to 12000 B.T.U./lb. This figure sets an upper limit on energy needed to 'take cellulose apart' for recycling. However in recycling not nearly all the energy content (with respect to combustion) need be consumed. It is estimated that from 10-25% of this figure, i.e. from 10000 to 30000 B.T.U. energy/lb. may be needed to deaggregate cellulose so it may more easily be recycled. Cellulosics which have already been modified are rather less energy demanding, having lost some of their crystalline character.

II. Calorimetry of water vapor (or other solvent vapor) adsorption has been carried out, based on our construction of a differential heat conduction instrument for the purpose. We have carried out two main kinds of measurements on cellulose and cellulosics with it: (i) Measurements to obtain the characteristic heat of adsorption of water, from known vapor pressures of water (using A.S.T.M. hygrostats). For crystalline cellulose, these heats are close to 8 Kcal of heat (exothermic)/mole of H_2O. This should be equal in magnitude but opposite in sign, i.e. endothermic for drying the cellulose. (ii) Measurements to obtain the surface area of cellulosics, recycle cellulosics, or modified cellulosics, assuming the 8 Kcal/mole is about constant.

III. Most of the work on cellulose energetics has been carried out with rather pure cellulose, e.g. Avicel. The next main group of energetics or energy content measurements, should be done with the derivatized celluloses, and recycle celluloses. These celluloses are expected to be lower melting, with decreased heat of water adsorption-desorption.

IV. Combustion Energy Value:

Several cellulosic films (CA, CAP, CAP/MA, CAB, some organic waste materials and commercial cellophane were measured for heat of combustion.
Energy value increased with increasing carbon chain. The increase of combustion energy value depends on different original materials, the increase order are paper towel>poplar>sawdust for all three kinds cellulosic films. Energy values of our cellulosic films are 20-40% higher than commercial cellophane. Combustion energy values were not affected significantly by grafting, energy values reduced about 0.7% after grafting.

V. Recycled materials for Making Carbon

One of our aims is to develop carbons for production of esters, in which esters are made from ethanol. Carbons can be used as catalysts, as absorbents, antioxidants, in water purification.

One of the 3M company's division is already involved in pyrolysis and carbon manufacture, also in feasibility studies. We found that two forms of carbon are efficient, relatively inexpensive, and completely recyclable for this.

Conversion of packaging material to carbon, is being set up with a small pyrolyzer, able to take 20-40 gm of material in about 10 minutes. Depending on quality of the carbon, this should be scaleable. The data gathered so far is intended to provide a basis for industrial feasibility prospects for carbon from - recycle.

Carbon in several forms is used on a large scale in industry, also for domestic use. Pelletted carbon is much favored for removing toxic and organic materials from both air and water, and for capturing solvent to either recycle them, or to purify other materials. Carbon decolorizes materials, including beverages, and removes bad odors. Carbon is useful for many other purposes (such as catalysts, or protection agents for catalysts). Hence discard package [illegible]ials for partial pyrolysis under [illegible]ing conditions may have potential for this market. High[illegible]st carbons retail from $5 to $15 per pound. These are made from pure petroleum hydrocarbons. Pyrolyzed packaging very likely cannot compete with those carbons. However as lower cost carb. for recovering toxic materials as an absorbant and similar applications, lower grade carbons should have good demand, as in air and water filters and treatment.

We report here physical characterization (Table 28) of four carbons gotten by heating packaging materials in a nitrogen atmosphere, to make the carbons. These parameters are the most useful parameters for gauging performance as adsorbants for compounds of kinds wanted to trap. In addition, usually it is very desirable to recycle the carbon to use it again, and remove the toxic compound or other compound trapped out, as a concentrate, isolated. For this, we Soxhlet extracted compounds trapped on carbons with low boiling alcohols. All three components can then be recovered, well separated from one another, by removing the carbon particles from the Soxhlet extraction device (upper chamber), and distilling away (for recovery) of the solvent. This leaves the contaminating chemical behind in the stillpot. This is far more effective than using an anion exchange resin: Such resins are powerful in trapping out TCA. But it is very difficult indeed to recover the resin, fee to TCA, for it has a tremendous affinity for the resin, much greater than any other anion we've found (so it can't be displaced). Thus we expect 'recycle carbon', lower grade carbons from mixed recycle material, is much preferred in an application of this kind.

VI. <u>Energy Requirements in Recycling Cellulosic and Packaging Materials</u>

Feasibility of recycling any waste materials most basically depends on how much energy, how much chemicals if any and their costs, needed to do the recycling.

There are three categories of energy involved: (i) The intrinsic energy content of the material. The intrinsic energy content of gasoline, and also of coal, is close to 18,000 B.T.U. per pound. Of course to use them efficiently, different technologies have to be used in their combustion. But complete burning either one (to CO_2 and water) gives off between 17,000 and 19,000 B.T.U./lb. (ii) The second category of energy is energy wasted (usually as waste heat) during whatever process is involved. Most engines waste about 70% to 75% of their fuel's total energy, as waste heat. (Very efficient large scale electric generating plants waste only about 50-60% of their input energy as waste heat. (iii) The third category of energy, needed to know, is how much energy is made either into useful work, or left in a product after paying for the waste energy. Applied to recycled materials such as cellulosic materials, they mostly have combustion energy contents of 11,000 to 14,000 B.T.U. per lb., depending on their carbon, hydrogen, oxygen content ratios. These values are not much different from that of pure cellulose (12,000 B.T.U./lb.

However even though cellulosic wastes such as cellulose acetate butyrate have energy contents in the range of 15,000 B.T.U. per lb, as a measure of their worth, it takes more energy than that, to recycle them. However it does not require as much energy to recycle, as to make the same packaging material new, in our estimation.

Perspective concerning that last point - energy of recycling vs energy needed to manufacture the same material new - can be seen in the case of cellulose itself. Although its energy content is about 12,000 B.T.U. per lb., it takes roughly 50,000 B.T.U./lb to extract it from wood (chipping, delignification, removal of water, filtration, regrinding if necessary). Furthermore, the costs of chemicals needed (sulfite-chlorine process) to do the delignification, and costs of treatment of waste water and oxidation of lignosulfonate wastes-if those are indeed expended-have not been added in. We do not actually know these latter costs, although they could be determined in another project. Possibly, some of our paper companies know them, but we do not have them at hand.

Recycling cellulosics may take only one mechanical step (regrind, remelt) to make ready for remanufacture, or it may take an additional step, derivatization to convert to an ester, currently carried out by Rayonie, Hercules, companies on the East Coast.

VII. <u>Means fo[illegible]rmination of Mechanical Processing Energy Dissipatio [illegible]t), and as Stored Energy.</u>

Power input. P.I. = Power lost as heat - Energy stored in the material being processed

$$P.L. = P.L.-E.S.$$

Since we measure P.I. and P.L., then E.S. is possible to determine. Under grinding conditions we were able to achieve, E.S. is relatively small, about 5 ±4% of the total power input P.I. In small laboratory milk which probably are rather inefficient, most power input in brinding packaging materials becomes waste heat. Averaging over seven different packaging samples, five Green Giant vegetable packaging, and two cereal boxes (General Mills), percent of input energy given off as waste heat, ranged between 82 to 95%. The average was 9.1%. Thus about 9% of the input energy becomes stored in the sample. This energy is the increased surface energy of the grind, of the particulate material, relative to the energy content of the bulk, unground form.

VIII. <u>Separability of Chopped Packaging Material for Recycling</u>

Some packaging materials are mixtures, of paper or cellulosics, and plastic films like polyesters. Some of these plastics are soluble enough to be extracted by hot solvent as in Soxhlet extraction. However others such as polyethylene are quite resistant. Solvents such as THF (tetrahydrofuran) are fairly good solvents or at least softening agents for such polymers, besides being reasonably low boiling, in the 60-90°C range. However such a process will require recycling the solvent, by redistilling it off the extracted resins and plastics, leaving the latter behind at residue. Because of the length of time for carrying out such a process, all the heat needed to carry out both main steps (extraction, redistillation), also the fire hazard of large amounts of flammable solvents, hot organic solvent extraction to separate out cellulose and cellulosic derivatives, from resins or plastics, does not appear practical. For expensive materials, hot solvent extraction may be useful because of its flexibility. However it is not simple, and can be hazardous because of the flammability problem

IX. <u>Derivatization of Cellulosic Recycle Packaging</u>

After grinding, converting bulk packaging to small particles, one of the ways to try to recycle is to derivatize enough by for example acetylation or propionylation, so the recovered and derivatized material can be made into films, cast, or molded. It is not necessary to convert all material to be recycled, to a product which is close to a pure plastic. The intent is to modify cellulosics so they can be remolded with the aid of heat, formed into films that are barriers against water and water vapor, be nontoxic, able to be refabricated.

To gauge the softening and film forming capacity of acetylated and propionylated recycle cellulosics, stretch-temperature profiles, and break point-temperature profiles method were used, with some modifications to compare with Saran wrap film in these characteristics. They also were compared with standard Saran wrap in 'cling' character, by measuring the weight, of a drag (a weighted object) necessary to peel such films lengthwise, off a 1/4" rod around which 2 layers had been wrapped. This is a rough comparison, but probably reasonable means of measuring 'cling' character. The data concerning cling takes into account the thickness of the films, both the standard against which we make comparison and the modified recycle film.

Recycle materials that are heavily loaded with printing and sizing additives, especially clay-like materials and Bentonite-like materials, neither derivatize readily nor have good mechanical, thermal, or cling properties, from treatment. It appears that cardboard, paper and related packaging based on cellulose, will not be practical to recycle via mild chemical treatment to derivatize it. Cellulose relatively free of such agents however, does take on properties compatible for using them again, such as ability to cling, keep reasonable tensile strength.

B. 6. Benefits:

Recycling of cellulosic rayon packaging material could (1) maximize income from marketable products, (2) reduce quantities of residue for disposal, (3) obtain maximum benefit from necessary separation/screening processes and off-setting waste handling conveying activity over more products and (4) reduce economic risks by providing flexibility (with careful planning and design) to accommodate fluctuations in markets for different products. The improvement in recycling technology resulting from this project would open the field for a number of new industrial (pulp paper) and environmental (waste paper) application.

C. Basic Parameters Needed for A Recycling Recovery and Reuse Strategy: Color Tagging Cellulosics For Recycle Identification

C1. Narrative

The energy saving through recycling and use of waste cellulosic materials varies considerably by quality of waste paper and type of end product. To the extent that further recovery of waste cellulosics packaging materials will be from more contaminated sources, requiring energy intensive preprocessing, the unit energy savings potential will be restricted.

Composting sewage sludge prior to land application may be a good way to utilize municipal and animal wastes in or near metropolitan areas. Large amounts of sludge can be stored in composts with minimum undesirable effects on the environment. During composting some organic matter and N are reduced and pathogenic microorganisms are eliminated. Composting processes require the carbon: nitrogen ratio to be within given limits. Extra nitrogen is readily available from animal manure or sewage sludge. However, paper is the main carbon source and would prove more difficult to substitute if removed.

When recycling, recovery and reuse becomes the norm, it is made easier if one can categorize recyclables by color. That is, pick out cellulosics. Accordingly, FDA approved dyes shall be incorporated in cellulosics, covalently linked if possible, to provide visible tags for recycling.

C2. Procedures

Recycling of plastics both cellulosic and petrochemicals based is reliant on grinding and chipping, in the initial stages of recycling. In order to follow this and relate it to energy inputs, the amount of additional surface added as grinding proceeds is the best index. This shall be evaluated in a surface measurements calorimeter. It is an easily used, precise way of obtaining surface development. Integral heat of absorption of water vapor, alcohol vapor, etc. onto preweighed samples are measured. As surface area increases from grinding, e.g. ball milling, above 10-20 m^2/gm, specific heats of absorption increase linearly.

If incineration is used for getting rid of waste, also heat recovery, a principal question is whether the material produces toxic compounds. We shall use two methods of measurement, aimed at elemental chlorine, and at heavy metals. Measurements shall be carried out on recycle particulate materials, petrochemical, and cellulosics, and agglomerates or mixtures of the two. For heavy metals the technique is to ash the plastics, then use either atomic absorption analysis, or spectrophotometry . Organochlorines shall be analyzed via electron capture mass spectrometry .

Composting will be practiced with operations using a combination of city garbage that includes cellulosic packaging materials and animal manures or sewage sludge, adding water to about 50% water holding capacity, and allowing the mixture to digest for several weeks until the compost is mature. Time required to achieve maturity will be studied with different cellulosic contents. Fertility value will be analyzed for each compost pile.

Dye (food grade dye) tagging, visible indicators identifying a recyclable cellulosic, will be carried out. We shall simply dissolve such dyes in hot melts, cool the melt, and regrind it. This shall permanently [illegible] or occlude the dye, until remelted or ground again. We [illegible] covalently link such dyes to cellulose itself, or to cellulosic plastics. We believe that simply [illegible]ing in" the dyes, without doing any chemistry, is best for practical purposes to provide imbedded identifying colors for recycling.

C.3. Budget

		LCMR Funds	Matching Funds
a.	Amount budgeted:	$ 50,000.00	-0-
b.	Balance:	$ 23.02	-0-

C.4. Timeline for Product/Tasks

	Nov 91	May 92	Nov 92	May 93	Oct 93
i. Categorization of recyclables by colors (dye tagging)	x-------	--------	--------	------x	
ii. Recycling technology and packaging engineering (energy input)	x-------	--------	--------	------x	
iii. Composting		x-------	--------	--------	------x
iv. Incineration (waste gas output)			x-------	------x	
v. Final Report					x

C. 5. Status Reporting:

Due to the delay in funding allocation, this research element was not initiated until the beginning of November, 1991.

Two food grade dyes have been incorporated into fibers by precipitating them via the solvent treatment process (evaporation of solvent after treatment). They are intended to enable easy visual identification of the kinds of cellulosics that may be recycled, or kinds that should go to incineration or composting if incineration or composting is used. Such dyed cellulosics are being determined for their stability. The reason for using food grade dyes for this purpose even if they are less stable is that they are safe to be used as recycled materials for food packaging.

I. Recycle Identification

The two additional food grade dyes have been incorporated into cellulose, for visualization of the kinds of cellulose products suitable for recycling. (Or for incineration, or composting).

II. Recycling For New Products, Upgraded Products

A product for stabilizing soils against water erosion is being developed with cellulosics. The product is a network of recycle cellulosic fibers, derivatized enough to biodegrade only slowly. The cellulosic network protects against washing while allowing some w[illegible]er penetrance, and acting as a [illegible] for clayey soils.

Another product partly developed is absorbent for proteins and enzymes. In many industries including food processing industries and food production, absorbed proteins are rather high value-added products. This is especially the case, for certain enzymes. Foreign made cellulosics are imported into the U.S. for this purpose, and as chromatography supports. Some of our work is aimed at competing with these using our own cellulose and if possible recycled cellulose.

III. Recycling packaging for conversion to carbon: Consultations with 3M specialties product division (Curt Larson's group).

If recycling old packaging to make more new packaging, is marginal from 3M's point of view, there are good prospects for using some kind of packaging for making salable absorbents, especially carbon. That is, by pyrolyzing used packaging to the extent of turning most of it into carbon, analogous to charcoal briquet. A number of carbons are fairly high added value materials. Activated carbons retail for $5 to $15 per pound. They are used in very large quantities for about fifty industrial and domestic purposes. Many of these uses are for absorbents of polluting chemicals, removing off-flavors from refrigerated rooms, from food products in some cases (especially fish and meat products in storage), as clarifying and decolorizing agents. Carbons are used fro purification of other chemicals, including synthetic chemicals, even proteins, and sugars. Often thy are called charcoals, and in many respects are close to cooking charcoal, except they have higher surface areas than ordinary charcoals (100-500 m^2/gm).

We developed a very significant pollutant chemical stripping method with a carbon. Trichloroacetate (TCA is a large volume, very toxic chemical produced in industry. Working with Lifecorps Inc. of Minneapolis, we developed a means for recovering TCA from water and industrial fermenter solutions, by carbon. The carbon absorbed all the TCA our in about 20-30 minutes.

It looked very much as if carbon gotten from recycling used packaging, can be used industrially, in a simple process cycle, at low cost, for removing toxics from water. Adsorbent carbon has been used in this way before, but these are far more expensive carbons than the materials from recycle.

Because some packaging has chlorinated polymers in it we are thinking now that leaving some of the chlorine in them to make a lower pyrolysis temperature carbon, would have advantages for removing chlorinated organic pollutants. The TCA example is removal of a toxic inorganic pollutant that has been causing considerable trouble. We look forward to collaborating more with the two industries that have helped us with these materials, also advice, 3M people, and Lifecorps, Inc.

IV. Biodegradation test

A natural sandy soil was used as the source of the soil microorganisms and two separated cellulosic film groups were cut into small pieces and mixed with soil. The final products of biodegradation are carbon dioxide and water.

From our biodegradation results it can be concluded that 1) all of our cellulosic films are biodegradable, although they are less biodegradable than cellophane; 2) biodegradation rate of cut film is higher than the whole piece film because microbial intrusion increase with increasing surface areas of film; 3) cellophane and cellulosics were degraded into simpler sugars by enzymes produced by microorganisms which are readily degraded by many microorganisms to form end products - carbon dioxide and water; and 4) cellophane was degraded faster than all of our cellulosics, this is probably because cellophane is much more soluble than cellulosics.

Nine cellu[illegible] packaging product samples were mixed into three replic[illegible] each of the three soils and th[illegible]s with soil only were used as a base indicator for natura[illegible]gen absorption. Each sample was cut into small pieces (approximately 1 mm. x 5 mm.), 0.15 grams of each product were placed in 16 oz. glass jars with approximately 150 grams of wet soil.

Percentage of degradability was lowest for clay soil (#3) and higher in sand (#1) and humus soils (#2). The commercial cellophane was degraded at a higher rate in humus clay soil (#2) and clay (#3) but slowly in sandy soil (#1).

In all cases CAP was degraded faster than samples graft with methyl acrylate. This could be due to more complicated structure of the graft sample and higher molecular weight, Although molecular weight of the films were unattainable due to testing implications and security reasons, it is fairly safe to assume that graft sample will have higher molecular weight than ungraft samples. There have been studies that suggest that low molecular weight increases biodegradability and branching inhibits degradation. It has been suggested that the length of degradation time depends on the ratio of natural to synthetic compounds the graft co-polymer contains.

The effects of polymer structure on biodegradation is very important. Many synthetic polymers that claimed to be degradable contain hydrolyzable linkages along the polymers. Natural macromolecules are generally degraded by hydrolsis followed by oxidation. If the synthetic polymer is flexible enough to fit into the active site of the enzyme it can be degraded by enzyme catalysis. Therefore the morphology of synthetic polymers is very important. Regularity enhances crystallinity making the hydrolyzable groups on the polymer inaccessible to enzymes. Synthetic polymers with long repeating units are less likely to crystallize and are thought to degrade faster. The orientation of the polymer molecules can increase or decrease the secondary valence forces acting between polar chains. The more symmetrical a polymer is the stronger the tensile strength and increase elastic modulus. It is suggested that enzymatic degradation is selective of semicrystalline polymer samples where during degradation, the crystalinity of the sample increases rapidly at first while enzymes attack the amorphous portion of the sample first. As crystallinity approaches 100% the rate of degradation levels off to a much slower rate leaving the crystalline lattice degradation last. Therefore molecular weight and the degree of crystallinity are the dominate factors for determining degradability, depending on the existing indigenous microorganisms.

Both the SB and CB showed lower oxygen uptake than natural rate determined in the empty jar which may mean the plastic is having an inhibiting effect on degradation and effect of SB on microbial activity is greater than GB. This could mean that no autooxidation is taking place. This could be due to coatings on the plastic films or the nature of linear hydrocarbons to be less readily oxidizable. But it should be able to be metabolized more readily by microorganisms if proper microorganisms are present in the soils.

Degree of cellulose degradation is dependent on the presence of impurities. Cellulose and cellophane have the same structural formula but different morphology. Cellulose was degraded to carbon dioxide and water. The rate of cellulose degradation is controlled by its hydrolysis to glucose. Water allows hydrolysis to take place, therefore, moisture content is important. CA, CAB, CAP and samples graft with MA are all considered to be cellulose esters. Acetylation takes place to different degrees, resulting in varying properties in the presence of different acids and catalysts. There are three hydroxyl groups per chain unit (glucose) and the properties of the polymer depend on the number that have been substituted. The degree of substitution (D.S.) used mainly in cellulose chemistry, measure (0-3), the substitution of reactive hydroxyl groups on each of the anhydroglucose units. Cellophane is a non-thermoplastic that absorbs water easily while the cellulose esters are considered thermoplastic. CA is lighter than regenerated cellulose and moisture sensitive, its molecular weight is dependent on acetic acid content. CA is as thermoplastic resistant to oil and many chemicals. CA made from hybrid poplar also showed better degradative property than CAP and CAB probably due to degree of substitution. Cut pieces that degraded at faster rates than whole pieces of the same film type can be due to increased surface area of cut pieces, allowing microorganisms more surface area to react upon. CAB has one hydroxyl group and four anhydroglucose units. CAP is more soluble than CA and shows lower weatherability than CAB, this may explain why CAP was degraded slightly faster than CAB.

Comparative results of biodegradability of films made from sawdust, h[illegible]d poplar and paper towel sho[illegible] difference. CAP and MA/CAP made from all three ce[illegible] bases degraded to abo[illegible] same extent.

V. Incineration

Environmental and food safety can be directly or indirectly affected by the incineration of petroleum base plastic packaging materials. The U.S. Environmental protection Agency (EPA) considers six pollutants produced from incinerators might be present in sufficient quantities to pose a threat to public health. They are arsenic, cadmium, dioxins, and furans, hydrogen chloride, lead and mercury. Pathways for the production of these emissions are not well understood because of the high tempertaure and heterogeneous mixtures associated with incineration of MSW. All of these emitted materials can enter human body directly by inhalation or indirectly through water consumption and the good chain, thereby increasing our exposure.

Elemental chlorine and heavy metals are two main items measured in our incinerated samples.

1. Chlorine

Measurement of total chlorine contents gives the sum of water soluble chlorides and the combusted organically bound chlorine compounds present in a specimen.

Chlorine presented in various cellulosic materials indicates that part of the chlorine in film products was introduced mainly from raw materials pretreated with sodium chlorite and chlorine production decreased with chemical reaction presses extensively.

Despite the fact that there is a broad difference in chlorine production among the three final products (MA/CAP film) made from three raw materials, chlorine in MA/CAP; poplar is much higher (10--folds) than MA/CAP, paper towel, but it is still close to or below that of cellophane.

2. Heavy Metals

Heavy metal in cellulosic film or commercial plastic, was measured using oxygen flask technique for the combustion of specimens, similar to the method of chlorine measurement. After absorption liquid (diluted sodium hydroxide) was neutralized with diluted nitric acid, acidity of solution was adjusted further with 0.1 N hydrochloric acid and concentrated to 10 ml in volume. Heavy metals were determined by Model-902 Atomic Absorption spectrophotometer. Heavy metal contents (Cd, Zn, Cu, Pb, Ni and Mn) in manufactured films are much lower than raw material (sawdust) and most metals are below the detection limit.

VI. Color Tagging

According to our previous work, three colorants were chosen as color tagging, visible indicators for the identification of recyclable cellulosic films. Experiments were set in three colorants with two time intervals (4 hr and 24 hr°. Six groups of treatment were conducted. A: UV exposed: B: freeze; C: water immersion (20°C); D:oven dried at 50°C, E: microwave oven heated at high power; F: autoclave. Three cellulosic films treated with different colorant in the same way were stored in the desiccator before weighed. The results showed that (1) [1]color tagging in films does not change during the test at room temperature (CK) 2) food yellow 4 colorant is the most stable among three colorants but food red 14 colorant is the least stable in our color tagging tests. Food yellow 4 colorant could be recommended in the future color tagging of cellulosic film manufacturing process 3) direct red 2 and food red 14 colorants, both are more sensitive to Uv. 4) the colorants have not been affected significantly by B,C,D. and E, except in food red 14 color[illegible] 5) direct red 2 and food yellow 4 both colorants in MA/[illegible]lm displayed completely differe[illegible]fects by autoclaving treatment.

Although dyeing technology of cellulosic materials has not been studied extensively, we believe dyeability and dyeing fastness of cellulosic films will be improved greatly with dye fixatives or fading inhibitors added or change of dyeing conditions. More colorants will be identified and used as color tagging in cellulosic film study according to the FDA regulations.

RECOMMENDATIONS

Throughout the R & D of this project we recommend that following R & D parameters should be further pursued:

A. To utilize other waste sources that are rich in cellulose.
B. To choose pretreatment pathways and conditions of raw materials that will increase reactivity and yields.
C. To improve synthesis techniques and optimize the reaction conditions, control degree to polymerization, improve tearing strength and elongation properties of products.
D. To study different proportions in each formula that are suitable for various uses of packaging products.
E. To further study techniques of forming, dyeing and packaging in final products.
F. To study recycle system of reaction reagents, extraction and redistillation of waste effluent during the manufacturing process to further reduce material consumption and minimize environmental pollution.
G. To conduct a detailed cost/benefit analysis and raw materials/reagents/products equilibrium in order to reduce the cost of goods and maximize yield efficiency.

C. 6. Benefits

Provide manufacturing opportunities for new salable packaging based on renewable resources-cellulose-in Minnesota. Enhance recycling, recovery and reuse in an environmentally compatible way through categorizing recyclables by dye tagging. The main benefit comes from production of packaging that is completely recyclable, nontoxic when incinerated, easily biodegraded, and compatible with current packaging manufacture in laminates, film forming, and extrusion.

IV. EVALUATION

Four general means of evaluation will be used.

(i) Our own evaluation and summary, based on how much energy is required in the recycling of cellulosic based packaging and rayons under the conditions described above.

(ii) Other institutes and agencies will be asked to evaluate the data, also use it if they indeed can. Namely, NRRI (Natural Resources Research Institute) at Duluth, Minnesota. The M.P.C.A. and Office of Waste Management in St. Paul will also be requested to evaluate and distribute the data.

(iii) Arrangements are being made with 3M Company, to evaluate our data, with respect to likely interest in manufacturing cellulosic based packaging raw material of enhanced recyclability.

(iv) Certain national organizations, and individual companies likely shall be interested if 3M Company does not have a great interest. A number of these companies e.g. American Hoechst, Mercules, Monsanto are likely prospects.

V. CONTEXT. RELATED CURRENT AND PREVIOUS WORK

A. Previous [illegible] on packaging by the packaging industry has been in the wrong direction with respect to biodegradability . Much of present packaging is based on chlorinated organics which when incinerated make either HCl or volatile organic chloride conjugates. Practically all 'plastic' packaging such as the styrenes relies on petroleum, not on cellulose nor on compounds from renewable or agricultural products.

Current plastics based packaging has two legs: (i) Petrochemicals, (ii) Ease with which plastics form films, blow mold, injection mold, extrude, seal, adhere, cling. Cellulose derivatives, rayons, etc. can help bridge the gap and make more sense, particularly to Minnesota which ought to sell cellulose.

B. Proposed work is supplementary in that it will provide a new material for current packagers to work with. The intent here is not to try to replace current packaging industry. Rather, it is to provide better alternatives, in different directions than the petrochemicals alternative since there is a huge, developable market for recyclable packaging cellulose rayons. We propose to use Minnesota agricultural and forestry biomass to produce cellulosic derivative packaging.

C. Both Chang and Lovrien have not accomplished any cellulosic packaging material R & D work without LCMR funds. Chang has been working on bioconversion of peat to ethanol and other useful products funded by U.S. Department of Energy through MN Department of Administration and LCMR (oil overcharge fund). Chang has been investigating microbial cellulases and lignocellulases system that can convert Minnesota peat to reducing sugars and then through fermentation process to convert reducing sugars to ethanol. He has isolated two bacterial species and four fungal species from peat bog that can be induced to produce these enzymes and result in high reducing sugar yields (up to 15,000 mg/l). Chang is also working on composting technology research and development. Lovrien has not had LCMR funds before, no planned LCMR proposals other than this one. However, if this one is successful, we might try to extend, or newly apply, this proposal.

D. Not applicable.

E. Biennial Budget System Program Title and Budget for this project for FY 92-93: None available at this time.

VI. Qualifications

1. Program Manager:

Fu-Hsian Chang
Professor of Environmental Microbiology
Bemidji State University
Bemidji, MN 56601-2699
Ph.D. Soil and Environmental Microbiology, University of California, Davis, CA 1979.
M.S. Biology (Microbiology Major and Biochemistry Minor)
University of North Texas, Denton, TX 1974.
Specialization: Biodegradation of xenobiotic compounds and biotechnological utilization of naturally occurring polymers.

Dr. Chang has refereed publications and conducted research in the areas of microbial degradation of crude oil and hydrocarbons in subsurface environments, biodegradation of toxic organics in waste water, microbial utilization of peat and bioconversion of peat to ethanol and other useful products. Current projects include "Biodegradation of crude oil in ground water environment" fun[illegible]y the U.S. Geological Survey, and "Bioconversion of pe[illegible]ethanol and other useful produ[illegible]unded by the U.S. Department of Energy through the M[illegible]partment of Administration and LCMR. Besides research, Chang also teaches Environmental Microbiology, Wastewater Treatment and Phytochemistry. He also team teaches Environmental Chemistry with four faculty members of the Chemistry Department (Chang's primary role is to coordinate this group and teach organic chemistry and biochemistry parts).

2. Coprincipal Investigator

Rex E. Lovrien
Professor of Biochemistry
Biochemistry Department
University of Minnesota
St. Paul, MN 55108
Ph.D. University of Iowa
Specialization: Naturally occurring polymers conversion, applied biochemistry.

Dr. Lovrien has worked on the Rosemount P. C. B. dump project for two years, and Diesel exhaust pollution projects, mutagenicity testing. Lovrien has worked with about ten projects involving microorganisms (bacteria), publishing 15 or so papers. Lovrien carried out several researches with enzymes and proteins, including several for cellulase enzymes and published those, about 20 papers. Lovrien also has researched and published six papers in synthetic polymers including vinyl polymers, and about 20 projects and papers in electronic instruments building. Lovrien also teaches analytical chemistry and analytic biochemistry, which pertain pretty directly to the proposed project.

A new means for assaying enzymatic degradation of cellulose, also for degradation of lignin compound which also are from wood, were designed and proven out in 1986-1989. New means for isolating cellulase enzymes and characterizing them were developed in 1982-1986 (list of papers are below). Biodegradation of cellulosic and wood materials by wood degrading soil fungi, tracked via "affinity gold" electron microscopy, was developed in collaboration with plant pathology people in St. Paul and at U.S.D.A. (Northern Region Laboratories, Peoria), and published on. Extraction and analysis, both chemical analysis and mutagenic analysis in two different pollutants projects were performed over a period of about three years, funded by private and institutional organization including the Federal E.P.A. A new instrumental analytic method based on microbial heat generation, heat conduction calorimetry, was developed for monitoring water pollutants related to petrochemicals. In connection with this we designed and build several calorimeters for Dow Chemical Company (pesticides pollutants) and Gulf South Research (river pollutants).

There are two Institutions involved in this proposed project. The principal research will be conducted parallelly in Lovrien's lab at the University of Minnesota and in Chang's lab at Bemidji State University. The headquarters for management of the project are at Bemidji State University.

1991 Research Project Abstract
For the period ending October 31, 1993.
This project was supported by the MN Future Resources Fund.

Title:	Cellulose Rayons for Packaging
Program Manager:	Fu-Hsian Chang
Organization:	Bemidji State University
Legal Citation:	M.L. 91 Ch. 254, Art. 1, Sec. 14, Subd. 13(g)
Approp. Amount:	$150,000

STATEMENT OF OBJECTIVES

The goal of this research project is to develop cellulose-based polymers, attractive to large manufacturers to switch from petrochemicals based plastics to a safer and more recyclable materials. Specific objectives are three folds: 1) develop cellulosics with desirable physical properties, including recyclability; 2) recycling of cellulosics - aiming at getting central physical data for selecting energy efficient means and paths, in re-use and recycling cellulosics and 3) basic parameters needed for a recycling recovery and reuse strategy, color tagging cellulosics for recycle identification.

OVERALL PROJECT RESULTS

Synthesis and derivatization of thermoplastic cellulosics were conducted using aspen hard wood sawdust, ground hybrid poplar and waste paper towel. A sequential of pretreatments were required to treat raw materials before major chemical manufacturing processes were undertaken. Various chemical synthetic processes were used, i.e. esterification, etherification and xanthation. Physical and chemical properties of esters vary with various degree of substitution levels and acyl-acyl ratio of the ester in mixed esters. Physical and chemical properties included in our test are water absorption capacity, water vapor transmission rate, water retention capacity, permeability to gases, clarity and heat stability. The tensile strength, tearing strength and elongation of cellulosic film products were measured and the results showed that tensile strength in an increasing order are MA/CAP blended >MA/CAP=CA >CAP>CAB and it increased more than 100% after grafting, crosslinking and blending. Tearing strength and elongation of our products are similar to commercial cellophane. Water absorption capacity decreased with increasing length of the carbon chain and thickness of cellulose esters and decreased with graft. Poplar wood made packaging material had a highest WVTR and WAC among three kinds of raw materials used. Recycling cellulosic waste of various kinds has its energy costs but not all steps in recycling can be accounted for. It is probably less expensive in terms of energy inputs, to recycle a number of cellulosic materials (kinds we have worked on) rather than manufacture them new, if they can be gathered for processing. Combustion energy value increased with increasing length of carbon chain. The increase of combustion energy value depends on original raw materials, the increasing order are paper towel > poplar > sawdust for all three kind cellulosic films. Energy values of our cellulosic films were 20-40% higher than the commercial cellophane. Comparative results of biodegradability of films made from sawdust, ground hybrid poplar and waste paper towel show little difference. Their biodegradabilities ranged from 13.9 to 26.5% after 105 days incubation period with an increasing order of CA > CAP > MA/CAP = CAB. When the films were incinerated there was very little chlorine and heavy metals produced in the waste gases. We recommended that the following R & D parameters ought to be pursued further; 1) utilizing other waste sources that are rich in cellulose 2) choosing pretreatment pathways and conditions that will increase reactivity and yields 3) improving synthesis techniques and optimizing the reaction conditions, controlling degree of polymerization to improve tearing strength and elongation properties of products 4) studying different proportions in each formula that are suitable for various uses of packaging products 5) studying further on techniques of forming, dyeing and packing of final products 6) conducting a detailed cost/benefit analysis and raw materials/ reagents/products yield coefficient in order to reduce the cost of goods and maximize yield efficiency.

PROJECT RESULTS USE AND DISSEMINATION

The results presented in this final report and the recommendation made above could make these cellulose based packaging materials attract large scale manufacture, compatible with package engineering, production and performance, and make cellulose products produced in Minnesota compete with current large scale imports of petrochemicals resins based packaging by virtue of recyclability and disposability plus performance by cellulosies. The processes we developed in this project could enable more investment in recovery facilities that can convert waste paper to packaging films and significantly reduce waste paper disposal to sanitary landfill. Part of the results reported here have been presented at 1993 American Chemical Society Annual Meeting in Denver, Colorado by Ms. Jennifer Wang and Dr. Fu-Hsian Chang. Another paper will be reported by the same authors at the 1994 American Society for Microbiology General Meeting in Las Vegas, Nevada. Besides, two manuscripts are being prepared and will be submitted to Polymer Chemistry Journal for review and publication.

November 15, 19[illegible]

LCMR WORK PROGRAM 1991 (Detailed Version)

I. Cellulose Rayons for Packaging-Waste 18

Program Manager: Fu-Hsian Chang
Center for Environmental Studies
Bemidji State University
Bemidji MN 56601-2699
(218) 755-4104

A. M.L. 91 Ch. 254 Art. 1 , Sec. 14 Subd: 13 (g)
Appropriation: $150,000.00
Balance: $ 94.02

Cellulose Rayons for Packaging: This appropriation is to the Commissioner of Administration for a grant to Bemidji State University, Center for Environmental Studies, to research and develop cellulose rayons.

B. Compatible Data Language: Not applicable.

C. Match Requirement: Not applicable.

D. Appropriate patents will be filed to protect any discoveries and pursued according to the patent and royalty language set by the LCMR in subd. 20 of SC9400-1.

II. Narrative

A. Statement of the problem: The goal is to develop cellulose-based polymers, attractive to large manufacturers to switch from petrochemicals based plastics to a safer and more recyclable materials. The raw material will be Minnesota grown cellulose, thus potentially creating a demand for Minnesota products. The questions to be answered are: (i) What forms of cellulose give optimum recyclability plus feasibility and performance in making package material? (ii) Can these cellulose based packaging materials attract large scale manufacture, compatible with package engineering, production and performance? (iii) Can cellulose products produced in Minnesota compete with current large scale imports of petrochemicals resins based packaging, by virtue of recyclability and disposability plus performance by cellulosics? (iv) Can multimarket outlets be developed for cellulosic rayon waste product, either as material, compost or heat? Can this enable more investment in recovery facilities to be considered and less paper simply being disposed of to landfill?

B. Importance

Waste reduction and reuse of materials is a top priority of many municipalities. Plastics pose a disposal problem, regardless of whether they are incinerated or landfilled. Alternative products which can reduce the problems created by plastics are needed. This project will compare plastic to cellulosics, which is a cellulose derived material that can be converted to a thermoplastic material and used in packaging. Other cellulose derived materials have been developed previously, including cellophane, food additives, and 'plastic wood.' Recyclability of other cellulose based products offers encouragement that cellulosics can also be recycled efficiently. Derived celluloses are completely burnable at reasonable temperatures. They are also biodegradable, but at different rates depending u[illegible]ow they are substituted and made into packages. Thus s[illegible]tuting cellulosics for plastics would reduce Minnesota's dependence on petroleum products, and reduce the amount of environmentally harmful waste generated.

C. Extent of the problem.

The problem is multiheaded. It can be outlined best by listing the questions that bear.

(i) Can Minnesota produce cellulosic packaging materials, in competition with current petrochemicals (plastics) based materials?
(ii) What happens if petroleum gets more expensive?
(iii) Can cellulosic packaging be recycled?
(iv) How much energy will it take to recycle cellulosics? Also, what are the central energy costs of petrochemicals plastics recycling?
(v) Can cellulosics and rayons be made to fit process engineering requirements (thermoplasticity tensile strength, film forming, body forming properties)?
(vi) If solvents have to be used for recycling, can nontoxic, completely recoverable solvents serve?
(vii) If burning (energy recovery) is carried out, what is the energy value of derivatized celluloses-cellulosics such as rayons?
(viii) May regenerated cellulose have a role in packaging?
(ix) Can Minnesota expect to become an exporter rather than importer of packaging raw materials?

III. Objectives

A. Develop cellulosics with desirable physical properties, including recyclability.

A1. Narrative

This objective will review other work on cellulosics, develop new cellulosic compounds, and test the compounds for water absorbability and recyclability. Several process engineering characteristics need to be addressed to determine workable combinations for manufacturing, including tensile strength, extrudability (formability), shear modulus, thermoplasticity, and hot flow indexes such as melt viscosity. Recycling requirements as defined by the OWM also need to be met by the new compounds.

A2. Procedures

Materials

Categories of rayons and derivatized cellulose polymers referred to generally as cellulosics shall be worked with as follows.

(i) Already available commercial rayons such as HWM (high wet modulus) and LWM (low set modulus) cellulosics. A number of the commercial rayons have been developed for high tensile strengths such as tire reinforcement, fabrics. Some rayons are being developed, not primarily for packaging but adaptable to packaging and tape, because they are cellulose and are cost effective. They are regarded as probably less expensive than petrochemicals raw materials. Microcrystalline celluloses are included in this category. Certain cellulosics lend themselves to non-viscose manufacturing processes. They are increasingly of interest because they are considered a good basis for more ecologically sound, more efficiently manufactured cellulosics than the older viscose and cuprammonium cellulosics (4).

(ii) Rayons and cellulosics already available, and cellulosics which are thermoplastic, esterified with C_4-C_8 fatty acids. Related materials are the corresponding ether cellulosics. Such alkyl groups are biodegradable in packaging (20). Cellulose polymers derivatized by alkyl groups are thermoplastic, logous to conversion of conventional plastics from brittle lexible substances by pla ers (2).

(iii) We are going to derivatize cellulose in our own laboratories, Chang's in Bemidji, Lovrien's in St. Paul. Namely, acetylated, propylated and butylated cellulosics which confer properties suitable for package fabrication, function, and recyclability. Reaction media include the anhydrides of the derivatization compounds (acetyl propyl, butyl anhydrides), which drive the derivatization reactions by contributing as substituents plus removing water as the reactions proceed. Catalysts for driving derivatization are those which are easily leachable and destroyed by small amounts of alkali after isolation of the polymeric products. Best catalysts for this purpose are the methyl methane sulfonic acid and homologous series. We do not consider that derivatization with aromatics should be first priority because they tend to be somewhat more toxic in incineration if burned, than all-alkyl derivatives. Also, alkylation agents are in a class which Minnesota companies likely will produce from growing fermentation and distillation industries. Aromatics derivatizing agents, e.g. benzylating agents, mainly are petrochemicals based.

The kind of cellulosic material gotten from derivatizing cellulose depends on three principal factors: (i) How substituted (whether ether, ester, xanthate, grafted oligomers, etc.). (ii) Degree or extent of substitution. (iii) Form of the cellulose starting material; crystalline, amorphous, dissolved, ramie-type cellulose. Cellulosic derivatives that are likely the best compromises between cost, ease of fabrication, biodegradability are the principal factors that determine our choice of modified, derivatized cellulosics for packaging development. The two main kinds of derivatives we have been making here (in connection with cellulose-based chromatographic support agents), which we expect to make for the LCMR work, are cellulose propionates and butyrates (esters), and cellulose ethers. We expect to form some xanthates also. However most of the xanthates which are likely packaging candidates, especially higher tensile strength materials, are commercially available. Aliphatic alcohols shall also be used to form cellulose esters under conditions outlined by Hiatt and Rebbel (21), conditions close to those used in industrial R and D for making cellulose esters on bench scale.

Cellulose ethers shall be made by ethyl chloride and ethylene oxide reaction with cellulose. These derivatives are 'self plasticized' cellulose, having water adsorption capacities of ca 5-10% of their weight as water, depending on humidity (water tension) and the degree of ether substitution. Alkyl ethers of cellulose will be formed via propylene oxide derivatization at low to intermediate propylene oxide concentrations, 1 to 3%. Variation of propylene oxide concentration during derivatization gives control over the degree of substitution, the mechanical and thermal properties of such etherated cellulosics, and their water penetrability or uptake (22,16).

The degree of substitution on cellulose derivatives will be measured by formylation (23) and by periodate oxidation uptake. The course of periodate oxidation is gotten from measuring oxidant consumption via analyzing simply for periodate left after incubation of standard periodate and the sample.

All derivatizing agents and any solvents used to handle them in prospective manufacturing processes are picked to be largely (probably completely) recoverable. In case there is any difficulty in this regard, derivatizing agents and solvents also are available which are completely biodegradable and nontoxic when diluted. For example, acetic anhydride, ethyl acetate, the solvents used in the pulping processes for making cellulose (11) and esterifying it, have these specifications. There is no need to rely on heavy metal catalysts in cellulose technology, in much contrast to making polymers in petrochemicals plastics. Some petrochemicals plastics are finished off, still containing small amounts of heavy metals.

A.3. Budget	LCMR Funds	Matching Funds
a. Amount Budgeted:	$ 50,000.00	-0-
b. Balance:	$ 31.00	-0-

A. 4 Timeline f ucts/Tasks

Nov 91 May 92 Nov 92 May 93 Oct 93

i. Laboratory survey of rayons X------------X

ii. Synthesis and Derivatization of thermoplastic celluloses X--X

iii. Relations of mechanical strength and packaging parameters to recyclability of both commercial and modified cellulose materials X--X

iv. Water absorbability and penetration of packaging celluloses X--X

V. Coordination with actual manufacturing needs X-------------X

A. 5. Status :

Due to the delay in funding allocation, this project was not initiated until the beginning of November, 1991.

Synthesis and derivatization of thermoplastic celluloses have been undertaken using aspen hard wood sawdust. Sawdust was obtained from Georgia-Pacific Corporation, Bemidji, MN. The characteristics of sawdust need to be investigated since the degree of chemicals reaction and quality of cellulosic film are mediated by the properties of the raw-material.

A. Determination of physical and chemical characteristics of sawdust or ground hybrid poplar wood:

1. Moisture content:

The moisture content of sawdust is determined according to the method described in the ASTM and the analytical result show that its moisture content is 2.79% (mean of seven replicates)

2. Acidity:

The pH value of sawdust is determined at different ratios of sawdust to water (wt: vol=1:5, 1:0, and 1:20). The results are given in Table 5. Even though the pH was affected by the pH of the distilled water it is considered medium acidic.

3. α -, β-, and γ - cellulose contents:

α - cellulose, also known as pure cellulose, is defined as the portion of material insoluble in 17.5% sodium hydroxide. The α - cellulose test served as a method of cellulose evaluation for a [illegible] variety of purposes. β-cellulose and γ- cellulose are [illegible] cellulose. β-cellulose, believed to be degraded low DP (degree of polymerization) α - cellulose, is soluble in 17.5% sodium hydroxide, but precipitates upon acidification. γ- cellulose is completely soluble at any pH and is thought to be the hemicelluloses, ie, xylans, mannans, galactants, etc.

a. α - cellulose content

Three methods have been used for the determination of α - cellulose content in sawdust. Although the concentration and amount of reagent used, treatment procedures and time of reaction varied, their fundamentals are identical. The α - cellulose contents of sawdust and other materials are given in Table 6. In same senses, this is the oldest and best known alkaline solubility test, the α - cellulose content of a pulp show a wide range of values.

b. β-, and γ- contents

β- cellulose and γ- cellulose contents are determined less frequently than α - cellulose content. The filtrate from the α - cellulose determination is used. The β- and γ- cellulose contents of sawdust are 9.15% and 7.34%, respectively.

4. Pentosan content

The cellulose is treated with boiling hydrochloric acid to hydrolyze the pentosans to pentoses, which is then converted to furfural. The furfural is distilled and collected. An aliquot of the distillate is treated with orcinol reagent and after standing for 2 hrs. the absorbance is measured at 630 um wavelength on spectrophotometer. The pentosans content (in percentage) is calculated by reference to a calibration curve prepared from known furfural solutions.

This test is used to measure the level of hemicellulose in wood pulps (sawdust). The amount of pentosans, primarily arabinose and xylose are measures of the purity of wood pulps used in chemical cellulose applications.

The analytical results of some raw materials and pulps are listed in Table 7.

5. Lignin

Lignin is an aromatic, amorphous material which forms a part of the cell wall and middle lemella in wood, but is not a definite chemical compound, and its chemical structure has not been fully elucidated. There is no single "lignin" which is of uniform composition regardless of source. Sometime Lignin has strong chemical activity, and sometime it does not. There are many chemical reactions can be carried out in lignin.

The most generally useful methods for determining lignin have been those based on hydrolysis and solution of the polysaccharides with strong mineral acids, leaving a residue which, after washing and drying, is weighed as lignin.

The lignin contents of sawdust (treated or non-treated) and other materials are given in Table 8.

6. Carboxyl Content:

The carboxyl content of sawdust is determined by sodium chloride - sodium bicarbonate method. It is an indication of the surface charge of the pulp which is important in the industries.

The measured result showed that cation-exchange capacity (CEC) of sawdust is 9.59

milliequivalents [illegible] g.

7. Ashing cellulose in sawdust

The ash content of sawdust or ground poplar wood is determined according to ASTM, by ashing cellulose at 575°C and sulfated ash in cellulose at 575°C. It gives an estimation of the inorganic content of cellulose samples. It also provides a rough estimate of silica content which can have a significant effect on the performance of filters in cellulose derivative manufacturing facilities.

The ash contents in sawdust and poplar wood range between 0.935% - 1.43% and 1.83-3.94%, respectively). It varies significantly in different raw materials, ie, ash contents in rice straw, bagasse and viscose rayon are 16.64%, 2.04% and 0.10% (ash in cellulose at 575°C), respectively.

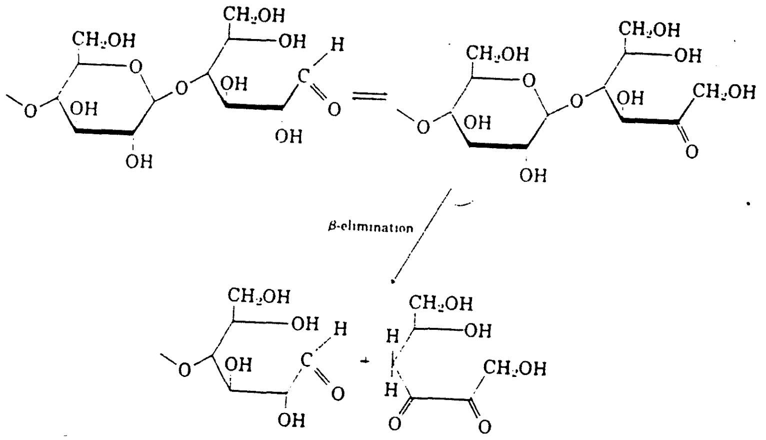
B. <u>Pretreatment</u>

The purposes of pretreatment are to improve purity and to increase reactivity of raw material. Generally, purifying processes include physical washing, chemical reaction or extraction process in appropriate reagents or solvents and the removal of impurity such as grease, lignin and other trace organics from the raw materials. Activation process is known to swelling the cellulose by water and other reagents, to reduce crystallinity and to increase accessibility. Attack of cellulose by swelling agents may be divided into two categories: intercrystalline swelling, caused by penetration of the amorphous regions between crystalline micelles, and intracrystalline swelling, caused by actual penetration and breakup of microcrystallike region of cellulose.

Swelling power generally increases in the order of bases > acids> salts> water> organic solvent. Important cellulose swelling agents include alkali hydroxides (especially NaOH), inorganic acids (eg, sulfuric, hydrochloric, and phosphoric), and solutions of metal salts.

1. Breakdown of raw materials by alkaline solution

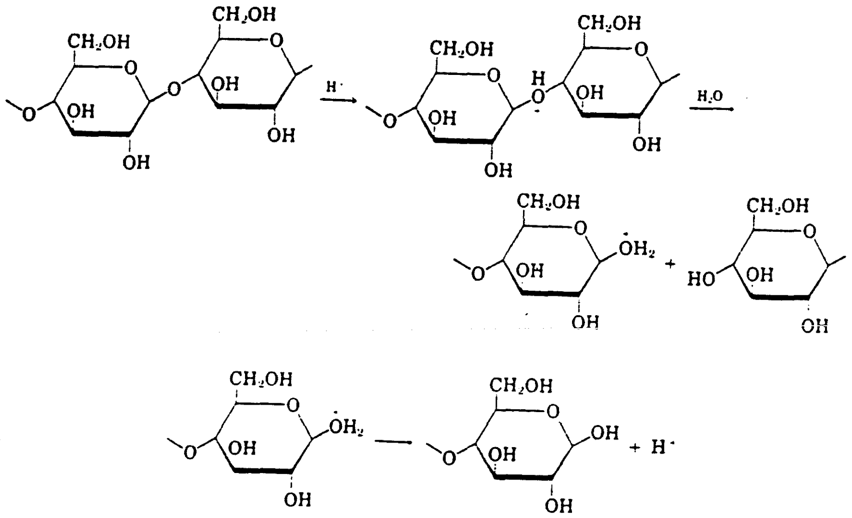
Under alkaline conditions at elevated temperature, cellulose is subject to β- elimination to produce smaller cellulose derivatives.



Sawdust was immersed in sodium hydroxide solutions (0.5%, 6%, [illegible] or 17.5%) for 2 hr. at 80-90°C [illegible] toclaved at 121°C for 30 min. One part of raw material [illegible] immersed in 10 parts of 3% H_2O_2 and 15% mixed solution (V:V=1.20) and autoclaved at 121°C 15 atm for 30 min. The treated mixture was collected by filtration through Buchner funnel and air-dried at room-temperature.

2. Acid Hydrolysis

The susceptibility to the degree of acidic hydrolysis varies according to the region, amorphous or crystalline, concentration and type of acid and temperature.



For sulfuric acid treatment, the dried sawdust was suspended in 1 N and 6 N H_2SO_4 solution, heated for 2 hrs at 80-90°C, or autoclaved at 121°C for 2 hrs. The pretreatment of raw materials was suspended in 1N or 0.5N H_2SO_4 solution and autoclaved for 30 min as final products.

3. Sodium chlorite - chlorite holocellulose

This is a procedure for the preparation of holocellulose by delignification with acidified chlorite solution. At appropriate condition, a reaction equilibrium of acidified chlorite established as follows:

$$10\,HClO_2 \rightarrow 5\,ClO_2 + 2\,ClO_3^- + 3\,Cl^-$$

However, complete delignification can not be obtained without excessive quantity of polysaccharides, and it is necessary to allow a few per cent of lignin remained in the preparation. The color of sawdust became slightly yellow color by chlorited treatment.

4. Salt soluti

The sawdust was treated with saturated sodium chloride solution and 10% sodium carbonate solution for 2 hrs at 80-90°C or autoclaved at 121°C for 30 min.

5. Benzene-ethanol extraction

The sawdust was extracted successively with Benzene-ethanol, followed by ethanol in a Soxhlet extractor in a glass - extraction thimble for 5 hrs. then was boiled in a flask for 3 hrs, filtered and air-dried at room temperature.

6. Dimethyl sulfoxide

The sawdust was placed in a mixture of dimethyl sulfoxide (4.0% consistency), and paraformaldehyde and heated at 80-90°C for 2 hrs. The excess paraformaldehyde was removed above 100°C.

7. Water Treatment

The dried ground poplar was immersed in distilled water (wt:vol=1:20) and autoclaved at 121°C and 15 atm for 30 min.

C. Esterification

Cellulose, a polyhydroxy compound, forms esters with inorganic or organic acids, anhydrides, and acid chloride. In some cases, wood pulp is the principal source of chemical cellulose, except for special plastic-grade acetates requiring low color and high clarity, where cotton tinters were used.

Cellulose esters may be divided into inorganic and organic esters. Among organic cellulose esters, the acetate is the most important one because of its broad application in plastics and fibers. It can be prepared with various degree of substitution (DS) ranging from water-soluble monoacetate to fully substituted triacetate depending on different needs. Generally, plastic-grade cellulose acetate contains 38 to 40% acetyl.

It has been proven that cellulose acetate ester is unsatisfactory in plastic and fiber application due to its comparatively limited solubility in low-cost solvents and limited compatibility with resins and high-boiling point plasticizers, its poor flexibility at low relative humidities and low temperature and its low moisture resistance. Therefore, acetate propionate and acetate butyrate are more widely used in plastic industry

Physical and chemical properties of esters vary with various DS levels and acyl-acyl ratio of the ester in mixed esters. Generally plastic-grade cellulose ester range in substitutions percent are: acetate (CA) 38-40 acetyl; acetate propionate (CAP), 2-9 acetyl and 40-49 propionyl; acetate butyrate (CAB), 12-14 acetyl and 35-39 butyrul.

Almost all cellulose esters are prepared by a solution process employing sulfuric acid as the catalyst with aliphatic acid anhydride in the corresponding acid solvent. The mixed esters, CAP or CAB are manufactured by combining the desired acyl components in the liquid esterification mixture in form of acid or acid anhydrides. The ratio of acetyl to higher acyl groups in the product is proportional to the concentration of the components in the esterification solution. The preparation of cellulose esters consists of four steps: activation, acylation, hydrolysis and recovery of polymer. However, reaction conditions must be modified when different raw materials are used.

Cellulose esterification flow sheet is given in Fig. 27.

1. Material

The bleached, unmilled sawdust and ground poplar wood that have been autoclaved in H_2O_2-NaOH solution were chosen as raw material for esterification according to the results of pretreatment.

2. Choices of reaction condition

To use cellulose in the esterification process, it must be adequately swollen in the pretreatment process, there must be catalyst penetration into the fibers without excessive hydrolytic degradation, the rate of reaction must be such that the process is economically feasible, and the product should be easily filterable. Thus, different reaction conditions, such as concentration, reaction time, and temperature may affect final properties of the product.

(a) Swelling

Since the esterification of cellulose occurs heterogeneously, preswelling of the cellulose prior to reaction is extremely important. For acetylation cellulose may be activated by pretreating it with water, aqueous acetic acid, acetic acid glacial or a mixture of acetic acid glacial and sulfuric acid catalyst, giving a fraction of the total required sulfuric acid catalyst. This swells the fiber and reduces intramolecular hydrogen bonding, thus increasing the rate of diffusion of the reactants. The small amount of catalyst serves to reduce the molecular weight of the cellulose to an acceptable level. When water or aqueous acetic acid is used, the cellulose is dehydrated by displacing the water with glacial acetic acid before the start of acetylation. Usually, the efficiency of activation is increased by increased temperature reaction time and amount of catalyst. Some conditions used for swelling is as following:

Swelling agents: Water, aqueous or glacial acetic acid, glacial acetic acid with sulfuric acid.
Amount of catalyst (wt. % H_2SO_4 based on sawdust): 1%, 2%, 3.5%, 25%.
Temperature: 40°C, room temperature
Time: 0.5 h, 3.0 h, 5.0 h, 15 hr (overnight) and 15 hr with magnetic stirring.

The preferred swelling condition was found to be in glacial acetic acid with 2% H_2SO_4 for 15 hrs. at room temperature.

(b) Acetylation

The acetylation is the most important process during the esterification. The chemical equilibrium is $C_6H_7O_2(OH)_3 + 3\,(CH_3CO)_2\,O = C_6H_7O_2(O.CO.CH_3)_3 + 3\,CH_3COOH$ or $C_6H_7O_2(OH)_3 + 3\,(CH_3CO)_2O = 2C_6H_7O_2(O.CO.CH_3)_3 + 3H_2O$.

The ratio of reactant cellulose to acetic anhydride is 1:1.88; exactly, an excess amount of anhydride is used and the ratio is about 1:2.5-4.0. The mixed esters in the chemical reaction described above are similar to acetylation except hydroxyls are substituted by acetyl and butyryl (or propionyl).

A heating water bath was used to carry out the two exothermal reactions in the acetylation process: the esterification of cellulose with acetic anhydride and the reaction of acetic anhydride with trace water from the pretreatment. The optimal temperature range for acetylation is 30-35°C, otherwise the polymer may be decomposed or produce cellulose.

Sulfuric acid is the most common and effective catalyst used because it is sorbed by the cellulose. In the presence of acetic anhydride, sulfuric acid rapidly and almost quantitatively forms cellulose sulfate [illegible]n unstable intermediate and it affects stability of cellulo[illegible]tate. Usually, high H_2SO_4 catalyst concentration (10-15 wt. % based on cellulose) and low catalyst concentration (<7wt.% H_2SO_4) are the two main variations in the solution process.

Various conditions for acetylation are presented as follow:s

The amount of esterifying agent: 1:25, 1:3, 1:4, and 1:5.
(ratio of sawdust to Ac_2O, wt/vol).

The amount of catalyst: 3%, 7%, 10%, 15%, and 25%
(wt. of H_2SO_4 based on sawdust, wt/wt)

The amount of solvent:
(the ratio of sawdust to HAc, wt/vol) = 1:6, 1:8, 1:10, and 1:20

Temperature*: <12°C and 30°C, room-temp. and 30°C, room-temperature.

Time: 2 hr., 3 hr., 5 hr., 8 hr., 12 hr., and 36 hr.

The function of solvent is to improve solubility of product and to increase ratio of liquid to "solid".

The preferred condition for acetylation is as follows: esterifying agent 1:4 ratio, catalyst 7%, solvent 1:10 ratio, at room temperature for 8 hr. We did not do any more detailed work on reaction condition for mixed esters except the composition of acetyl and butyryl (or propionyl) because it will change their physical properties.

The best ratio of cellulose to acetic acid to butyric acid to butyrate anhydride is wt:vol: vol:vol=1:1.5:5.0:5.0 and the best ratio of cellulose to acetic acid to propionic acid to propionate anhydride is wt:vol:vol:vol=1:1.5:5.5:5.0.

(c) Hydrolysis

The acetylation reaction is stopped by the addition of water, which destroys the remaining acetic anhydride and promotes rapid desulfation. In order not to precipitate the cellulose acetate, the water is added in the form of aqueous acid. The rate of hydrolysis is controlled by temperature, catalyst concentration and, to a lesser extent, by the amount of water. But the rate of combined sulfate removal is strongly influenced. Normally, 5-20% water in the final solution is used for hydrolysis.

The hydrolysis temperature and time can affect the degree of substitution, hydrolysis at higher temperature may entail polymer degradation and reduce yield. The percentage of water in the solution: 10, 12, 15, 26. Temperature (C°) room-temperature, 45, 50, 55.
Time (hr), 0, 3, 6, 12, 16, 66.

The best condition for hydrolysis is 15% of water in the solution and hydrolysed at 50°C for 16 hrs.

(d) Polymer recovery

Precipitation, washing, and drying are the final steps in polymer preparation. However, because of some particle, un-and non-reacted, are still retained, the hydrolysis solution must be centrifuged before precipitation. The shape of product, powder or flake, can be separated by precipitation. The precipitated cellulose acetate is filtered and washed to remove the acetic acid and the residual salts formed from neutralization. This is to eliminate cellulose sulfate acid ester to prevent excessive depolymerization of the cellulose acetate.

Precipitating agent: Water or dilute acetic acid.
Precipitating process: 1) addition of dilute acetic acid or water to the solution
2) addition of the solution to water or dilute acetic acid.
3) the solution was precipitated before or after neutralization.
Neutralizing agent: Sodium carbonate or magnesium acetate.
Drying process: 1) oven-dried under 60°C
2) air-dried at room-temperature.

3. Results:

(a) Morphology:

The shapes and types of cellulose acetate vary with degree of substitution, degree of polymerization and precipitation form. They are usually white, odorless, and nontoxic material.

(b) Microscopic observation

Cellulose behavior during the preparation of cellulose acetate was observed under microscope: When cellulose is swollen by acetic acid glacial, the crystalline regions is extended and swollen. In this swollen process, the hydroxyls became more accessible and reactive. After acetylation, cellulose fiber was colloidizated and became paste-like substance slowly. After hydrolyzed solution was centrifuged, there is hardly any residual fibrous mass in the supernatant.

(c) Yield

Of the two raw materials used in packaging material R &D researched, the hybrid poplar is preferred to the aspen sawdust (Table 10) since it produced significantly higher esterified products than the aspen sawdust (Note, the pretreatment procedures of hybrid poplar are different from that of sawdust). The yield % decreased slightly with increasing carbon-chain length (the reactivity decreases with increasing carbon-chain length).

(d) Moisture Content

Cellulose esters have low moisture content in their final granular products. The moisture contents (%) of CAB, CAP and CA are 1.29, 1.12 and 2.70, respectively.

(e) Solubility

Cellulose acetate, like other cellulose derivatives, has typical solubility characteristics of high polymers. However, its solubility varies according to its combined acetic acid (acetyl) and molecular weight. Frequently, mixed solvents are better than single solvent. Thus, with some types of cellulose acetate, mixed solvent of methylene chloride and ethyl alcohol is a better solvent than methylene chloride alone, in spite of the fact that ethyl alcohol is not a solvent for cellulose acetate. Solubility of organosoluble cellulose derivatives was generally increased with increasing temperature. Tw[illegible]ne solvents were used in the solubility test and good sol[illegible] for cellulose acetate with DS (degree of substitution) range 2.2-26 are:

DMS0, pyridine, Dioxane, Toluene, cyclohexanone, Acetic acid glacial, Dichloromethane + Methanol and Methylene chloride + Methanol.

Partially soluble solvents are: Alkyl chloride, Acetone, Acetic ether and Methyl ethyl ketone.
Insoluble solvents are: Alcohols and butyl acetate.

The CAP and CAB have wider solubility range than CA. They can be dissolved in almost any organic solvent. Acetone is preferred to other solvents because of its low cost and low toxicity.

(f) Degree of substitution

Although degree of esterification of cellulose acetate can be described by many different physical and chemical index, the most important parameter is percentage of acetyl (acetic acid) combined or called degree of substitution, how many hydroxyl functional groups are substituted.

In theory, the highest percentage of acetyl, propionyl and butyl groups are 44.8, 51.7 and 57.3, respectively. Usually DS values can be calculated according to the percentage of acyl group.

$DS = 3.86\ A/102.4-A \qquad C=2$
$DS = 2.89\ P/101.8-P \qquad C=3$
$DS = 2.31\ B/101.4-B \qquad C=4$

Where A, P and B are acetyl %, propionyl % and butyl %, respectively.

DS of mixed esters can be calculated as follows:
DS for CAP = DS (Acetate) + DS (Propionate)
DS for CAB = DS (Acetate) + DS (Butyrate)

The DS's of CA under different esterifying conditions were measured and the results are presented in Table 11. It is obvious that (1) DS's are not different and the same acetylation condition, (2) DS's in the supernatant are slightly higher than those in the residuals if aspen sawdust was used as a raw material for esterification, and (3) pretreatment of ground poplar wood, using any methods described earlier, increased DS significantly.

The analytical results are given in Table 9. The degree of substitution (DS) was affected greatly by the quantity of acetyl agent, acetylation and hydrolysis time. In general, DS increased with increasing amount of acetyl agent and acetylation time (Fig. 1 and 2). However, it decreased with hydrolysis time (Fig. 3). The highest DS obtained was 2.6 which was manufactured in a solution process.

(g) Degree of polymerization (DP), Molecular Weight (MW_t) and Viscosity

Both DP and MW_t are important parameters that affect physical mechanical properties of polymers, these properties include tensile, impact, and flexural strengths, elongation, etc. The mechanical strength increased with DP, but it should have an appropriate mechanical strength and film-forming conditions. In general, the minimum DP and MW_t for useful cellulose derivatives are in the range of 50-100 and 10^4, respectively. Below this range, products do not form suitable films, filters, or plastics. As the DP increased from about 100 to 250, there is a fairly rapid improvement in mechanical properties.

Viscosimetric method is commonly used in the measurement of DP and MW_t. It is not an absolutely reliable method since it may differ appreciably from average values obtained by common osmotic measurements. However, the results are quite close to the average M [illegible] culated from light scattering o [illegible] centrifugal measurements.

DP values may be calculated by means of the empirical equation, $[\eta] = K'm(DP)^a$ and $[\eta] = KmM^3$. In both equation K and a are empirical constants $K'_m = K_m M_o^3$ (M_o is MW_t of the monomeric unit).

The expression $[\eta]$ is defined as

$$[\eta] = \lim_{c\to 0} \left(\frac{\eta\ \text{solution}}{\eta\ \text{solvent}} - 1\right)/c,$$

where c is the concentration of the solution in weight of solute per unit volume of solution.

The term intrinsic viscosity is most commonly used for $[\eta]$. However, it is not really a viscosity, but has the relationship with concentration. In practice, the intrinsic viscosity is determined by measuring the flow times of a solution of known concentration and also of the solvent used and making a calculation by means of the appropriate equation.

According to the different reaction conditions, a range of intrinsic viscosity value is obtained and corresponding average value of DP, 180, is given. In general, the DP value is related to acetylation and hydrolysis time, but there is no obvious relationship between DP value and amount of acetyl agent used.

Intrinsic viscosity of a polymer solution is strongly dependent on the polymer concentration. In addition, it depends on the solvent power of the solvent, degree of substitution of cellulose derivatives, shear rate in the viscosimeter and temperature.

Cellulose acetate has the following relationships in (methylene chloride)-methanol (90:10 w/w) solution

$$DP = 147[\eta]^{1.20}$$
$$MW_t = DP(162 + 42\ DS)$$

Cellulose butyrate acetate or cellulose propionrate acetate has the following relationships in acetone solvent:

$$DP = 102.2[\eta]^{1.14} \qquad MW_t = DP(162 + 56\ DS) \qquad \text{CAP}$$
$$DP = 102.0[\eta]^{1.18} \qquad MW_t = DP(162 + 70\ DS) \qquad \text{CAB}$$

The results of intrinsic viscosity, DP and MWt are illustrated in Table 11 & 12 which show that (1) intrinsic viscosity decreased with increasing C chain, (2) it decreased with increasing esterified time (Fig. 4), (3) it increased with hydrolysis time (Fig. 5), (4) the relationship of intrinsic viscosity with DS has been found and (5) intrinsic viscosity decreased with increasing butyryl% (propionyl %) and decreasing acetyl %.

4. Film-forming

The granulated cellulose acetate, one of the basis and original materials for the preparation of plastic or film, is thermoplastic and adaptable to compression molding, injection molding, extrusion and solution casting. In fibers, plastics, and film made from cellulose acetate, mechanical properties such as tensile, impact, elongation and flexural strength vary with DP and DP distribution. The mechanical properties improve significantly when the DP of cellulose acetate is increased from about 100 to 250.

In order to test the characterization or possibility of film-forming from cellulose acetate, cellulose acetate is dissolved in appropriate solvent with appropriate ratio of liquor to mass and dissolution condi [illegible] e solvent is then volatilized off to form coarse product. [illegible] or plastic sheet is thus obtai [illegible] However, its many properties (chemical, electrical and me [illegible] nical) must be improved with a variety of additives, such as plasticizers, pigments, stabilizer and so on, but the modifiers used in the greatest quantity are plasticizers.

The processing of the cellulose-derivatives to obtain the blended, homogeneous mass in a suitable form for subsequent molding processes can be accomplished by two major type of processes: (1) solvent process, and (2) thermal process (injection molding, extrusion molding). The organic cellulose esters can be processed by either method, but the additional solvent cost dictates the less expensive method of solventless processing whenever it can be used. The solvent process is used in our lab condition.

Solvent process is to dissolve polymer in appropriate solvent, methylene chloride and methanol (90:10 v/v) mixed for CA and acetone for CAP or CAB, with appropriate ratio of solvent to mass and dissolution condition, the solvent is then volatilized off to form coarse product. Film or sheet is thus obtained. The additives such as plasticizers, stabilizers and colorants are also added and combined with cellulose esters before solvent is volatilized off.

5. Additive

Many of the uses of cellulose esters require a different balance of properties (chemical, electrical, and mechanical) than the unmodified cellulosic derivatives. Several types of modifiers used in the greatest quantity are plasticizers.

a. Plasticizer

Plasticizers can give and increase plasticizalbe of cellulose derivatives, which can be shaped (or formed) easily. They are generally stable organic chemicals, compatible with polymer in certain range, for thermolysis and other chemical reagents.

The plasticizers used usually can be selected according to their compatibility with the particular cellulose acetate and suitable for food packaging application by the Food and Drug Administration. Therefore, dietyl phthalate and acetyl triethylcitrate are used in cellulose acetate preparation.

The type and quantity of plasticizer will influence the physical properties of the plastic composition, softening points or flow temperature. From finger-tip test of the product, both plasticizers have strong plastication, but diethyl phthalate seems to be better than acetyl triethyl citrate. The optimal range of quantity of plasticizer is about 30% (ratio of wt. of plasticizer to wt. of solution of cellulose acetate).

Although the film product obtained by esterification of chlorited sawdust has a certain strength and transparency nature, lots of studies will be carried out, such as the improvement of physical characterization of film, tensile and flexural strength, permeability of water, ventilate; the compatibility with stabilizers, pigments and plasticizers; the inter-compatibilty among additives and the effect of additives on physical and mechanical properties of film product.

To be considered a satisfactory modifier, a plasticizer, in addition to being low in cost, should be nonvolatile, heat and light stable, and insoluble in water, it should yield a clear molded product in combination with the cellulosic derivative; and, finally, it should present no additional stability problems after compounding. Other side, plasticizer must be nontoxic by the FDA regulation when it is used for food packaging application.

The quantity and effect of both plasticizers are given in Table 13 and result showed that they both have strong plastication, but diethyl phthalate seems to be better than acetyl triethyl citrate. The optimal range of quantity of plasticizer is about CA, 40%; CAP, 30%; and CAB 20%. However, the quantity of plasticizer will be increased if the thickness of film increases.

The stability of plasticizer was studied in cellulose ester film. The result showed that:

(1) both have a little bit volatility during long-term testing (three months), (2) the dioctyl phthalate is much more stable [illegible] acetyl triethyl citrate, (3) the degree of volation increas[illegible] increasing plasticizer % used.

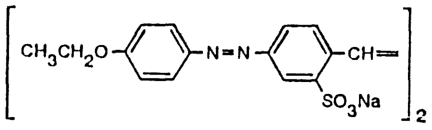
b) Colorant

The use of colorants in the cellulosics varies from a very small quantity of dye in a clear transparent to 1% or more of dye and/or pigments, either organic or inorganic, where translucent to completely opaque colors are desired. The most important factors to be considered in the proper selection of colorants for cellulosics are the type of processing conditions to be used, the quantity to be incorporated in the plastic, and the end-use application for the finished product.

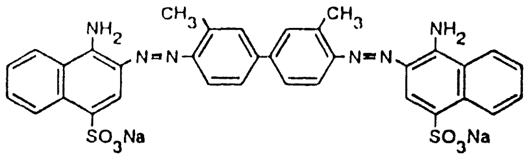
Dyes produce bright, strong and transparent colors. Organic pigments produce colors not as bright as dyes although still brighter than inorganic pigments. The selection of the specific colors must be made after testing for resistance to heat, lightfastness, resistance to outdoor weathering, resistance to migration, chemical resistance and cost. In other words, the non-toxicity is one of the factors use din food packaging applications.

Five kinds of food grade pigment and two direct dyes that conform to FDA regulation were chosen as colorants used in our cellulosic products. Their absorption curve are listed in Fig. 28.

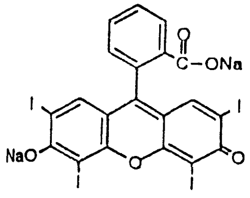
#1 Direct Yellow 12 Chrysophenine



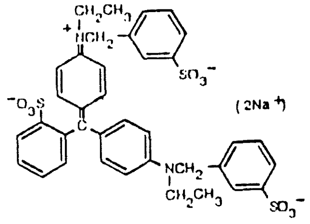
#2 Direct Red 2 Benzopurpurin 413



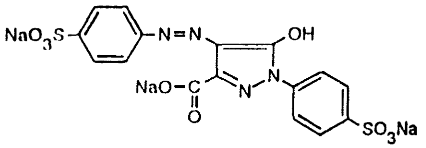
#3 Food Red 14 Erythrosin B



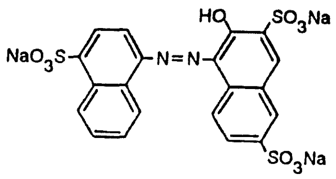
#4 Food Blue 2 Erioglaucin



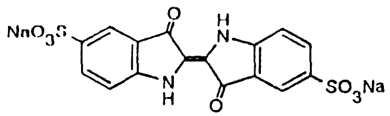
#5 Food Yell Tartrazine



#6 Food Red 9 Amaranth



#7 Food Blue 1 Indigo Carmine



The colorant is dissolved in methanol to prepare complete solution because they only partially dissolved in solvent that made cellulosic film and then mixed with cellulosic derivative solution in appropraite proportion. After forming, film was fixed with dyeing auxiliary.

Usually, the quantity of colorant is about only tens to hundeds ppm to get transparent film.

Various colorants can be obtained at various proportions when two colorants were mixed together.

Stability of colorants to light, compatibility with solvent derived film and declorization in film were studied. Comprehensive review of three colorants, Benzopurpurin 4B (direct red 2-#2); Erythrosin B (food red 14-#3); and Tartrazine (food yellow 4 - #5) are chosen as color taggin used in the following test.

(i) Removal rate

Various removal rates were observed at different immersing time after different amount of Erythrosin B (#3 colorant) is added into cellulose acetate film.

The results show that (1) methanol was a good solvent for removing dye from CA film, (2) removal rate increased with increasing immersing time, after 8-10 hr, the removal rate reached highest value (>99%, Fig. 6), (3) the concentration of pigment in immersing solvent increased with increasing concentration of one solvent used in film and had a good correlation (Fig. 7), (4) removal rate decreased with increasing concentration in film (Fig. 8), (5) immersing time had much effect on higher pigment concentration and increased with increasing pigment concentration in film, (6) plasticizer did not affect r[illegible]l rate, (7) methanol [illegible] in the removal test can be recovered and reused convenie[illegible].

Although, we did not get more detailed information about two other colorants but they had some removal rates.

(ii) Decolor test

Decolor is also one of considerable properties during color tagging procedure. Usually used concentration in CA film is less than 50 PPM for Erythrosin B. From testing results, pigment in film has slight decolor and increased with immersing time and pigment concentration (Fig. 9). In general, they can be neglected if abstraction rate is less than 5%. On the other hand, inter-molecular linkage of pigment with cellulose derivative is much weaker in the lab conditions. Usually, it can be improved in industrial conditions. The abstraction rate will be decreased further.

c) Stabilizers, Ultraviolet Inhibitor

In the compounding and molding processes for cellulose derivatives to be used as plastics, small quantities of special chemicals are used to prevent or retard thermal degradation, discoloration, or the adverse effects of photochemical reactions.

RMB (resorcinol monobenzoate), UVinul 400 (2,4-dihydroxybenzophenone), and polyethylene glycol are chosen and their effect will be determined later.

D. Etherification

Cellulose ethers comprise of a class of cellulose derivatives that are soluble in water or organic solvents function as thickeners, flow-control agents, suspending aids, protective colloids, water binders, liquid crystals, filmers or thermoplastics.

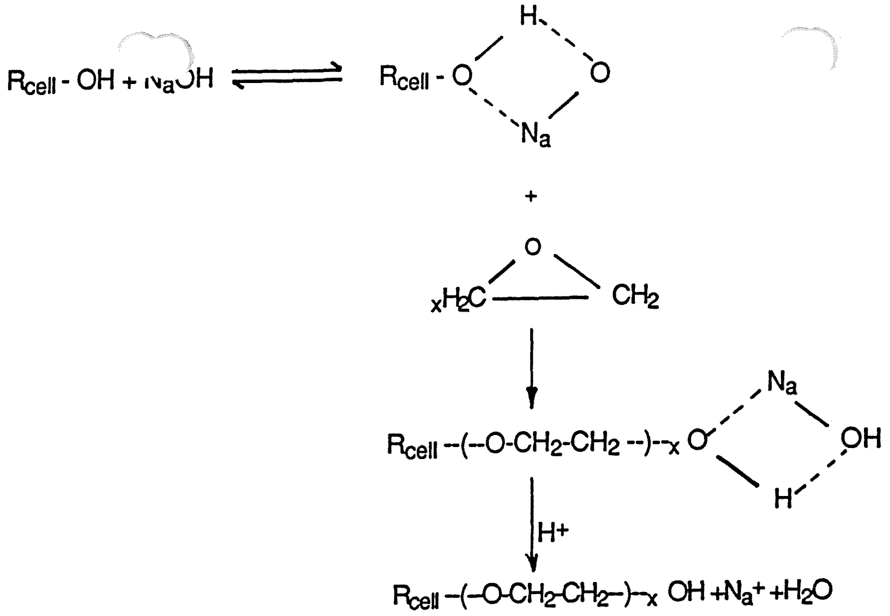
Two types of reaction are employed in the preparation of cellulose ethers. The most common one is nucleophilic substitution, and another is Michael addition.

Cellulose ethers may be soluble in water or in organic solvent depending on the nature of the substituent and on the degree of substitution. The final product depends upon factors which are inherent to the cellulose structure or reagents used in the preparation. Such factors are the cellulose accessibility, hydroxyl group reactivity, and reagent reactivity.

Cellulose ethers, hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC) was prepared in our laboratory.

The preparation of alkali cellulose was the first step for the manufacturing of cellulose ethers. Swelling and decrystallization were the two main processes occurred during the activation of cellulose by alkaline metal hydroxides and sodium hydroxide that were used almost exclusively for this purpose.

Ethylene oxide and propylene oxide were used for the preparation of HEC and HPC. The reactions are SN$_2$ displacements by the alkalic cellulose complex on the epoxide which generates a new reactive site at the end of the side chain. HEC reaction is illustrated as follows:



HPC is more hydrophobic than HEC due to the presence of the methyl groups on the side chain. Thus, hydroxypropylation would be expected to occur at about a quarter of the rate of hydroxyethylation.

Through a series of activation and hydroxypropylation (or hydroxyethylation), HPC (or HEC) product was obtained from poplar and formed clear and flexible film in cold water. However, these products are soluble in water, so they can not be used as packaging material.

E. Xanthation

Strictly speaking xanthation is one kind of esterification, too, but it does not result in any change in stucture of final products. These products are not the same as other esterified products. eg. cellulose acetate etc. Usually xanthation improves the properties of the regenerated cellulose.

Cellophane is the name given to a thin transparent film consisting of a base sheet of cellulose, regenerated from viscose. Cellophane was manufactured with cellulose, sodium hydroxide, carbon disulfide, modifiers and water as the raw materials.

A flow diagram of the various processes to produce viscose is given in Figure 11. Due to experimental equipment limitation, semifinished products of cellophane have been obtained from raw materials in our laboratory. Usually, they have a high strength.

F. Further Derivalizations of Cellulose

1. The earlier work used epichlorohydrin to attach some hydroxypropyl groups on cellulose to make cellulose more thermoplastic. Because a compound like epichlorohydrin rapidly reacts, when cellulose is in bulk form, not finely divided, it appears that reaction tends to occur mainly at the surface unless large amounts of epichlorohydrin are used, e.g. 2-5% by weight. Accordingly we presoaked the cellulose and steam autoclaved it to swell it, before epichlorohydrin addition. Under these conditions about one third as much epichlorohydrin has to be used, to get more uniform penetrance of chopped packaging. These more uniformly derivatized cellulosics are

analyzed for by chloride ion release from the condensation product to find the efficiency of coupling.

To obtain cellulosics that have thermoplastic properties suitable for re-using or recycling them, we used mixtures of derivatizing agents to add more than one kind of functional group. We used in addition to epichlorohydrin, acetic anyhdride and chloroacetic acid with zinc chloride catalyst to esterify packaging cellulosics. When substituted enough these cellulosics become partly clear (transparent in thin layers), and stretchable. Further addition of benzyl groups via heat and benzoyl chloride gives cellulosics which are less penetrable by water. We continue to use formaldehyde as a derivatizing agent up to levels of about 1-2%, to try to test plasticity properties to enable recycling.

Organic solvents have been used for a long time to aid cellulosic polymers processing (e.g. in making film). Although organic solvents when pure, can be somewhat expensive, they are fully recoverable by distillation-condensation. For industrial workup of cellulosics to process them, organic solvents need not necessarily be pure. There are large quantities of discard and surplus organic solvents available which, in fact, should be used again if possible. (In order to avoid manufacture of new solvents). These surplus solvents are mixtures, in some cases of unknown composition. However if they are simply distilled, driving off first the very low M.W. volatiles and then any water, intermediately boiling (110-160°) solvent mixtures can be recovered which are fairly effective in handling some of the derivatized cellulosics. these derivatized, and solvent treated cellulosics were used to make recycled cellulosics for tensile strength measurements.

2. Graft Copolymerization

The graft polymerization approach, to produce a composite containing a biopolymer and a graft synthetic polymer, provides a method to prepare new and novel polymeric materials with specific and improved properties for a wide range of applications. Graft polymerization routes can be divided into mainly two kinds: free-radical-polymerization, and ionic-polymerization.

The best known example of direct oxidation which is one of free-radical-polymerization is the use of the ceric ion. Although the actual reaction is known to be quite complex, the principles of the reaction can best be illustrated in the following way:

$$R_{cell}H + Ce^{4+} \rightarrow R_{cell}\bullet + Ce^{3+}$$

$$R_{cell}\bullet + M \rightarrow \text{Graft copolymer}$$

where Ce^{4+} is as an initiator. M means various monomers.

Although in principle no homopolymer should be formed, in fact some homopolymer always appears to be produced due to reactions of the ceric ion with the monomers themselves.

The ceric ion method is particularly rapid and appear to be suited for commercial production.

Grafting conditions were chosen as follow in our lab,

Grafted monomers: methyl acrylate (MA), and methyl methacrylate (MMA)

Reacted material: cellulose acetate (DS 2.2-2.4)

Initiator concentration:	3 mmole/L in the polymerization system
Temperature:	38-40°C
Time:	2-4 hrs

Homopoly extracted	toluene or methanol for 24 hrs

Clarity and flexibility of film formation have been improved after graft copolymerization, the grafting yield is too low to have enough economic value and potential for commericalization if cellulose is derivatised as grafting materials because grafting decreased with increasing degree of polymerization of the cellulose. In order to change this status, another synthetic pathway, which involve two-stage grafting with original materials treated with acid (or base) and holocellulose and then esterified to cellulose acetate propinate. The conditions for grafting and esterification are similar to those for previous esterification or grafting, except that nitrogen was filled in this grafting system, due to the inhibitory effect of oxygen that caused a decrease in grafting yield. Grafting effeciency was affected mostly by properties of raw materials, eg lignin. In general, the grafting percentage increased as the lignin content decreased.

The percent grafting, the efficiency of grafting, and total conversion were calculatedd from the following relations:

$$\%\ \text{grafting} = \frac{(\text{total wt of grafted copolymers}) - \text{wt of pulp}}{\text{Wt. of pulp}} \times 100$$

$$\text{Efficiency of grafting } (\%) = \frac{\text{Wt. of PMA grafted}}{(\text{wt. of PMA grafted}) + (\text{PMA homopolymer})} \times 100$$

$$\text{Total conversion } (\%) = \frac{\text{Wt. of polymer grafted and homopolymer}}{\text{Wt. of monomer charged}} \times 100$$

Some experimental results were illustrated in Table 14. It can be seen that paper towel has highest efficiency of grafting among three kinds raw material because its lignin content is lowest. The percent of homopolymer was seen to decrease with decreasing lignin content.

Usually, the reduction of polymerization rate of cellulose was the main reason for higher grafting rates. Increases in the surface area of cellulosic samples have been shown to increase grafting rates as well as grafting yields. However, the surface area of sample is too fine to increase the grafting rate. The reason for it is still unknown.

Multiple polymerization was carried out and corresponding reaction condition was controlled and changed in final products which have good mechanical strength and other physical properties that are required for manufacturing of good packaging material.

Due to the constrained patent application procedure, detailed synthetic pathways and reaction conditions will not be reported here. We intend to carry out more investigation before filing our patent application.

3. Blending

The method of a cellulose ester blended directly with some resin (synthetic or natural) can also improve physical properties of film-forming as compared to the cellulose ester composition by itself.

Polyester-10 and ethylene/vinyl acetate copolymers are chosen to be used as blending agent with cellulose ester. However, physical properties of cellulosic film were restricted by various factor, eg. blending way, ratio of cellulose ester to blending agent, compatibility with other additives because blending degree may be limited in solvent process. Even so, perfect data are still expected to get through further studies.

After studied, both are not good blending agent. There are two majo[illegible]ons that limited the improvemen[illegible] mechanical properties of cellulosic film blended with p[illegible]ester-10. One is its low molecular weight that exists as glassy state; another is its compatibility with cellulosic graft and ester product. Ethylene/vinyl acetate copolymers exist as rubbery state, but its compatibility with cellulosic limited it as a blending agent, even though it can improve flexibility of film-formation.

Two polymers, one is copolymer and another is homopolymer was synthesized and used as blending agent in our laboratory. Both have not only good compatibility with cellulosic in appropriate ratio but also function to improve mechanical properties in the formation of cellulosic film.

G Mechanical properties of products

1. Tensile Strengths

By the magnetic tensiometer method, derivatized and parent celluloses in the previous report gave wet tenacities in the range of 2 to 3 gm./denier with elongations of 5-15%. The newer products have extended this range to 2-6 gm/denier in cellulosics derivatized with benzylic acid and acetyl groups. Their water penetrabilities are somewhat decreased by 10-20%.

The tensile strength of cellulosic film products was measured and the results show that strength in a decreasing order are CA>CAP>CAB in all cellulosic films. However, this strength value was affected by raw materials. Generally, product derived from sawdust has highest value among three raw materials. The tensil strength of the film can be increased by an incorporation of graft copolymer. usually, the tensile strength increased more than 100% after grafting. Despite that the strength of cellulosic films was improved, our products are still not as strong as the commercial cellophane product, but they are as strong as commercial plastic bags that indicates tensile strength of our products is strong enough to be used as packaging material (Table 18).

2. Tearing strength and elongation

Table 19 describes tearing strength and elongation of cellulosic and commercial plastic films. Both properties of our films are similar to commercial cellophane. However their cellulosic structural characteristic results in low tearing strength and elongation properties. Commercial plastic of petrchemical base has greater tearing strength and elongation peoperties but they are affected by orientation of film. Usually, vertically orientation is much better than horizontal orientation.

3. Different formulas.

In order to further improve mechanical properties of products two blending agents synthesized in our laboratory were used and different ratios of blending with MA/CAP or CAP were studied. Fig. 29 ~ 31 illustrate some testing results which indicate tensile strength, tearing strength and elongation increased 16.7, 40.0 and 29.3% in blending 1, and 25.5, 25.4 and 49.8 in blending 2.

Either before or after blending tensile strength of our products showed several times higher than that of film made from starch graft copolymers, starch-polyethylene plastics and composite of chitosan and homogenized cellulose.

4. The change of environment conditions

One interesting matter is to find out if mechanical properties of film changed with changing environment conditions. There are several ways to evaluate this change. The change of solution viscosity is the most common and simple way used in the evaluation of film resistance to environment conditions as an important and reference parameters. For food packaging,

temperature chan[illegible]aviolet radiation, water immersion and autoclave or mic[illegible]e oven have been used as effective means. Chosen environment factors which may affect mechanical properties of MA/CAP (sawdust) film and corresponding viscosity were illustrated in Table 20 and statistical analysis results were given in Table 21. The results showed that no significant difference was found within four replicates, but very significant difference existed among total average of affecting factors. Thus, LSD and LSR were chosen to compare and evaluate these differences.

LSD, Fisher's Least Significant difference was analysed based on a t test. The goal is to test if any significant difference was present within a single environmental factor before or after change (to compare with a standard value - ie. normal condition). If the treatment groups are all of equal size n. Then two samples were averaged, $\bar{y}_1$, and $\bar{y}_2$, for example, can be tested for a significant difference by the statistical relationship.

$$t = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\frac{s_p^2}{n} + \frac{s_p^2}{n}}} = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\frac{2s_p^2}{n}}}$$

where, sp^2 is the pooled sample variance. Thus the difference y_i-y_j is significant if

$$|y_i - y_j| \geq t_{\alpha/2,a(n-1)} \sqrt{\frac{2\mathrm{MS}_e}{n}}$$

LSR: Duncan's New Multiple Range Test. This test should be used to find significant differences among group means. It not only test difference in comparison with a standard value, but also test difference in between two factors.

$$|\bar{y}_i - \bar{y}_j| \geq d_{\alpha,r,a(n-1)} \sqrt{\frac{\mathrm{MS}_e}{n}}$$

There is a very significant difference ($P \leq 0.01$) within treatment of ultraviolet radiation for 24h, and a significant difference ($P \leq 0.05$) appear in samples autoclaved for 15 min. Due to the fact that Duncan's test is slightly more conservative than Fisher's. That is, it will sometime find less significant differences. Similar results were found in autoclaving treatment. No significant difference was obtained by LSR test. However, there is about 95% confidence agreement between the two procedures.

From statistical analysis no significant differences were found among various factors even though their viscosity has increased or decreased than normal treatment conditions. LSR analysis results indicates no significant difference was found among factors except ultraviolet radiation treatment.

Viscosity of MA/CAP solution decreased with exposing time of Uv radiation. Because cellulose may be photochemically degraded in a number of ways, one is direct photolysis which is a high energy process and leads to direct scission of chemical bonds within the cellulose molecules. Rapture of C-C or C-O bonds requires about 335-377 J/mol, and C-H bond cleavage requires approximately 418 J/mol. Light wavelength of $\lambda = 300$ nm is equivalent to 397 KJ. An adsorption of lightg at $\lambda = 340$ nm is sufficient to initiate cellulose degradation. Thus, choice and use of ultraviolet stabilizer needs to be studied further.

H. Analysis by Periodate

Periodate analysis has been calibrated, and applied to measurement of degree of substitution of several cellulosics. It likely is capable of measurement to within about ±5% accuracy, degree of substitution of cellulosics. If there is time we shall correlate the periodic method with other analytic methods, especially FTIR which we have in the department. However processing FTIR data is somewhat time consuming. Hence it will be used for definitive or 'absolute' analyses, in only about 30% of the samples which however will be correlated with periodate analysis."

I. Moisture Permeability

1. Water absorption capacity (WAC)

Various cellulose ester products, CA-MA, cellulose acetate graft with methyl acrylate; CA, cellulose acetate; CAP, cellulose acetate propionate; CAB, cellulose acetate bulyrate, MA/CAP, grafted with methyl acrylate + esterified products of three kinds raw material (poplar, sawdust and paper towel) and commercial cellophane were tested for water absorption capacity. Measurements were done by gravimetric method in accordance with ASTM. One group of specimens were placed in a container supported on the edge and immersed entirely in distilled water that was maintained at a temperature of 50 ± 1° C. At the end of 24 h, the specimens were removed from the container, water outside the specimens was wiped off, and weighed to the nearest 0.001 g immediately. Another group of specimens was immersed in boiling water. At the end of 120 min, the specimen was removed from the water and cooled in distilled water for 15 min. The percentage of water absorption capacity was calculated based on the increasing weight before and after the immersion in water. The results were depicted in Fig. 10, 32 and 33). Water absorption capacities of the cellulose ester products were about one order of magnitude less than cellophane product. Water absorption capacity decreased with increasing length of the carbon chain and thickness of cellulose esters and decreased with graft. Similarly, WAC of MA/CAP films is low too. Product made from poplar seems to have the highest WAC among three kinds of raw material used. Further observation, WAC of various films tested did not increase with increasing immersing time. WAC of films at the end of 48h was very close to the one at the end of 24h. Specimens after boiled 2h in boiling water had a slightly higher WAC than the one immersed in 50°C water for 24h. WAC (20°C) of cellulosic films were 3.0-8.5, 2.0-4.5, 1.0-2.0 and 45-115%, for cellulose acetate, cellulose triacetate, cellulose acetate butyrate and cellophane, respectively.

2. Water Vapor Transmission Rate (WVTR)

The protection of foods against their environment until consumption is becoming one of the most important preoccupation in food preservation and packaging materials. Water is one of the factors that influence the stability. The water migration between the product and its surrounding atmosphere may be responsible for a modification of texture and appearance. Determining the WVTR through packaging materials is a simple method of assessing the polymer permeability. The permeability of films prepared by solvent casting may be influenced by many factors, including polymer hydrophobicity, solvent composition and plasticizer content, and may be modified by changing the structure of the polymer. In a series of polymers with a similar backbone structure, but with different substituent groups, differences in permeability may be ascribed to the properties of the substituent group.

The cups used in this study consisted of a plastic body with a screw cap with a hole cut in the center. A circular section of 4.46 cm diameter was cut from cellulosic films, each was placed between cup contained 20 ml of a saturated salt solution and screw cap and was sealed with parafilm strips. Each assembly was weighed and placed in a desiccator. At predetermined time the

cup assemblies w oved, reweighed and replaced in the desiccator. The e ent was continued for 72 hours.

The control for all experiments was the commercial cellophane at the same procedure.

The relative humidites (RH) within the cup were maintained with saturated salt solution in contact with undissolved salts: $CaCl_2 \cdot 2H_2O$ (32% RH), NaBr (58% RH), and $ZnSO_4 \cdot 7H_2O$ (90%RH). These solutions were kept at 20°C and 1 atmospheric pressure.

The uniformity of the film thickness is of some importance because other properties in turn depend on it, especially the water vapor permeability.

Three replications were done for each vapour transmission experiment.

From the measured WVTR the corresponding permeability is calculated as

$$\mathrm{WVTR} = \Delta w / \Delta t \cdot l / A$$

where $\Delta w/\Delta t$ is the amount of moisture gained per unit time of transfe, l is the film thickness, A is the area exposed to moisture transfer.

The value for the water vapour transmission rates thus obtained were considered as relative rather than absolute value because, during reweighing of the cups, time was required to return the environment within the desiccator to the dehydrated state. Therefore the relative humidity difference across the film was not constant at all time.

A plot of amount of water vapour permeated per unit surface area versus time yielded a straight line (Fig. 12) and a simple linear correlation relationship was obtained. An increase in WVTR with an increase in relative humidity (RH) was obseved for every polymer film studied. However, the relationship was not linear. (Fig 13) The factor may be responsible for the lack of linearity: a build up of moisture and a change in the permeability coefficient. At the higher relative humidities the environment within the desiccator outside the cups may not have been completely dehydrated by the desiccatant, allowing a build up of moisture.

The permeability coefficient is dependent on the physiochemical characteristics of the polymer and is, therefore, influenced by the tupe of substituent used to make the cellulose polymer. A change in the permeability coefficient would alter the water vapour transmission rate constant (ko). The influence of substituent type on ko is most apparent at higher relative humidites. When the WVTR constants ko were averaged over the relative humidites the following rank order of substituent types was observed: MA/CAP<CAB<CAP<CA<cellophane (Fig. 14, 15, and 16). However, a decreasing order of WVTR (CAP>CAB>CA) was observed at low RH condition. Comparison of results of WVTR of cellulosics or cellophane suggests that the WVTR of cellophane is higher than cellulosics at higher RH. It appears that cellophane is more sensitive to moisture than cellulosics.

In general, poplar had a highest WVTR among three kinds of raw materials used. This result is similar to WAC, but no significant difference (Fig. 34, 35) in WVTR was observed in cellulosic films that were made from three different raw materials. Diffusion of a gaseous medium through a polymer may be influenced by several structure related factors, such as polymer molecular weight, cross-linkage and crystalinity. Fig. 36 and 37 showed that WVTR decreased with copolymer or homopolymer blended wherever in MA/CAP or CAP film. Polyethylene film had very low WVTR usually ranged from 0.3-0.6, at 37.8C. It was 0.26 (90% RH, 20°C) and 0.10 (58% RH, 20°C) in our test.

3. Water Retention Capacity (WRC)

The water retention capacity of the cellulosic substances was measured by a suction technique. An oven-dried (80°C) sample (1g) was placed in a previously dried and weighed glass funnel, which was then filled with water (60 ml). Suction was gently applied from a vacuum of water pump until the sample was completely drained. The glass funnel was weighed, dried overnight at 80°C, and then reweighed. The amount of water in grams retained per gram of the dry material was expressed as the water retention capacity.

The WRC of cellulosic materials is generally thought to result from the interaction through hydrogen bonding of the hydroxyl groups on cellulose with water molecules. In our results (Table

15). WRC of cellulosic have not been affected significantly by the increase o n chain length, however, it was ed by grafting and reduces the water retention capacity.

J. Permeability to Gases

The same assemblies were used in permeability to NH_3 and CO_2 experiments as WVTR, except water and basic solution were used for the NH_3 and CO_2 permeability within each cup, respectively. The assemblies were placed into a system filled with NH_3 or CO_2 for a specified time, the solution absorbed gas was then titrated with standard acid solution.

NH_3 and CO_2 were produced by the following chemical reactions

$$NH_4OH \rightleftharpoons NH_3\uparrow + H_2O$$

$$CaCO_3 + 2HCl \rightleftharpoons CO_2\uparrow + CaCl_2 + H_2O$$

The results of permeability of some cellulosic films to gases showed (Fig. 17) the permeability of cellulosic films was about 0.1 to 0.25 of that cellophane except cellulose acetate propionte product made from sawdust which do not show significant difference among three cellulosic films. Averaging speaking, the permeability of NH_3 is about 50% more than that of CO_2. The results of permeability of MA/CAP films to CO_2 are showed in Fig. 38, the permeabilities are between commercial plastic and cellophane.

K. Clarity

A strip sectionof 5 cm^2 cut from each cellulosic or cellophane film, was measured at 400nm spectrophotometerically and compared with color standards of platinum-cobalt. The thickness of each film was measured in randomly selected places with a micrometer.

Clarity of cellulosics films derived from three kinds raw material are all as good as that of cellophane and have little difference among raw material used (Table 16). Clarity of films have not been affected obviously by grafing. In all cases, the clarity decreased with increasing film thickness.

L. Heat Stability

Heat a 1g sample of 4 h at 110°C, 2 h at 140°C, 2 h at 160°C and 2 h at 190°C. After cooling, the heated sample was dissolved in methylene chloride-methanol mixture. Color of the solution can be measured spectrophotometerically at 400nm and compre with standard solution of platinum-cobalt.

In general, color of cellulosic solution increased with increasing temperture, the increasing order of heat stablity of cellulosic is CAP, CA and CAB, and was charred or decomposed over 190°C (Fig. 18, 19 and 20). However solutions can maintain good clarity at 160°C for most cellulosics as shown in Figure 21. When solution clarity is 100 PPM, the temperatures of heat stability for cellulosics obtained from relative equation are given in Table 17. The heat stability of cellulosics differ among three raw materials. It was affected not only by physical and chemical properties of raw materials, but also by the content and comosition of acetyl, propionyl and butyryl groups on the compounds.

M. Mechanical strength and other physical properties of packaging celluloses

Edge tearing of cellulosic films were carried out by a modified TAPPI method (TAPPI publication T470-OM-80), clamping each film in a stirrup and using weighted brackets to exert force, as specified (elongation rate close to 1 inch per minute, followed by micrometer on the stirrups). The data is in kilonewtons for two orthogonal (90°) directions on the film. Conversion factor for a kilonewton is 0.00448 x pounds force at the tear point. The data can be converted to

force per unit len ear, but according to TAPPI, this is not necessary. Th PUT and 160 PUT cellulosics withstand 15 to 20 kilogram force to start tearing, exerted on a 5 mm. clamp.

Wet tensile strength (ASTM D829-48) and dry tensile strengths for 150 and 160 range from 50 to 80 gm/denier.

Diffusivity of water was measured by clamping films over beakers, with four beakers containing neutral water and phenolphthalein, one beaker containing dilute aqueous ammonia. Diffusion of aqueous ammonia through the film transports ammonia to the adjacent beakers containing neutral water and phenolphthalein, one beaker containing dilute aqueous ammonia. Diffusion of aqueous ammonia through the film transports ammonia to the adjacent beakers, making them alkaline enough to turn possibly pink. This method is developed to compare with the standard ASTM D1251-79 method which involves successive weighings of the sample vessels while in presence of dessicants that absorb the water. Both methods have to be calibrated, which is being carried out at the time of this writing. Preliminary results are that the PUT films slow the outward diffusion coefficient of water through from saturated water vapor by a factor of over one thousand. The full ASTM method is a cycling method, which is also being put in place.

Adsorption capacity of the PUT films for water under hygrostate water vapor pressure form relative humidities of 10% to 100% (25°C) (hygrostats set up also according to ASTM specifications), indicate the films adsorb water from zero to 1.8 in 2.0% of their dry weight. Heats of absorption of water on these films, measured by heat conduction calorimetry (Talanta (1992), In Press) give adsorption heats from 6 to 12 exothermic Kcal per mole of water absorbed. Desorbing energies are similar in magnitude, but of course endothermic, positive in sign.

O. Permeabilities of cellulosic packaging in relation to film forming properties

In order for packaging to form films (to be useful as recycled materials in packaging) they need to have physical properties in the following ranges. Tenacity; 1,2-3.2 gm/denier; Elongation, 20-30% dry and about 20-40% wet. Derivatized cellulosics and rayon-like materials which fall in this range also may adsorb, and be permeable to some extent toward water, low M.W. flavor-taste components. Accordingly relatively uniform cellulosics were evaluated (regenerated cellulose), also regrinds from recycle cellulosic packaging, for their permeabilities to ethyl acetate, acetic acid, and ammonium ion. These were analyzed for by gas chromatography, and by colorigenic reaction using dichloroisocyanurate for ammonium. For estimating how lower M.W. food-flavor permeant behave, thiazole and oxazole were used as calibrating compounds (Tr. in Food Sci. Tech 329-332 (1991)).

Film recasting was carried out by partial dissolving of regrind cellulosics in a pressure tube at autoclave temperatures, then cold-wire redrawing out the film from the melt. This technique does not produce a film of the desired thickness in each draw. However, by reasonably careful attention to conditions, experimentation, one can produce several square centimeters of films in 2-10 mils thickness, uniform to ±20% relative to overall thickness. The films can be squeezed to make them thinner, by heating metal plates and inserting them quickly in the jaws (insulated) of a vise, with the plastic material in between the plates. The latter kind of technique is more recent. Most of our data pertains to cold wire draw materials.

Adsorption of test compounds was determined by a standard A.S.T.M. method which is related to the isospiestic technique for determining relative humidities, except that in this case we are transferring organic compounds instead of water. The test compound (such as oxazole) is dissolved in concentrations ranging from 0.01 to 0.2%, in dibutly phthalate. Dibutyl phthalate is almost completely non vaporous, even though it is a liquid. A container of this is equilibrated with a container that has the film wrapped around it, all confined inside a dessicator. Probe molecules (oxazole in this example) leave the 'food substitute' (D.B.P. solution of the volatile probe molecule), and transfer to the film dependent on two variables. Namely, affinity of the film of recycle cellulosic for the probe molecule, and the vapor pressure of the probe compound.

DERIVA ED CELLULOSICS, FILM-CAST RECYCLE RIAL

Material	Permeability to ethyl acetate (Previous report)	Tenacity	Thinning temperature (vice technique)	Thiazole uptake
Cellulose acetate	0.14			
Cellulose acetate propionate	0.34	1.52 g/d		
Cellulose hydroxy-propyl film	0.09			
Cellulose acetate butyrate	0.92	3.3 g/d		
Food package cellulose laminate (1)		1.4 g/d	150-160°	0.2 mg/gm
Food package cellulose laminate (2)		4.4 g/d	180-190°	0.8 mg/gm
Food package cellulose laminate (3)		3.2 g/d	200-220°	1.6 mg/gm

The thiazole uptake values refer to films of 5-8 mil thickness (5 to 8 thousandths inch). The permeabilities are cm^3 (STP) x cm/cm^2 of film area x sec x Pascal pressure.

There is expected a correlate of these food-flavor uptakes, with cellulose contents of the films, both test films and recycle packaging. Accordingly we have carried out measurements for total cellulose by the technique we developed in 1984 (B. Odegaard et al., J. App. Biochem.). In this, we dissolve 2 to 8 mg. of samlple, in sulfuric acid-dichromate. All cellulose is oxidized at the expense of dichromate to make the green chromous ion. The latter, Cr^{++}, is readily measured by spectrophotometry. The technique is sensitive and accurate. Cellulose contents of the materials in the table, range from 62-90% by weight. These cellulose contents are useful in case these cellulosics are to be biodegraded. They roughly predict long-term biological oxygen demand, the B.O.D. Also they should predict, contingent on further determinations, approximately how much nonbiodegradable, or slowly biodegradable, material remains to be handled by any other disposal process. We should expect this latter (non-readily degradable) material, are plasticizer-organic compounds used in original manufacture, which should be recycled if possible, or otherwise reused. Increasingly it looks likely that some of these materials, instead of recycling aimed at packaging, could advantageously be used for recycling their carbon. That is, to make adsorbent and catalytic carbons. This is explained in the next section, based partly on discussion with Donald Eaton at 3M Company, and some of our own work.

A. 6 Benefits: A successful development of cellulosic packaging material will help combat the disposal problem of plastics at the landfill site by recycling, reuse and composting. It will produce completely nontoxic packaging and salable technology.

B. Recycling

The project shall include R and D for cellulosics: Aim at getting central physical data for selecting energy efficient means and paths, in re-use and recycling cellulosics.

B1. Narrative

Several possible paths for recycling cellulosics are apparent. These are either single operations, or combinations, or grinding, low temperature fracture, solvent extraction, melting, reprecipitation, hydrolysis, critical point gas (CO_2) extraction. Choice of these depends on the cellulosic material at hand, also on what the resource recovery use actually shall be. Recycled cellulosics headed for re-use as packaging materials, reblending with other recycled products, would be recycled in a different way than cellulosics which might be hydrolyzed and partly fermented if fermentation is possible.

We shall carry out three areas of work that we view as probably most practical at this point to carry out, useful in most recycling paths. Namely, determination of regrinding energetics, reprecipitation and melting energetics, combustion energies.

There are several technical factors which hinder plastics recycling: the production of thermosetting plastics requires the setting into permanent shape of the resin by the application of heat and pressure. These plastics are thus by their nature impossible to recycle as a material, though they do offer limited potential for by-product generation; thermoplastics are frequently mixed with plastics based on different resins or with completely different materials during the course of fabrication and conversion. As different thermoplastic polymers are incompatible they must be separated before they can be used for re-processing.

Effective recovery technology declines rapidly as the virgin resin moves towards the end use item. The more mixed, the dirtier, the wetter and the less consistent the scrap, the cruder and less consistent are the products that can be made from it and the greater the cost of converting it.

All processes, including recycling, have a 'cost', meaning energy costs. It is logical to find what those energy requirements actually are. That is, minimal energy requirements. Although incineration or burning of cellulosics is not recycling them as polymeric materials, burning can produce process heat. Process heat shall be needed in almost any recycling strategy. Therefore the combustion energy content of cellulosics (oxygen bomb combustion) is wanted in order to determine what fraction of packaging material might be used to supply adequate process heat to drive the rest of the process. Or, to drive recycling processes for other materials, i.e. other plastics.

B2. Procedures

Two kinds of calorimeters shall be used to make the energetics measurements. About twenty such instruments have been constructed here, for "energy" (thermodynamics) research, associated with Biotechnology Reactions Instruments projects (29) and several other projects in the past. These are Seebeck effect (heat conduction instruments capable of making accurate (±3%) heat measurements in ranges down to a few millicalories. We expect that 50-500 mg. samples should be adequate for such measurements. The Seebeck instruments are used for any class of reaction which takes place at temperatures lower than about 80°C. E.g. reprecipitation of recycled cellulose or cellulosics, for recovery of them, extraction of them via alkaline hydrolysis, etc.

For burning energies values, we need a bomb combustion (oxygen bomb) calorimeter. There exists one such calorimeter at the Center for Environmental Studies, Bemidji State University and another unit at the U of M - St. Paul campus. We hope to construct one and use in Lovrien's lab. (To do so requires a steel cylinder and a safety shield, about $800 for the central unit). We can make the necessary sensor elements and D.C. amplifiers here, and heat sinks, for about $1000. These operate efficiently for reactions which proceed at very high temperature.

We are also equipped with a complete ball mill. Low temperature grinding to make plastic materials brittle, is done by adding dry ice to the load to freeze it. Energy costs of dry ice are well known. D.S.C. (scanning calorimetry) - also available here - gives the energetics of thermal treatment of either cellulosics, or petroleum plastics, for recycling. Energies o[illegible]ding and milling are found [illegible]wattage measurement of the motors used to carry out eac[illegible], to a particular state of subdivisi[illegible] recycled material. (As in standard engineering practice (30) for particulate formation).

A path for recycling of cellulosics is likely to involve extraction of them out of packaging particulates. They likely will be re-incorporated again in packaging, probably via light crosslinking of recovered cellulosics to rebuild their polymeric nature. We shall carry out such extraction with environmentally compatible solvents such as ethyl acetate (already a solvent used for cellulosics, nail polish, etc.) and related nontoxic esters. These extractions shall be carried out at intermediate temperature, from ca. 20° less than the boiling point of the solvents, up to the boiling point. After extraction, temperatures are kept at the boiling point, pressure is relieved, solvent is distilled off and recovered (condensed). The energy costs are primarily the heat of evaporation of whichever solvent is chosen, less whatever heat can be gotten by recycling heat from the condenser to raise temperatures of incoming material ("cogeneration"). Again, these heats can be determined via either Seebeck calorimetry, or by conventional means involving thermistor thermometry (30).

Extraction of cellulosics out of mixed materials such as cellulosics agglomerated with other plastics, likely will aid in recovery of them also. That is, recovery and purification of other plastics the cellulosics were mixed with beforehand. This should accrue if the second plastic is made more porous, less aggregated, or in effect attains a lower melting or softening point as cellulosic is removed. It can be argued that "unmixing" such polymers should raise the melting point of each one, because each one may become more crystalline. We simply do not know the answers to this particular problem. However they probably are of some moment - may be very important - in recycling. In order to deal with these questions, both basic and applied, we want to carry out measurements of packaging materials that should be recycled, as in the next section.

III. Extraction of cellulosics out of mixed materials such as cellulosics agglomerated with other plastics will be studied. This should accre if the second plastic is made more porous, less aggregated, or in effect attains a lower melting or softening point as cellulosic is removed.

B. 3 Budget

		LCMR Funds	Matching Funds
a.	Amount Budgeted:	$ 50,000	-0-
b.	Balance	$ 40.00	-0-

B. 4. Timeline f[illegible] Products/Tasks

	Nov 91	May 92	Nov 92	May 93	Oct 93
i. Determination of regrinding energetics	x----------	----------	x		
ii. Determination of reprecipitation and melting energetics	x----------	----------	----------	x	
iii. Determination of combustion energetics		x----------	----------	x	
iv. Extraction of cellulosics with environmentally compatible solvent		x----------	----------	----x	
v. Extraction of cellulosics out of mixed materials		x----------	----------	----------	x
vi. Final Report					x

B. 5. Status:

Due to the delay of funding allocation, this research element was not initiated until the beginning of November, 1991.

The 'energy value' of a large variety of cellulosics involved in packaging are intended to be measured. Dr. Chang has acquired or is acquiring several of these from companies who manufacture and sell diverse cellulosics. These cellulosics shall be partly solubilized or regenerated using nontoxic solvents such as ethyl acetate, insofar as ethyl acetate can soften them. Ethyl acetate (or other solvents intended to use for recycling or for derivatization) need be recovered by distillation, for reuse, the calorimeter is intended to measure the actual energy costs for that part of recycling.

Heats of combustion of pure (mainly crystalline) cellulose are close to 12000 B.T.U./lb. This figure sets an upper limit on energy needed to 'take cellulose apart' for recycling. However in recycling not nearly all the energy content (with respect to combustion) need be consumed. It is estimated that from 10-25% of this figure, i.e. from 10000 to 30000 B.T.U. energy/lb. may be needed to de-aggregate cellulose so it may more easily be recycled. Cellulosics which have already been modified are rather less energy demanding, having lost some of their crystalline character.

Our estimates for these are based on DSC calorimetry, which gives T_m values via heat capacity measurements as a function of temperature, through the temperature ranges necessary to get partial "melting" when "melting" can be reached. Melting here means phase transitions, not true melting to convert to a liquid. The direct combustion calorimeter for measuring these energetics is still under construction. It should be ready for operation in 2-3 months.

Calorimetry of water vapor (or other solvent vapor) adsorption has been carried out, based on our construction of a differential heat conduction instrument for the purpose. We have carried out two main kinds of measurements on cellulose and cellulosics with it: (i) Measurements to obtain the characteristic heat of adsorption of water, from known vapor pressures of water (using A.S.T.M. hygrostats). For crystalline cellulose, these heats are close to 8 Kcal of heat (exothermic)/mole of H_2O. This should be equal in magnitude but opposite in sign, i.e. endothermic for drying the cellulose. (ii) Measurements to obtain the surface area of cellulosics, recycle cellulosics or modified cellulosics, assuming the 8 Kcal/mole is abou [illegible] ant.This latter assumption may [illegible] e exactly right, but as an approximation there is good reason to believe it will approximately hold for reasonable ranges of surface water content of cellulosics. More precisely determined figures, to correct this provisional heat value, can be gotten in the next few months.

Most of the work on cellulose energetics has been carried out with rather pure cellulose, e.g. Avicel. The next main group of energetics or energy content measurements, should be done with the derivatized celluloses, and recycle celluloses. These celluloses are expected to be lower melting, with decreased heat of water adsorption-desorption. It is difficult to estimate what their surface areas will be like, as a result of grinding, ball milling or other workup as usually done in industry. They shall have to measure directly. The calorimetric means is very helpful for that purpose.

A. Energy Requirements in Recycling Cellulosic and Packaging Materials

Feasibility of recycling any waste materials most basically depends on how much energy, how much chemicals if any and their costs, needed to do the recycling.

There are three categories of energy involved: (i) The intrinsic energy content of the material. The intrinsic energy content of gasoline, and also of coal, is close to 18,000 B.T.U. per pound. Of course to use them efficiently, different technologies have to be used in their combustion. But complete burning either one (to CO_2 and water) gives off between 17,000 and 19,000 B.T.U./lb. (ii) The second category of energy is energy wasted (usually as waste heat) during whatever process is involved. Most engines wate about 70% to 75% of their fuel's total energy, as waste heat. (Very efficient large scale electric generating plants waste only about 50-60% of their input energy as waste heat. (iii) The third category of energy, needed to know, is how much energy is made either into useful work, or left in a product after paying for the waste energy. Applied to recycled materials such as cellulosic materials, they mostly have combustion energy contents of 11,000 to 14,000 B.T.U. per lb. , depending on their carbon, hydrogen, oxygen content ratios. These values are not much different from that of pure cellulose (12,000 B.T.U./lb). When carbon-hydrogen contents are high and oxygen contents are low, energy contents of plastics and some derivatized cellulosics containing extra hydrocarbon as some rayons do, are larger, about 15,000-16,000 B.T.U. per lb. We arrived at the figures, for cellulosics by burning them in a combustion calorimeter constructed here under this project, joint with food science department who also are interested in such combustion energies for foods (to get Calories contents).

However even though cellulosic wastes such as cellulose acetate butyrate have energy contents in the range of 15,000 B.T.U. per lb, as a measure of their worth, it takes more energy than that, to recycle them. However it does not require as much energy to recycle, as to make the same packaging material new, in our estimation.

Perspective concerning that last point - energy of recycling vs energy needed to manufacture the same material new - can be seen in the case of cellulose itself. Although its energy content is about 12.000 B.T.U. per lb., it takes roughly 50,000 B.T.U./lb to extract it from wood (chipping, delignification, removal of water, filtration, regrinding if necessary). Furthermore, the costs of chemicals needed (sulfite-chlorine process) to do the delignification, and costs of treatment of waste water and oxidation of lignosulfonate wastes-if those are indeed expended - have not been added in. We do not actually know these latter costs, although they could be determined in another project. Possibly, some of our paper companies know them, but we do not have them at hand.

In any case, once cellulose has been isolated and reasonably purified, its actual value in terms of the energy needed to get it, is between 4X and probably about 8X, that of its intrinsic combustion energy content. Recycling cellulosic waste of various kinds, has its energy costs also, and some of these are reported below. Not all steps in recycling can be accounted for, in terms of energy costs, but this project has put us in a position to make some estimates. The principal conclusion is that it is probably less expensive in terms of energy inputs, to recycle a number of cellulosic materials (kinds we have worked on) rather than manufacture them new, if they can be

gathered for proc [illegible] Because cellulosic materials especially from municipa [illegible] es are mixed, and vary considerably unless sorted, there can be some degradation of quality compared to starting with completely pure homogeneous materials. The same occurs in plastics: Virgin plastics, sorted plastics, completely randomly mixed plastics, are usually very different in quality, both for manufacturing and in ultimate use. (Reground mixed plastics tend to be brittle, no good for electric wire insulation, suitable perhaps for flower pots, one - use containers, etc.).

Recycling cellulosics may take only one mechanical step (regrind, remelt) to make ready for remanufacture, or it may take an additional step, derivatization to convert to an ester, currently carried out by Rayonie, Hercules, companies on the East Coast.

1. Combustion Energy Value

Incineration is a viable solution to decreasing the municipal solid wastes (MSW) volume. Usually four types of incinerators exist: mass burn, refuse-derived fuel (RDF), fluidized bed combustion, and pyrolysis. Mass burn incinerates heterogeneous MSW in an excess supply of oxygen at about 1,800°F. RDF systems employ mechanical means to produce a heterogeneous fuel and are able to produce energy from MSW (about 5,000 BTU/lb), of which an estimted 50% can be converted into electricity. Mass burn and RDF systems would be applicable to the incineration of plastic and could be employed to reduce the volume of plastic food packages entering landfills if hazardous emissions were to be lowered.

A bomb combustion (oxygen bomb) calorimeter was used to measure combusiton energy values. A pellet of samples (0.5 gram) was made and put into bomb combustion calorimeter filled oxygen to incinerate completely. The following equation was used to determine the energy value (BTU content).

BTU/pound = [2483(change in temp. °C) - 1400(wire grams burned)] / pellet wt. grams
x 1.8

1 BTU/lb = 0.002326 KJ/kg

Several cellulosic films (cellulose acetate, CA; cellulose acetate propinate, CAP; celllose acetate propinate grafted with methyl acrylate, CAP/MA; cellulose acetate butyrate CAB), some original waste materials(OWM) and commercial cellophane were used as measuring materials.

Heat of combustion means energy value evolved by the complete combustion of an amount of the substance. An organic substance combusted completely means this carbon containing substance is changed into carbon dioxide, and hydrogen can be changed into water. Therefore, the energy output increased with CO_2 and H_2O release. The combustion energy value and the increasing percentage of combuston energy as compared with original materials or cellophane are shown in Fig 22 and 23, respectively. Those results show that energy value increased wtih increasing carbon chain, because the proportion of oxygen decreased with structure unit in which carbon chaing length increased. The increase of combustion energy value depends on different original materials, the increase order are paper towel > poplar > sawdust for all three kind celulosic films. Energy values of our cellulosic films were 20-40% higher than the commercial cellophane.

In general, petrochemical fims have higher combusiton energy value, because they contain C-H bond in their structure units.

Combustion energy values were not affected significantly by grafting, energy values reduced about 0.7% after grafting.

ENERGIES OF COMBUSTION TO OBTAIN INTRINSIC ENERGY CONTENTS

Material	Calorimetric combustion energy content (n = number of determinations) (B.T.U. per lb)
Cellulose	
Filter paper	12800±900 (n=2)
Powdered α -cellulose	12600±1000 (n=3)
Cottom	13100±900 (n=2)
Solka-floc commercial bulk cellulose	10600±1000 (n=3)
Derivatized cellulose rayons	
Cellulose acetate	9100±800 (n=2)
Cellulose acetate butyrate	1300±700 (n=3)
Hydroxypropylated cellulose, one-two groups per monomer unit	10800± (n=3)
Methyl cellulose	12200±800 (n=4)
Carboxymethyl cellulose (CMC) acid form	9600±700 (n=3)
Modal rayon	9800±1000 (n=3)
HWM rayon	10200±1200 (n=2)
Prima rayon	10800±800 (n=2)
Packaging (cellulosic packaging, primarily cellulosic but in some case partly laminated admixed glazed)	
Frozen vegetable packaging (Green Giant)	12200±1100 (n=2)
Paper food sack	9800 ±1200 (n=2)
Cereal box (cornflakes, GM)	10500±800 (n=3)
Cereal box (cornflakes, Post T)	11600±700 (n=4)
Cardboard, shipping	11800±1000 (n=3)
Newsprint	12700±1100 (n=2)

2. Energy of drying from 100% humidity to near dryness via vapor flow-heat conduction calorimetry

α -Cellulose, 100-200 mesh	8000 calorie/gm.
Ground paper: (100-200 mesh)	
newsprint "	7000
paper backs "	7500
ground cardboard "	7700
Powdered C.M.C.	6200

3. Energy of grinding to 20-60 mesh (coarse) and 100-150 mesh (medium) particles. Waste heat substracted out from overall energy input.

	Coarse 0.40 Kilowats hr	Medium 0.90 Killowats hr
Cellulose acetate butyrate	lb	lb
Paper sack	0.85	1.40
Paper sack	1.25	2.20
Paper sack	1.10	1.80
Veg. packaging (Green Giant)	0.70	1.20
Cereal packaging (Gen. Mills)	0.50	1.05

4. Energy of dissolving cellulose acetate and hydroxypropyl cellulose in DMSO (Mixing calorimetry).

Cellulose acetate	52 calories/gm
Cellulose acetate butyrate	72
Hydroxypropyl cellulose (low substitution)	31
Hydroxypropyl cellulose	36
Methyl cellulose (high substitution)	43

5. Energy to achieve thermoplastic behavior measured by DSC calorimetry, ' 1 midpoint t emperature c momechanical yield behavior plot. (Derivatized cellulos

Material	Midpoint Temperature (starting from 25°C)	B.T.U. per lb(n=2)
Cellulose acetate	240°C	3800±600
Hydroxypropyl cellulose (degree of substitution, 1 group per monomer	210°	2600±400
Hydroxypropyl cellulose, 1.5 group per monomer	180°	1850±400
Cellulose acetate butyrate	320°	6900±800
Methyl cellulose (1 group per 2 monomer, i.e. D.S. = 0.5)	230°	5300±700
HMW rayon	350°	7100± 800
Prima low rayon	220°	4200±500

B. Means for Determination of Mechanical Processing Energy Dissipatio (as Heat), and as Stored Energy.

In an electric motor driven grinding or milling machine, we can measure the input energy by measuring input voltage and current. Over time, e.g. 5 minutes, this is a measurement of total input power (Volts x Current = Watts, Watts x Time = kW hr). If this is done in a closed insulated box, the temperature rise in the box may be measured. It can be produced by using a resistance heater (also dissipating a known amount of power) so such temperature rises can be calibrated, in terms of heat dissipated, of either the resistance heater, or the electric machine of interest. Thus, when the machine is in place and running, the amount of heat it gives off, can be found from the temperature rise it produces which in turn was calibrated in terms of heat for the particular box or enclosure. If the box is fairly well insulated, there is not much error, from external "drag", loss of heat to the surrounding, the laboratory, during short runs. (At steady state maximum temperature of course, losses to the outside equal rate of heat generation inside). Thus.

Power input, P.I. = Power lost as heat - Energy stored in the material being processed

P.L. = P.L. - E.S.

Since we measure P.I. and P.L., then E.S. is possible to determine. Under grinding conditions we were able to achieve, E.S. is relatively small, about 5 ±4% of the total power input P.I. In small laboratory milk which probably are rather inefficient, most power input in brinding packaging materials becomes waste heat. Averaging over seven different packaging samples, five Green Giant vegetable packaging, and two cereal boxes (General Mills), percent of input energy given off as waste heat, ranged between 82 to 95%. The average was 9.1%. Thus about 9% of the input energy becomes stored in the sample. This energy is the increased surface energy of the grind, of the particulate material, relative to the energy content of the bulk, unground form.

C. Separability pped Packaging Material for Recycling

Two means of separation of packaging material to be recycled appear practical, although both of them require such material to be chopped to pieces about the size of small wood chips. Namely, separation by settling-floatation, and separation by hot solvent extraction for removal of synthetic polymers.

Settling-flotation was carried out in the small scale device shown in figure 46. When the water-salt mixture-of adjustable density-has a density between the densities of the chopped particles, 'light' particles float and heavies sink. The system can be fed at either the top or bottom. It can be operated under fairly crowded conditions in the settling tower, if agitation using a propellor which can move up and down is used.

Some packaging materials are mixtures, of paper or cellulosics, and platic films like polyesters. Some of these plastics are soluble enough to be extracted by hot solvents as in Soxhlet extraction. However others such as polyethylene are quite resistant. Sovlents such as THF (tetrahydrofuran) are fairly good solvents or at least softening agents for such polymers, besides being reasonably low boiling, in the 60-90°C range. However such a process will require recycling the solvent, by redistilling it off the extracted resins and plastics, leaving the latter behind at residue. Because of the length of time for carrying out such a process, all the heat needed to carry out both main steps (extraction, redistillation), also the fire hazard of large amounts of flammable solvents, hot organic solvent extraction to separate out cellulose and cellulosic derivatives, from resins or plastics, does not appear practical. For expensive materials, hot solvent extraction may be useful because of its flexibility. However it is not simple, and can be hazardous because of the flammability problem.

D. Derivatization of Cellulosic Recycle Packaging

After grinding, converting bulk packaging to small particles, one of the ways to try to recycle is to derivatize enough by for example acetylation or propionylation, so the recovered and derivatized material can be made into films, cast, or molded. It is not necessary to convert all material to be recycled, to a product which is close to a pure plastic. The intent is to modify cellulosics so they can be remolded with the aid of heat, formed into films that are barriers against water and water vapor, be nontoxic, able to be refabricated.

To gauge the softening and film forming capacity of acetylated and propionylated recycle cellulosics, stretch-temperature profiles, and break point-temperature profiles by the TAPPI T470-Om-80 method and by ASTM-D828-60 method were used, with some modifications to compare with Saran wrap film in these characteristics. They also were compared with standard Saran wrap in 'cling' character, by measuring the weight, of a drag (a weighted object) necessary to peel such films lengthwise, off a 1/4" rod around which 2 layers had been wrapped. This is a rough comparison, but probably reasonable means of measuring 'cling' character. The data concerning cling takes into account the thickness of the films, both the standard against which we make comparison and the modified recycle film.

To measure the amount of derivatizing agent which becomes permanently attached to the material being derivatized, the raw material in 1 to 10 mil (0.001 to 0.010 thousandth inch thick, approximately) was treated with acetic anhydride, propyl anhydride, and epichlorohydrin in ethyl ether, from 30-40°C for 24 hrs (below reflux temperature) with stirring. Amounts left in the solvent were directly measured by hydrolysis of the supernate after filtering out the solid material, titrating the supernate, then subtracting that from the total amount originally put in. Typical derivatization recipes were 200-500 mg. of material to be derivatized, 20 ml. of solvent with 2% derivatization compound. Weight gain of the solid material, after derivatization and drying, is also indicative of amounts of derivatization gotten. For derivatization to ethers instead of esters, ethyl chloride in 2% sodium hydroxide, in a reflux system, going up to near reflux temperatues, was used (Table 27).

Perodiate ox[illegible]on also was used in some cases, for measuring the degr[illegible]bstitution. Table A summari[illegible]e data, connecting the kind of derivatization with behavior o[illegible]e materials after treatment. The values for cling behavior are relative to Saran wrap, as mentioned above.

Recycle materials that are heavily loaded with printing and sizing additives, especially clay-like materials and Bentonite-like materials, neither derivatize readily nor have good mechanical, thermal, or cling properties, from treatment. It appears that cardboard, paper and related packaging based on cellulose, will not be practical to recycle via mild chemical treatment to derivatize it. Cellulose relatively free of such agents however, does take on properties compatible for using them again, such as ability to cling, keep reasonable tensile strength.

E. Recycled Materials for Making Carbon

Carbons are used as catalysts, as adsorbents, antioxidants, in water purification. One of our aims is to develop them for production of esters, in which esters are made from ethanol.

The 3M company, in one of their divisions, is already involved in pyrolysis and carbon manufacture, also in feasibility studies.

Our preliminary work here pertains mostly to forming esters, although we also completed a project for Lifecore, Inc., using carbon to recapture TCA. (TCA = trichloroacetate; very toxic). The TCA compound has to be used in production of certain biologicals, but also has to be completely stripped out and recaptured at the end of the process. We found that two forms of carbon are efficient, relatively inexpensive, and completely recyclable (Soxhlet extraction of TCA with isopropanol) for this.

Conversion of packaging to carbon, is being set up with a small pyrolyzer, able to take 20-40 gm of material in about 10 minutes. Depending on quality of the carbon, this should be scaleable. The data gathered so far is intended to provide a basis for industrial feasibility prospects for carbon-from-recycle.

CARBON-FROM-RECYCLE; CONTENT, AND ADSORPTION CHARACTER

Raw Material	Approximate carbon yield	Adsorption capacity (for butyl acetate)
Food packaging number 1 (Green Giant)	28±4%	75 mg/gm
Food packaging number 2 (Green Giant)	32±6%	94 mg/gm
Food packaging number 3 (Kemps)	22±4%	106 mg/gm
Food packaging number 4 (General Mills)	39±6%	88 mg/gm

Carbon in several forms is used on a large scale in industry, also for domestic use. Pelletted carbon is much favored for removing toxic and organic materials from both air and water, and for capturing solvents to either recycle them, or to purify other materials. Carbon decolorizes materials, including beverages, and removes bad odors. Carbon is useful for many other purposes (such as catalysts, or protection agents for catalysts). Hence discard package materials for partial pyrolysis under reducing conditions may have potential for this market. Higher cost carbons retail from $5 to $15 per pound. These are made from pure petroleum hydrocarbons. Pyrolyzed packaging very likely cannot compete with those carbons. However as lower cost carb, for

recovering toxic [illegible]ls as an asbsorbant and similar applications, lower grade [illegible]ons should have good demand [illegible] in air and water filters and treatment.

In the previous report, we described our development of carbon for capture of TCA (trichloroacetate), and extremely toxic material needed to use, then remove, in an biomedical product manufacture.

We report here physical characterization (Table 28) of four carbons gotten by heating packaging materials in a nitrogen atmosphere, to make the carbons. These parameters are the most useful parameters for gauging performance as adsorbants for compounds of kinds wanted to trap. In addition, usually it is very desirable to recycle the carbon to use it again, and remove the toxic compound or other compound trapped out, as a concentrate, isolated. For this, we Soxhlet extracted compounds trapped on carbons with low boiling alcohols. All three components can then be recovered, well separated from one another, by removing the carbon particles from the Soxhlet extraction device (upper chamber), and distilling away (for recovery) of the solvent. This leaves the contaminating chemical behind in the stillpot. This is far mroe effective than using an anion exchange resin: Such resins are powerful in trapping out TCA. But it is very difficult indeed to recover the resin, free to TCA, for it has a tremendous affinity for the resin, much greater than any other anion we've found (so it can't be displaced). Thus we expect 'recycle carbon', lower grade carbons from mixed recycle material, is much preferred in an application of this kind.

B. 6. Benefits:

Recycling of cellulosic rayon packaging material could (1) maximize income from marketable products, (2) reduce quantities of residue for disposal, (3) obtain maximum benefit from necessary separation/screening processes and off-setting waste handling conveying activity over more products and (4) reduce economic risks by providing flexibility (with careful planning and design) to accommodate fluctuations in markets for different products. The improvement in recycling technology resulting from this project would open the field for a number of new industrial (pulp paper) and environmental (waste paper) application.

C. Basic Parameters Needed for A Recycling Recovery and Reuse Strategy: Color Tagging Cellulosics For Recycle Identification

C1. Narrative

The energy saving through recycling and use of waste cellulosic materials varies considerably by quality of waste paper and type of end product. To the extent that further recovery of waste cellulosics packaging materials will be from more contaminated sources, requiring energy intensive preprocessing, the unit energy savings potential will be restricted.

Composting sewage sludge prior to land application may be a good way to utilize municipal and animal wastes in or near metropolitan areas. Large amounts of sludge can be stored in composts with minimum undesirable effects on the environment. During composting some organic matter and N are reduced and pathogenic microorganisms are eliminated. Composting processes require the carbon: nitrogen ratio to be within given limits. Extra nitrogen is readily available from animal manure or sewage sludge. However, paper is the main carbon source and would prove more difficult to substitute if removed.

When recycling, recovery and reuse becomes the norm, it is made easier if one can categorize recyclables by color. That is, pick out cellulosics. Accordingly, FDA approved dyes shall be incorporated in cellulosics, covalently linked if possible, to provide visible tags for recycling.

C2. Procedures

Electronic tensiometry for materials of these kinds is carried out by using nulling or magnetic levitational techniques (31,32). We make the necessary D.C. amplifiers and electromagnet current source and current measurements devices (these are very simpole, with printed circuit units). They are calibrated with N.B.S. standard tensile strength calibrating fibers, or can be calibrated here with a vertical electronic balance.

The D.S.C. instrument is available from Dr. Tsong's laboratory. It is used to determine Tm values (transition temperatures for phase changes) via heat capacity measurements as a function temperature (33).

Recycling of plastics both cellulosic and petrochemicals based is reliant on grinding and chipping, in the initial stages of recycling. In order to follow this and relate it to energy inputs, the amount of additional surface added as grinding proceeds is the best index. This shall be evaluated in a surface measurements calorimeter. It is an easily used, precise way of obtaining surface development. Integral heat of absorption of water vapor, alcohol vapor, etc. onto preweighed samples are measured. As surface area increases from grinding, e.g. ball milling, above 10-20 m^2/gm, specific heats of absorption increase linearly. Therefore, integral heats of absorption up to saturation of probe or carrier gas onto the powder, are direct measures of surface area, when coupled with the calibration factor relating heat production and weight of probe gas absorbed. The latter is determined by direct weighing. This technique for surface areas measurement in general, also for cellulose [illegible] en developed her e(34) using Seebeck calorimetry. It [illegible] eveloped earlier, by oil company researchers using more cumbersome calorimeters (35).

If incineration is used for getting rid of waste, also heat recovery, a principal question is whether the material produces toxic compounds. We shall use two methods of measurement, aimed at elemental chlorine, and at heavy metals. Measurements shall be carried out on recycle particulate materials, petrochemical, and cellulosics, and agglomerates or mixtures of the two. For heavy metals the technique is to ash the plastics, then use either atomic absorption analysis, or spectrophotometry with chromogenic chelate agents for quantitation. Organochlorines shall be analyzed via electron capture mass spectrometry (the mass spectrometer is in St. Paul), also by the A.O.A.C. method using antimony oxide digestion (36).

Composting will be practiced with operations using a combination of city garbage that includes cellulosic packaging materials and animal manures or sewage sludge, adding water to about 50% water holding capacity, and allowing the mixture to digest for several weeks until the compost is mature. Time required to achieve maturity will be studied with different cellulosic contents. Fertility value will be analyzed for each compost pile.

Dye (food grade dye) tagging, visible indicators identifying a recyclable cellulosic, will be carried out as follows. We shall simply dissolve such dyes in hot melts, cool the melt, and regrind it. This shall permanently trap or occlude the dye, until remelted or ground again. We could covalently link such dyes to cellulose itself, or to cellulosic plastics. However, such linkers are triazine types of compounds, and might not pass FDA regulations (until proved harmless). Therefore we believe that simply "rolling in" the dyes, without doing any chemistry, is best for practical purposes to provide imbedded identifying colors for recycling.

C.3. Budget

		LCMR Funds	Matching Funds
a.	Amount budgeted:	$ 50,000	-0-
b.	Balance:	$ 23.02	-0-

C.4. Timeline for Product/Tasks

	Nov 91	May 92	Nov 92	May 93	Oct 93
i. Categorization of recyclables by colors (dye tagging)	x--------	----------	----------	x	
ii. Recycling technology and packaging engineering (energy input)	x------	----------	----------	--------x	
iii. Composting		x--------	----------	----------x	
iv. Incineration (waste gas output)			x----------	--------x	
v. Final Report					x

C. 5. Status Reporting:

Due to the delay in funding allocation, this research element was not initiated until the beginning of November, 1991.

Two food grade dyes have been incorporated into fibers by precipitating them via the solvent treatment process (evaporation of solvent after treatment). They are intended to enable easy visual identification of the kinds of cellulosics that may be recycled, or kinds that should go to incineration or composting if incineration or composting is used. Such dyed cellulosics are being determined for their stability. The reason for using food grade dyes for this purpose even if they are less stable is that they are safe to be used as recycled materials for food packaging.

A. Recycle Identification

The two additional food grade dyes have been incorporated into cellulose, for visualization of the kinds of cellulose products suitable for recycling. (Or for incineration, or composting).

B. Recycling For New Products, Upgraded Products

A product for stabilizing soils against water erosion is being developed with cellulosics. The product is a network of recycle cellulosic fibers, derivatized enough to biodegrade only slowly. The cellulosic network protects against washing while allowing some water penetrance, and acting as a sponge for clayey soils.

Another product partly developed is absorbent for proteins and enzymes. In many industries including food processing industries and food production, absorbed proteins are rather high value-added products. This is especially the case, for certain enzymes. Foreign made cellulosics are imported into the U.S. for this purpose, and as chromatography supports. Some of our work is aimed at competing with these using our own cellulose and if possible recycled cellulose.

Recycling packaging materials has been worked with pertaining to recycle materials permeability to low M.W. organic compounds. The measurements determine the extent to which recycle materials are barriers to water, and barriers to low M.W. (molecular weight) compounds such as off-flavors. They also determine the extent of adsorption of compounds. Recycle materials need to be evaluated for use in food packaging, in relation to their physical properties such as thermoplasticity and film forming capacity. They also need evaluation in how they behave in the biochemical sense with respect to giving off, or adsorbing, compounds depending on how used. Recycle plastics headed for motor oil use, obviously come under different criteria than those headed for food use.

Recycle materials also are being converted to absorbent carbon black (charcoal carbon), for its potential as a commercial product. We believe one of the divisions of 3M Company (specialty packaging) is interested in this because they are strong markets for absorbent carbon. Absorbant carbon is used for many purposes, in water purifiers, industrial and domestic filtration devices, in cleanup and decolorizing a large number of materials.

Our means for converting packaging is to grind it, heat it under a slow stream of nitrogen to partly pyrolyze it. The residues are dominantly carbon, with from 0.5 to 3% of other elements including chlorine, sodium, sulfur, calcium, silica. Contents of these depend of course on what the original packaging was made of. If it was mainly cellulose, or cellulose and polyethylene (or terephthalate), there is very little or no chlorine or sulfur in it. Sizing compounds based essentially on clay materials, leave some metallic elements in carbon residue. Off gases from pyrolysis were analyzed for chlorine. (Cellulosic materials are very low in chlorine, as expected. But films, or mixed packaging materials based wholly or partly on any polyvinylchlorides, contain chlorine, as expected (organochlorine)). In pyrolysis, chlorine compounds are driven off as low M.W. compounds with nt chlorine, perhaps as ethylene mono-and dichloride). ral residues in pyrolysis carbons were analyzed by assuming they are mostly alkaline earth metals, calcium and magnesium compounds, using murexide colorimetric analysis. Analysis for silica, and aluminum ion in pyrolysis carbons, is being calibrated.

C. Recycling packaging materials containing some lignin. Lignin is part of nearly all cellulose, except the most pure celluloses such as cotton. Wood and pulp cellulose always have some lignin, usually partly oxidized. We see no clear correlates of recyclability or of cellulose capacity to be modified, with moderate contents of lignin in cellulose, a few percent. Lignin contents are defined as amounts of Folin-active phenolic materials that can be bleached out of lignocellulose. It is likely that better measures can be gotten by FTIR, which is coming available now for our use.

D. Recycling packaging, for conversion to carbon: Consultations with 3M specialities product division (Curt Larson's group).

If recycling old packaging to make more new packaging, is marginal from 3M's point of view, there are good prospects for using some kinds of packaging for making salable absorbents, especially carbon. That is, by pyrolyzing used packaging to the extent of turning most of it into carbon, analogous to charcoal briquet. A number of carbons are fairly high added value materials. Activated carbons retail for $5 to $15 per pound. They are used in very large quantities for about fifty industrial and domestic purposes. Many of these uses are for absorbents of polluting chemicals, removing off-flavors from refrigerated rooms, from food products in some cases (especially fish and meat product sin storage), as clarifying and decolorizing agents. Carbons are used for purification of other chemicals, including synthetic chemicals, even proteins, and sugars. Often they are called charcoals, and in many respects are close to cooking charcoal, except they have higher surface areas than ordinary charcoals (100-5600 m^2/gm).

We developed a very significant pollutant chemical stripping method with a carbon. Trichloroacetate (TCA) is a large volume, very toxic chemical produced in industry. Working with Lifecorps Inc. of Minneapolis, we developed a means for recovering TCA from water and industrial fermenter solutions, by carbon. The carbon absorbed all the TCA out in about 20-30 minutes. Then the TCA was recovered by isopropanol-Soxhlet extraction. Since isopropanol boils off at a very different temperature than TCA does, they can easily be separated by simple distillation, recovering both the TCA and isopropanol. Thus carbon is the key first step, in a simple three step process, to completely recover and reconcentrate a very toxic chemical out of water, without using ion exchangers. Ion exchangers are also efficient in removing TCA from water. However it is almost impossible to remove TCA from any commercial ion exchanger we could find. Since these resin ion exchangers cost about $10-20 per lb., they are far too expensive to be used as a "one-time" means for stripping out a compound like TCA, or similar pollutants.

Therefore it looks very much as if carbon gotten from recycling used packaging, can be used industrially, in a simple process cycle, at low cost, for removing toxics from water. Adsorbant carbon has been used in this way before, but these are far more expensive carbons than the materials form recycle.

Because some packaging has chlorinated polymers in it, we are thinking now that leaving some of the chlorine in them to make a lower pyrolysis temperature carbon, would have advantages for removing chlorinated organic pollutants. The TCA example is removal of a toxic inorganic pollutant that has been causing considerable trouble. We look forward to collaborating more with the two industries that have helped us with these materials, also advice, 3M people, and Lifecorps, Inc.

E. Biodegradation

Traditionally, synthetic polymers have always been designed to be resistant to microbial attack and are usually stabilized with antioxidants, antiozonants, heat stabilizers and UV stabilizers in order to protect them from environmental degradation. Usually, most synthetic polymers are not biodegradable because they have not been on the earth long enough for the m[illegible]ganisms to evolve to utilize [illegible] as food. In the same way, most addition polymers are [illegible]t biodegradable because the com[illegible] micro-organisms do not contain the required extracellular enzymes capable of hydrolyzing or cleaving polymers containing only carbon to carbon bonds in the backbone to low molecular weight oligomers. Recently, it was determined that degradation of polyethylene (Mn = 18,000; Mw = 84,000) to be less than 0.2% by weight in a 10 year peiod. On the other hand, all naturally occurring polymers, such as starch, cellulose, proteins, nucleic acids, and lignin, are biodegradable since microorganisms have evolved which contain the necessary enzymes for the degradation of these natural polymers. However, there are still a lot of unanswered questions about biodegradable plastics. Among these questions are concerns about the definitions of degradation, degradation products and how they will affect the environment.

ASTM committee on Environmentally Degradable plastic has developed technical definitions that concentrate on the mechanism of degradation but do not address the time for degradation to occur. "Biodegradable" is considered simply as the ability of the molecular components of a material can be metabolized by the action of micro-organisms such as bacteria, fungi and algae, so that the carbon contained in that material can ultimately be returned to the biosphere. This definitions will be usd as a basis for discussion of the application of degradation to the food packaging. Generally, degradaton of plastic follows two steps; first, the plastic is physically deteriorated into oligomers; then the oligimers are degraded into their smaller molecular weight components. However, the rate of degradation of biodegradable plastics is largely a funciton of the monomer composition, polymer chan ends or degree of branching exposed surface area, molecular weight and conditions within the biodegradation environment. At present, the degree of biodegradation is measured by quantifying modifications in molecular weight distribution, carbon dioxide production, formation of carboxyl end groups and examination of the plastic structure via scanning electron microscopy (SEM).

Carbon dioxide evoluton is a measure of complete degradatio of organic compounds, with higher values indicating a greater extent of decomposition. The increase in the amount of carbon dioxide produced from the polymer, compared to that of the control was used as the measure of the rate of biodegradation on the time scale used.

Although rapidly rising costs of landfilling, as high or higher than $100 per ton in some parts of the U.S., and of alternative waste treatment methods, such as incineration, about 85% of the waste is currently disposed of in landfills. For these reasons, we have more interest in if or how cellulose film can be biodegrated in landfills condition.

In our biodegradation experiment, a natural sandy soil was used as the source of the soil micro-organisms and two separated cellulosic film gorups were cut small pieces and whole pieces and mixed with soil.

Into a 500-ml glass jar, 0.15g of both of cellulosic film groups were thoroughly mixed or buried in propotion with 150g soil, adjusted to 20% of water holding capacity, and were connected to the CO_2 collection apparatus, which is composited with small beaker that contained absorption alkine solution and was fixed in the centre of the bottle. The system was incubated at room-temperature. The carbn dioxide released from the sample was trapped in a 0.5 N KOH solution as potassium carbonate, which was then precipitated as strontium carbonate by the addition of stratium chloride. A piece of folded filter paper was placed in the KOH solution to increase the absorption surface area. The unreacted KOH in solution was then titrated against standardized hydrochloric acid and the amount of the carbon dioxide released was calculated by

$$\text{mg } CO_2 = (B-V)NE,$$

Where:
V = volume (ml) of acid to titrate samples
B = volume (ml) of acid to titrate blank
N = normality of acid
E = equivalent weight of carbon dioxide

After each determination, the systems were flushed with air. Al samples had five replicates. Control sample did not contain film test mateials.

$$\text{Biodegradation \%} = \frac{\text{carbon mineralized from added organic carbon (mg)}}{\text{Total added organic carbon in samples (mg)}} \times 100$$

$$= \frac{\text{mg}CO_2 \text{ of sample - mg}CO_2 \text{ of blank}}{\text{Wt. of film added x C\% x F}}$$

Where: F -- conversion factor of organic carbon to carbon dioxide.

The results of CO_2 evolution plotted in Figure 24, 25, and 26. From these results it can be concluded that 1) all of cellulosic film are biodegradable, although the introduction of ester linkages in the backbone of celulose indeed makes our products less biodegradable than cellophane. 2) Biodegradation rate of cut film is higher than the whole piece film because microbial intrusion increase with increasing surface areas of film. 3) Cumulative evolution of carbon dioxide increased with incubation time. In this experiment, a phenomenon of cellophane disappearance was observed when biodegradation rate of about 25%, corresponding with soil burial for 60 days. It can be explained that cellophane was degraded into oligomers by enzymes produced by microorganisms first thus loss its original film propety; further it was degraded gradually into glucose, which is a readily available carbon and energy source for many microorganisms, and finally in the form of low molecular weight compounds, carbon dioxide and water quickly and completely disappeared from the environment.

Biodegrability of cellulosic films was studied further by different soil samples. Three soils were chosen from the Bagley, Minnesota area. Soil one; sandy texture, soil two; a humus clay, rich in organic material, and soil three; clay. All three soils were passed through a #10 sieve, rocks and debris removed, and the moisture contents were determined to be 15%, 25%, and 20% respectively. Water was added to each jar and the moisture contents were maintained at 22%, 41% and 32% respectively. Type and composite of films used in this test was shown in Table 22.

Table 22. Test f sed in study.

NAME	DESCRIPTION	SOURCE
SD/MA	Cellulose acetate propionate made from sawdust graft with methyl acrylate.	prepared by CES, BSU
SD/CAP	Cellulose acetate propionate made with sawdust.	" "
P/MA	Cellulose acetate propionate made from hybrid poplar chips graft with methyl acrylate.	" "
P/CAP	Cellulose acetate propionate made from hybrid poplar chips.	" "
PT/MA	Cellulose acetate propionate made from used brown paper towels graft with methyl acrylate.	" "
PT/CAP	Cellulose acetate propionate made from used brown paper towels	" "
CELL	Commercial cellophane film type 128 PUT76	purchased from Flexel.
SB	A polyethelene sandwich bag made from low density polyethelene.	Glad product, mfg. by First Brand Corp.
GB	A 30% post consumer garbage bag made from recycled polyolefins, created from a combination of four types of linear low density polyethenes; butene, octene, hexene and polypropalene.	Shurfine-Central Corp manufactured by Presto Products

Nine proc mples were mixed into three replicates of each of the thr lls and three jars with soil only were used as a base indicator for natural oxygen absorption. Each sample was cut into small pieces (approximately 1 mm. x 5 mm.), 0.15 grams of each product were placed in 16 oz. glass jars with approximately 150 grams of wet soil.

Apparatus setup and determination procedures were the same as above described methodology.

Results were presented in figures 39-41. Percentage of degradability was lowest for clay soil (#3) and higher in sand (#1) and humus soils (#2). The commercial cellophane was degraded at a higher rate in humus clay soil (#2) and clay (#3) but slowly in sandy soil (#1).

In all cases CAP was degraded faster than samples graft with methyl acrylate. This could be due to more complicated structure of the graft sample and higher molecular weight. Although molecular weight of the films were unattainable due to testing implications and security reasons, it is fairly safe to assume that graft sample will have higher molecular weight than ungraft samples. There have been studies that suggest that low molecular weight increases biodegradability and branching inhibits degradation. It has been suggested that the length of degradation time depends on the ratio of natural to synthetic compounds the graft co-polymer contains.

The effects of polymer structure on biodegradation is very important. Many synthetic polymers that claimed to be degradable contain hydrolyzable linkages along the polymers. Natural macromolecules are generally degraded by hydrolysis followed by oxidation. If the synthetic polymer is flexible enough to fit into the active site of the enzyme it can then be degraded by enzyme catalysis. Therefore the morphology of synthetic polymers is very important. Regularity enhances crystallinity making the hydrolyzable groups on the polymer inaccessible to enzymes. Synthetic polymers with long repeating units are less likely to crystallize and are thought to degrade faster. The orientaton of the polymer molecules can increase or decrease the secondary valence forces acting between polar chains. The more symmetrical a polymer is the stronger the tensile strength and increase elastic modulus. It is suggested that enzymatic degradation is selective of semicrystalline polymer samples where during degradation, the crystalinity of the sample increases rapidly at first while enzymes attack the amorphous portion of the sample first. As crystallinity approaches 100% the rate of degradation levels off to a much slower rate leaving the crystalline lattice degradation last. Therefore molecular weight and the degree of crystallinity are the dominate factors for determining degradability, depending on the existing indigenous microorganisms.

Both the SB and GB showed lower oxygen uptake than natural rate determined in the empty jar which may mean the plastic is having an inhibiting effect on degradation (Fig. 42 and 43) and effect of SB on microbial activity is greater than GB. This could mean that no autooxidation is taking place. This could be due to coatings on the plastic films or the nature of linear hydrocarbons to be less readily oxidizable. But it should be able to be metabolized more readily by microorganisms if proper microorganisms are present in the soils.

The properties of soil, such as pH, organic matter and porosity etc. can affect enzymatic activity and microbial populations. Fig. 44 depicts cumulative CO_2 evolution in four soils. The degradation sequence is #2, #3, #4 and #1 in a decreasing order. However, kinds and population number of microorganisms in soil is also an important factor. A higher biodegradation rate of cellophane was obtained in #4 soil (Fig. 45), even though its cumulative microbial activity is not as high as #2 or #3 soil.

Degree of cellulose degradation is dependant on the presence of impurities. Cellulose and cellophane have same structural formula but different morphology. Cellulose was degraded to carbon dioxide and water. The rate of cellulose degradation is controlled by its hydrolysis to glucose. Water allows hydrolysis to take place, therefore, moisture content is important. CA, CAB, CAP and samples graft with MA are all considered to be cellulose esters. Acetylation takes place to different degrees, resulting in varying properties in the presence of different acids and catalysts. There are three hydroxyl groups per chain unit (glucose) and the properties of the polymer depend on the number that have been substituted. The degree of substitution (D.S.) used mainly in cellulose chemistry, measure (0-3), the substitution of reactive hydroxyl groups on each of the anhydroglucose units. Cellophane is a non-thermoplastic that absorbs water easily while the cellulose esters are considered thermoplastic. CA is lighter than regenerated cellulose and moisture sensitive, its molecular weight is dependent on acetic acid content. CA is a thermoplastic resistant to oil and many chemicals. CA made from hybrid poplar also showed better degradative property than CAP and CAB probably due to degree of substitution. Cut pieces that degraded at faster rates than whole pieces of the same film type can be due to increased surface area of cut pieces, allowing microorganisms more surface area to react upon. CAB has one hydroxyl group and four anhydroglucose units. CAP is more soluble than CA and shows lower weatherability than CAB, this may explain why CAP was degraded slightly faster than CAB (Fig. 24 and 25).

Comparative results of biodegradability of films made from sawdust, hybrid poplar and paper towel show little difference. CAP and MA/CAP made from all three cellulose bases degraded to about the same extent.

F. <u>Incineration</u>

Environmental and food safety can be directly or indirectly affected by the incineration of petroleum base plastic packaging materials. The U.S. Environmental protection Agency (EPA) considers six pollutants produced from incinerators might be present in sufficient quantities to pose a threat to public health. They are arsenic, cadmium, dioxins, and furans, hydrogen chloride, lead and mercury. Pathways for the production of these emissions are not well understood because of the high temperature and heterogeneous mixtures associated with incineration of MSW. All of these emitted materials can enter human body directly by inhalation or indirectly through water consumption and the food chain, thereby increasing our exposure.

Elemental chlorine and heavy metals are two main items measured in our incinerated samples.

1. Chlorine

Hydrogen chloride (HCL, MP-114°C, b.P -84.8°C), is emitted from a number of sources. Incineration of chlorinated plastics releases HCL as a combustion product. Thus, someone is extremely concerned over, if there is any risk of increased acidity of atmospheric deposition (wet and dry) once a vast scale of HCL released into atmosphere during the incineration processes. Because apart from the nitrogen and sulphur compounds, that can give a significant input of acid to a coniferous forest ecosystem, hydrochloric acid is probably the only compound of interest. However, the anthropogenic emission of HCL is small compared to emissions of sulphur and nitrogen, and since most of the chloride existing in the atmosphere comes from neutral sea salt, it does not give any imput of acid. In fact, chlorine content in cellulose is very low, the range is 5-1000 ppm. Therefore, the amount of HCL in atmosphere sourced from the incineration of cellulose is much less than evaporation of sea salt.

Total chlorine in raw materials, cellulosic films was measured according to the method described in the ASTM, respectively. This test method makes use of the oxygen flask technique for the combustion of the specimens. After the specimens was burned completely, the flask was allowed to cool until all vapors are absorbed by the dilute sodium hydroxide solution. The solution was transferred to a titration vessel and the flast rinsed with distilled water and neutralized with diluted nitrate acid until pH is less than 4.0. The solution was titrated with0.00282 M silver nitrate solution using a Corning ion analyzer-250. Chlorine content, C, was calculated in parts per million as follows:

$$C = (AB/W) \times 1000\,000$$

where

A = 0.00282 M $AgNO_3$ solution required for titration of the specimen, corrected for the blank, mL.

B. = chlorine equivalent of the 0.00282 M $AgNO_3$ solution, g/mL, and

W = specimens used, g.

Measurement of total chlorine contents gives the sum of water soluble chlorides and the combusted organically bound chlorine compounds present in a specimen.

Chlorine in various cellulosic materials are shown in Table 23 which indicates that part of the chlorine in film products was introduced mainly from raw materials pretreated with sodium chlorite and chlorine production decreased with chemical reaction presses extensively.

Despite the fact that there is a broad difference in chlorine production among the three final products (MA/CAP film) made from three raw materials, chlorine in MA/CAP; poplar is much higher (10--folds) than MA/CAP, paper towel, but it is still close to or below that of cellophane.

2. Heavy Metals

Although the concentration of air-borne metals is very low, people still pay more attention to their effects on human health. There is evidence suggesting that a number of trace metals that alter the physiology or function of macrophages can cause a significant increase in susceptibility to infection. Animals exposed to air-born nickel, cadmium, zinc. magnesium, and lead have modified susceptibility to aerosol challenge with bacteria. Inhalation of airborne nickel and cadmium not only altered alveolar macrophage function but also depress primary hormon immunity.

There are data illustrated airborne cadmium in the present-day workplace environment is generally less than 0.02 μg/m^3. Typical concentrations in ambient air in rural areas are 0.001 to 0.005 μg/m^3 and up to 0.050 or 0.060 μg/m^3 in urban areas. Respiratory absorption of cadmium is about 15-30 percent. Most airborne cadmium is respirable. A major nonoccupational source of respirable cadmium is cigarettes. One cigarette contains 1 to 2 μg cd, and 10 percent of Cd in a cigarette is inhaled (0.1 to 0.2 μg).

Batteries, gasoline additives and paint pigments are major uses, but combustion of gasoline additives is the major source of environmental pollution by lead. Thus, lead is primarily an atmospheric pollutant that enters soil and water as fallout. Air is a third source of lead exposure for persons in the genral population. Concentrations of lead in air vary widely and may be lower than 1.0 μg/m^3 in rural areas to 10 μg/m^3 in certain urban environments. Lead in the atmosphere exists either in solid forms, dust or particulates of lead dioxide, or in the form of vapors. Some metals emitted into the environment from combustion of fossil fuels in the United States are shown in Table 24. These include many of the metals most abundant in particulates in ambient air.

T 4. Toxicologically Important Metals Mobilized by Com n o ossil Fuel in U.S. (Column A), Concentrations in Particulates In Ambient Air (Column B) and in Raw Surface Water (Column C), and Best (Worldwide) Prevailing Standards for Threshold limit values (TLV) for Eight-Hour Occupational Exposure (Column D)

	A: From Fossil Fuels U.S.*	B: In Particulates In Air** Typical	C: In Water µg/liter and Frequency of Detection***			D:
	(10^3 tons)	(ng/m^3)	maximum	mean	%	TLV@ mg/m^3
Al	6000	3080	2760	74	31	10
As	27	10	ζ			0.2
Ba	300	100	340	43	99	0.5
Be	15	0.2	1.22	0.19	5.4	0.002
Cd	1	1	120	10	2.5	0.02 dust
Co	15	.5	48	17	2.8	0.05
Cr	0	20	112	10	25	0.05
Cu	9	500	280	15	75	0.1
Fe	6002	4000	4600	52	76	3.5
Li	39	4				0.025
Mg	1200	2000				5.0
Mn	33	100	3230	60	58	2.5
Mo	5	1	1500	68	38	10
Ni	11	20	30	19	16	0.1 sol.
Pb	126	2000	140	13	19	0.1
Sn		50				2.0 inorg.
Se	2	1				0.1
V	27	30	300	2	5	0.5
Zn	30	500	2010	79.2	80	1.0

* From Vouk and Piver, 1983, 1983, data from 1977 fuel consumption

** From Thompson, 1979, ten-day period, six U.S. cities.

*** From NAS, *Drinking WAter and Health,* 1977.

ζ Arsenic in water is extremely variable, 10 to 1100 µg/liter 728 samples surface water 22 percent in 10 to 20 µg range.

@ Levinson, 1972.

Heavy metal in cellulosic film or commercial plastic, was measured using oxygen flask technique for the combustion of specimens, similar to the method of chlorine measurement. After absorption liquid (diluted sodium hydroxide) was neutralized with diluted nitric acid, acidity of solution was adjusted further with 0.1 N hydrochloric acid and concentrated to 10 ml in volume. Heavy metals were determined by Model-902 Atomic Absorption spectrophotometer. Elements include Cd, Zn, Cu, pb, Ni and Mn and results are presented in Table 25. Heavy metal contents in manufactured films is much lower than raw material (sawdust) and most metals are below the detection limit.

G. Color Taggi

According to our previous work, three colorants were chosen as color tagging, visible indicators for the identification of recyclable cellulosic films. Although cellulose has such a good dyeability, people still are more interested in knowing if colorant in cellulosic film will be affected by various environmental factors, i.e. temperature, light (visible or ultraviolet), water immersion or microwave radiation. Experiments were set in three colorants with two time intervals (4 hr and 24 hr.) Six groups of treatment were conducted. A: Uv exposed; B: freeze; C: water immersion (20°C); D: oven dried at 50°C; E: microwave oven heated at high power; F: autoclave. Three cellulosic films treated with different colorant in the same way were stored in the desiccator before weighed. The films were dissolved in same volume of solvent to prepare completely clear solution. Solution were determined for their absorbance at maximum absorption wave-length by color chromatography (spectrophotometer). The concentrations of colorants in treated films were calculated and compared with colorant in non-treated films. The results showed that (Table 26): 1) color tagging in films does not change during the test at room temperature (CK) 2) food yellow 4 colorant is the most stable among three colorants but food red 14 colorant is the least stable in our color tagging tests. Food yellow 4 colorant could be recommended in the future color tagging of cellulosic film manufacturing process 3) direct red 2 and food red 14 colorants, both are more sensitive to Uv. 4) the colorants have not been affected significantly by B,C, D and E, except in food red 14 colorant 5) direct red 2 and food yellow 4 both colorants in MA/CAP film displayed completely different effects by autoclaving treatment.

Although dyeing technology of cellulosic materials has not been studied extensively, we believe dyeability and dyeing fastness of cellulosic films will be improved greatly with dye fixatives or fading inhibitors added or change of dyeing conditions. More colorants will be identified and used as color tagging in cellulosic film study according to the FDA regulations.

Recommendation

Throughout the R & D of this project we recommend that following R & D parameters should be further pursued:

A. To utilize other waste sources that are rich in cellulose.
B. To choose pretreatment pathways and conditions of raw materials that will increase reactivity and yields.
C. To improve synthesis techniques and optimize the reaction conditions, control degree of polymerization, improve tearing strength and elongation properties of products.
D. To study different proportions in each formula that are suitable for various uses of packaging products.
E. To further study techniques of forming, dyeing and packing in final products.
F. To study recycle system of reaction reagents, extraction and redistillation of waste effluent during the manufacturing process to further reduce material consumption and minimize environmental pollution.
G. To conduct a detailed cost/benefit analysis and raw materials/reagents/products equilibrium in order to reduce the cost of goods and maximize yield efficiency.

C. 6. Benefits

Provide manufacturing opportunities for new salable packaging based on renewable resources-cellulose-in Minnesota. Enhance recycling, recovery and reuse in an environmentally compatible way through categorizing recyclables by dye tagging. The main benefit comes from production of packaging that is completely recyclable, nontoxic when incinerated, easily biodegraded, and compatible with current packaging manufacture in laminates, film forming, and extrusion.

IV. EVALUATION

Four general means of evaluation will be used.

(i) Our own evaluation and summary, based on how much energy is required in the recycling of cellulosic based packaging and rayons under the conditions described above.

(ii) Other institutes and agencies will be asked to evaluate the data, also use it if they indeed can. Namely, NRRI (Natural Resources Research Institute) at Duluth, Minnesota. The M.P.C.A. and Office of Waste Management in St. Paul will also be requested to evaluate and distribute the data.

(iii) Arrangements are being made with 3M Company, to evaluate our data, with respect to likely interest in manufacturing cellulosic based packaging raw material of enhanced recyclability.

(iv) Certain national organizations, and individual companies likely shall be interested if 3M Company does not have a great interest. A number of these companies e.g. American Hoechst, Mercules, Monsanto are likely prospects.

V. CONTEXT. RELATED CURRENT AND PREVIOUS WORK

A. Previous work on packaging by the packaging industry has been in the wrong direction with respect to biodegradability . Much of present packaging is based on chlorinated organics which when incinerated make either HCl or volatile organic chloride conjugates. Practically all 'plastic' packaging such as the styrenes relies on petroleum, not on cellulose nor on compounds from renewable or agricultural products.

Current plastics based packaging has two legs: (i) Petrochemicals, (ii) Ease with which plastics form films, blow mold, injection mold, extrude, seal, adhere, cling. Cellulose derivatives, rayons, etc. can help bridge the gap and make more sense, particularly to Minnesota which ought to sell cellulose.

B. Proposed work is supplementary in that it will provide a new material for current packagers to work with. The intent here is not to try to replace current packaging industry. Rather, it is to provide better alternatives, in different directions than the petrochemicals alternative since there is a huge, developable market for recyclable packaging cellulose rayons. We propose to use Minnesota agricultural and forestry biomass to produce cellulosic derivative packaging.

C. Both Chang and Lovrien have not accomplished any cellulosic packaging material R & D work without LCMR funds. Chang has been working on bioconversion of peat to ethanol and other useful products funded by U.S. Department of Energy through MN Department of Administration and LCMR (oil overcharge fund). Chang has been investigating microbial cellulases and lignocellulases system that can convert Minnesota peat to reducing sugars and then through fermentation process to convert reducing sugars to ethanol. He has isolated two bacterial species and four fungal species from peat bog that can be induced to produce these enzymes and result in high reducing sugar yields (up to 15,000 mg/l). Chang is also working on composting technology research and development. Lovrien has not had LCMR funds before, no planned LCMR proposals other than this one. However, if this one is successful, we might try to extend, or newly apply, this proposal.

D. Not applicable.

E. Biennial Budget System Program Title and Budget for this project for FY 92-93: None available at this time.

VI. Qualificat

1. Program Manager:

Fu-Hsian Chang
Professor of Environmental Microbiology
Bemidji State University
Bemidji, MN 56601-2699
Ph.D. Soil and Environmental Microbiology, University of California,
Davis, CA 1979.
M.S. Biology (Microbiology Major and Biochemistry Minor)
University of North Texas, Denton, TX 1974.
Specialization: Biodegradation of xenobiotic compounds and biotechnological utilization of naturally occurring polymers.

Dr. Chang has refereed publications and conducted research in the areas of microbial degradation of crude oil and hydrocarbons in subsurface environments, biodegradation of toxic organics in waste water, microbial utilization of peat and bioconversion of peat to ethanol and other useful products. Current projects include "Biodegradation of crude oil in ground water environment" funded by the U.S. Geological Survey, and "Bioconversion of peat to ethanol and other useful products" funded by the U.S. Department of Energy through the MN Department of Administration and LCMR. Besides research, Chang also teaches Environmental Microbiology, Wastewater Treatment and Phytochemistry. He also team teaches Environmental Chemistry with four faculty members of the Chemistry Department (Chang's primary role is to coordinate this group and teach organic chemistry and biochemistry parts).

2. Coprincipal Investigator

Rex E. Lovrien
Professor of Biochemistry
Biochemistry Department
University of Minnesota
St. Paul, MN 55108
Ph.D. University of Iowa
Specialization: Naturally occurring polymers conversion, applied biochemistry.

Dr. Lovrien has worked on the Rosemount P. C. B. dump project for two years, and Diesel exhaust pollution projects, mutagenicity testing. Lovrien has worked with about ten projects involving microorganisms (bacteria), publishing 15 or so papers. Lovrien carried out several researches with enzymes and proteins, including several for cellulase enzymes and published those, about 20 papers. Lovrien also has researched and published six papers in synthetic polymers including vinyl polymers, and about 20 projects and papers in electronic instruments building. Lovrien also teaches analytical chemistry and analytic biochemistry, which pertain pretty directly to the proposed project.

A new means for assaying enzymatic degradation of cellulose, also for degradation of lignin compound which also are from wood, were designed and proven out in 1986-1989. New means for isolating cellulase enzymes and characterizing them were developed in 1982-1986 (list of papers are below). Biodegradation of cellulosic and wood materials by wood degrading soil fungi, tracked via "affinity gold" electron microscopy, was developed in collaboration with plant pathology people in St. Paul and at U.S.D.A. (Northern Region Laboratories, Peoria), and published on. Extraction and analysis, both chemical analysis and mutagenic analysis in two different pollutants projects were performed over a period of about three years, funded by private and institutional organization including the Federal E.P.A. A new instrumental analytic method based on microbial heat generation, heat conduction calorimetry, was developed for monitoring water pollutants [illegible]ed to petrochemicals. In connection with this we design[illegible] build several calorimeters for Dow Chemical Company (pesticides pollutants) and Gulf South Research (river pollutants).

There are two Institutions involved in this proposed project. The principal research will be conducted parallelly in Lovrien's lab at the University of Minnesota and in Chang's lab at Bemidji State University. The headquarters for management of the project are at Bemidji State University.

Bemidji State University
1500 Birchmont Dr. NE
Bemidji, MN 56601-2699

MEMORANDUM

NOV 24 1993

TO: Dr. Chang

FR: Dennis Burgess, Accounting Office, D201b (Bx13), ph.218-755-2903

RE: 520410 - LMCR Rayon

	Award Amt	Interest	Adm Exp	Total Exp	Unexpended Funds
FY 92		5,984	0	19,323	
FY 93		5,799	0	65,228	
FY 94		653	0	77,223	
	150,000	12,436	0	161,774	662

```
  11/24/93                  BEMIDJI SUB-LEDGER FILE SNAPSHOT
520410     CELLULOSE RAYON PKG                          F CHANG

S/C DESCRIPTION  RUN-BUDGET     CUR-MON        YTD-DISB      REQ & ENC      BALANCE
=== ==========================================================================
021 UNCL SALARY    19543.72     1926.85        13640.79       5902.93          .0
022 UNCL RETIRE     1256.86       32.95          238.56       1018.30          .0
024 UNCL FICA       1327.72       56.15          302.48       1025.24          .0
026 UNCL INSURA      570.16       21.23          168.20        401.96          .0
082 STUDENT HEL     1486.18         .00         1486.18           .00          .0
167 OTHER PROF     38930.00         .00        12169.97      26760.03          .0
167 OTHER PURCH       43.00       42.92           42.92           .00          .0
213 LIVING EXP-       56.75       56.75           56.75           .00          .0
223 LIVING EXP-     2525.44      682.79         2525.44           .00          .0
295 MEMBERSHIPS      129.00         .00          129.00           .00          .0
297 TUITION FEE      507.35         .00          507.35           .00          .0
300 SUPPLIES BU      662.20         .00             .00           .00      662.2
341 REFRIG & AC      498.00      498.00          498.00           .00          .0
353 HARDWARE &         8.86        8.86            8.86           .00          .0
366 LAB EQUIP       6985.00     3474.47         6776.36        208.64          .0
367 PHOTO             12.85         .00           12.85           .00          .0

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  11/24/93         FY 94    BEMIDJI SUB-LEDGER FILE SNAPSHOT

520410     CELLULOSE RAYON PKG                          F CHANG

S/C DESCRIPTION  RUN-BUDGET     CUR-MON        YTD-DISB      REQ & ENC      BALANCE
=== ==========================================================================
368 CHEMICALS         74.86         .00           74.86           .00          .0
375 OFFICE SUPP      101.70         .00          101.70           .00          .0
376 BOOKS             68.00         .00           68.00           .00          .0
466 LAB EQUIP       3097.23     2308.84         2308.84        788.39          .0
    *ACCT-TOT*-    77884.88     9109.81        41117.11      36105.49      662.2




BACS   94 520410
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 1./24/93                 BEMIDJI SUB-LEDGER FILE SNAPSHOT
520410      CELLULOSE RAYON PKG                        F CHANG           FLAG   R
B/C DESCRIPTION  RUN-BUDGET    CUR-MON      YTD-DISB     REQ & ENC     BALANCE
=== ===========================================================================
001 UNCL OT, OV    15000.00         .00     13523.77          .00      1476.23
019 FRINGE RESE     2172.32         .00          .00          .00      2172.32
21 UNCL SALARY     20443.95         .00      2745.77          .00     17698.18
22 UNCL RETIRE       383.77         .00       339.18          .00        44.59
24 UNCL FICA         210.05         .00       209.69          .00          .36
26 UNCL INSURA       229.22         .00       124.53          .00       104.69
82 STUDENT HEL      5492.60         .00      4185.90          .00      1306.70
42 PRINT STATE      1449.28         .00          .00          .00      1449.28
67 OTHER PROF      78635.00         .00     39705.00          .00     38930.00
67 OTHER PURCH        11.13         .00        11.13          .00          .00
02 PHONE RENTA       978.25         .00          .00          .00       978.25
13 LIVING EXP-      4185.00         .00       865.94          .00      3319.06
19                   125.00         .00        41.10          .00        83.90
23 LIVING EXP-      3500.00         .00       757.49          .00      2742.51
00 SUPPLIES BU      9689.48         .00          .00          .00      9689.48
47 PIPE               40.32         .00        40.32          .00          .00
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 1./24/93        FY 93    BEMIDJI SUB-LEDGER FILE SNAPSHOT
20410      CELLULOSE RAYON PKG                        F CHANG           FLAG   R
/C DESCRIPTION  RUN-BUDGET    CUR-MON      YTD-DISB     REQ & ENC     BALANCE
== ===========================================================================
66 LAB EQUIP        1354.41         .00      1354.41          .00          .00
68 CHEMICALS         395.26         .00       395.26          .00          .00
72 APPLIANCES         45.76         .00        45.76          .00          .00
73 OFFICE SUPP        23.10         .00        23.10          .00          .00
76 BOOKS             359.60         .00       359.60          .00          .00
   *ACCT-TOT*-    145223.50         .00     65227.95          .00     79995.55




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        EXP. DATE 00/70    F CHANG                CELLULOSE RAYON PKG                5-20410     DEPT NO. 00000
                                                  SUMMARY REPORT FOR 01/93

SUB                              ORIGINAL      PRESENT    D I S B U R S E M E N T S                                   BALANCE
CODE  DESCRIPTION                 BUDGET        BUDGET      CUR MONTH        TO DATE   REQUISITIONS  ENCUMBRANCES    AVAILABLE

001   UNCL OT, OVL                                                          3,596.00                    4,239.09     7,835.09-
002   OVL RETIREMENT                                                          292.72                                   292
004   OVL FICA                                                                274.38                                   274
019   FRINGE RESERVE                           1,189.95                                                              1,18
021   UNCL SALARY                             69,000.00                     7,872.05                                61,127.
022   UNCL RETIREMENT                            640.48                         3.20                      361.72       275.56
024   UNCL FICA                                  931.38                        26.27                      251.56       653.55
026   UNCL INSURANCE                             238.19                         3.07                                   235.12
082   STUDENT HELP                             7,925.00                     2,432.40                                 5,492.60
       0XX TOTALS                             79,925.00                    14,500.09                    4,852.37    60,572.54

123   REPAIR OTH EQUIP                                                         50.72                                    50.72-
142   PRINT STATE SHOP                         1,500.00                                                              1,500.00
167   OTHER PROF SVC                          79,460.00                       825.00                                78,635.00
       1XX TOTALS                             80,960.00                       875.72                                80,084.28

201   POSTAGE                                    100.00                        21.75                                    78.25
202   PHONE RENTAL                               900.00                                                                900.00
       20X TOTALS                              1,000.00                        21.75                                   978.25

213   LIVING EXP-IN-ST                         2,500.00                                                              2,500.00

222   TRAVEL-OUT STATE                           700.00                       690.00                                    10.00

       2XX TOTALS                              4,200.00                     - 711.75                                 3,488.25

300   SUPPLIES BUDGET                         16,679.62                                                             16,679.62
334   METALWORKING                                86.40                        86.40
366   LAB EQUIP                                  901.35                       901.35
368   CHEMICALS                                2,205.88                     2,205.88
376   BOOKS                                       41.75                        41.75
       3XX TOTALS                             19,915.00                     3,235.38                                16,679.62

       * TOTAL *                             185,000.00                    19,322.94                    4,852.37     160,82

                                                OPEN COMMITMENT STATUS
          ACCOUNT E/R REF.      DATE        DESCRIPTION         ORIGINAL AMOUNT       CURRENT AMOUNT
```

Table 5, pH Values of Raw Material in Distilled Water

Species		Sawdust	Poplar
Distilled Water		6.51	6.56
Ratio of Raw Material to Water	1:5	5.66	6.18
	1:10	5.79	6.27
	1:20	5.83	6.39

Table 6. Comparison of Alpha cellulose content in various raw materials and pulps.

Source	α-cellulose %	Source	α-cellulose %
Cotton linters	99.89	soft-wood paper pulp	86.88
Bagasse	41.70	Viscose rayon	89.55
Bagasse pulp	76.82	Viscose grade pulp	93.83
Bleached bagasse paper pulp	70.28	Sawdust	76.8-83.7 (43.5)*
Rice straw	39.30	Hybrid poplar (1mm)	69.9-81.5 (31.2)*
Wood chips (steam exploded	55.40		

*Cellulose content %

Table 7. Pentosans content of some raw materials and pulps

Source	Pentasans %	Source	Pentasans %
Cotton linters	——	Soft-wood paper pulp	9.87
Bagasse	27.50	Viscose rayon	2.31
Bagasse pulp	21.84	Viscose grade pulp	2.87
Bleached bagasse paper pulp	26.06	sawdust	18.60
Rice straw	21.7		
Wood chips (steam exploded)	20.3		

Table 8 The content of Lignin in some materials

Source	Lignin content (%)	Source	Lignin content (%)
Bagasse	17.9	Herbaceous plant	25-28
Rice straw	10.7	sawdust	19.9
Conifer wood	28-33	Poplar wood	
		non-treated	29.2
Deciduous wood	17-23	bleached	26.8

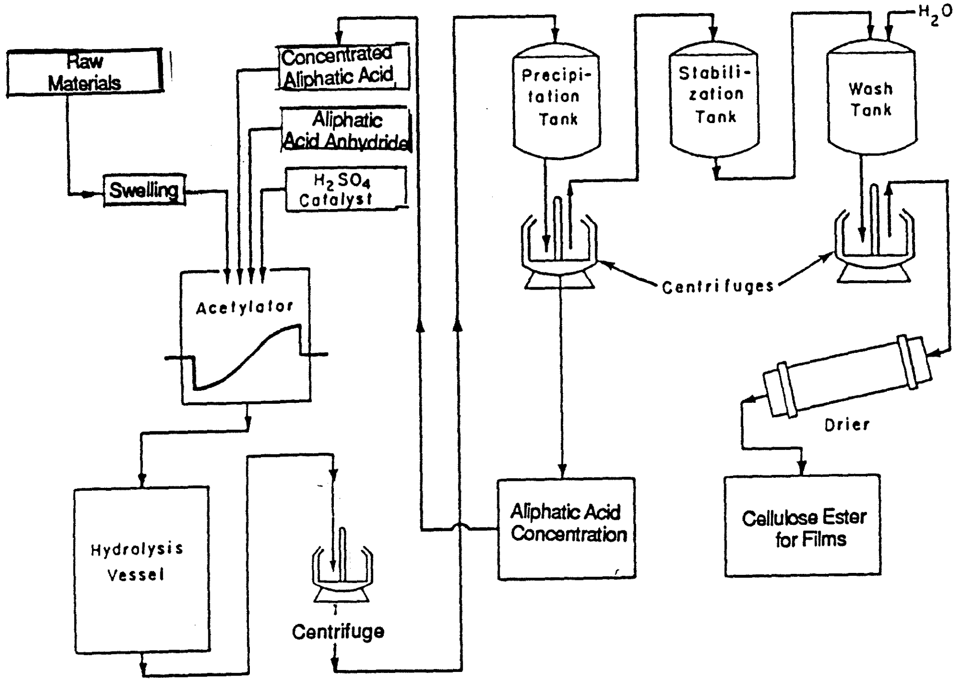


Fig.27 Cellulose Ester Manufacturing Flow Sheet

Table 10 **The yield % of esterified products (w/w)**

specise	CA	CAP	CAB
sawdust	57.8	53.4	117.0
poplar	152.4	143.2	141.2

Table 9. Degree of esterification under different reaction conditions

Index				Reaction Conditions**							
				Acetylation					Hydrolysis		
Acetyl%	Acetic acid %	DS*	Hydroxyl %	1	2	3	4	5	6	7	8
40.3	56.2	2.50	3.17	5.0	12.5	8.0	12~30°C	3.5	25.0	Room-T	-
41.6	58.0	2.64	2.25	4.0	6.0	6.0	12~30°C	18.5	25.0	55	6.0
40.4	56.4	2.52	3.10	4.0	10.0	7.0	12~30°C	5.0	25.0	45	3.0
37.8	52.7	2.25	4.96	4.0	3.0	6.0	12~30°C	2.0	12.0	45	3.0
34.3	47.8	1.94	7.42	"	15.0	"	"	"	"	"	"
39.7	55.4	2.44	4.93	4.0	3.0	10.0	Room-T	8.0	15.0	50	16.0
40.4	56.4	2.52	3.10	4.0	7.0	10.0	Room-T	60	15.0	50	6.0
37.9	52.9	2.27	4.86	2.5	7.0	20.0	"	12.0	15.0	53	12.0
36.5	50.9	2.14	5.85	"	"	"	"	36.0	"	"	"
40.6	56.6	2.53	2.96	4.0	10.0	6.0	"	8.0	15.0	50	12.0
34.1	47.5	1.92	7.54	3.0	10.0	12.0	"	8.0	12.0	52	16.0
29.9	41.7	1.59	10.5	"	"	"	"	"	"	"	66.0

*DS = Degree of substitution

**Acetylation
1 = The amount of esterifying agent, the ratio of sawdust to AC_20 wt/vol
2 = The amount of catalyst, wt. of sawdust to H_2S0_4 ratio (wt/wt).
3 = The amount of solvent, the raio of sawdust to HAc, wt/vol.
4 = Temperature, °C
5 = Time, hr.

Hydrolysis
6 = The percentage of water to total solution (vol. /vol).
7 = Temperature, °C
8 = Time, hr.

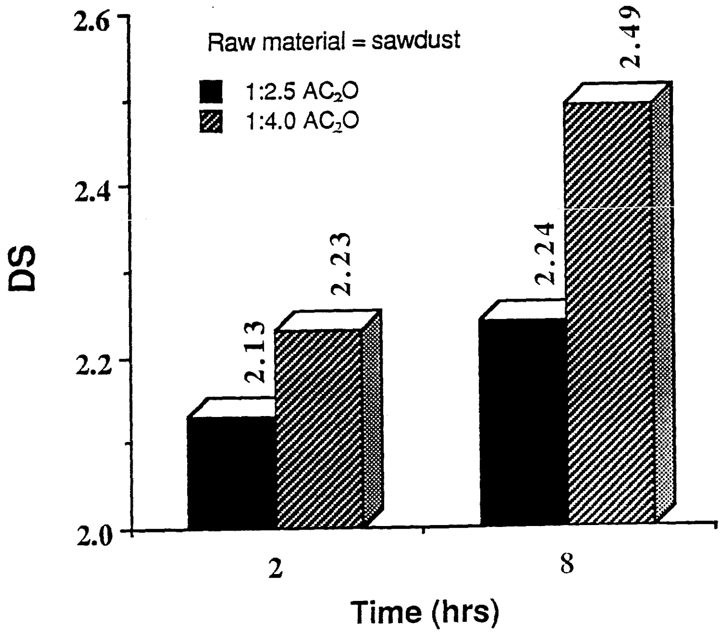


Fig.1 The relationship of DS,amount of acetyl agent and acetifying time

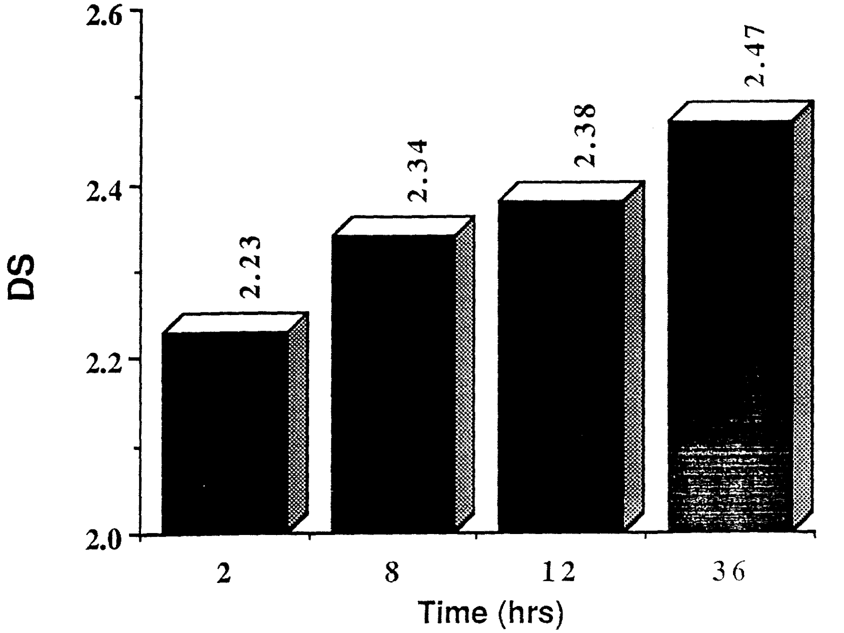


Fig.2 The relationship of DS and acetifying time at sawdust:AC O=1:4

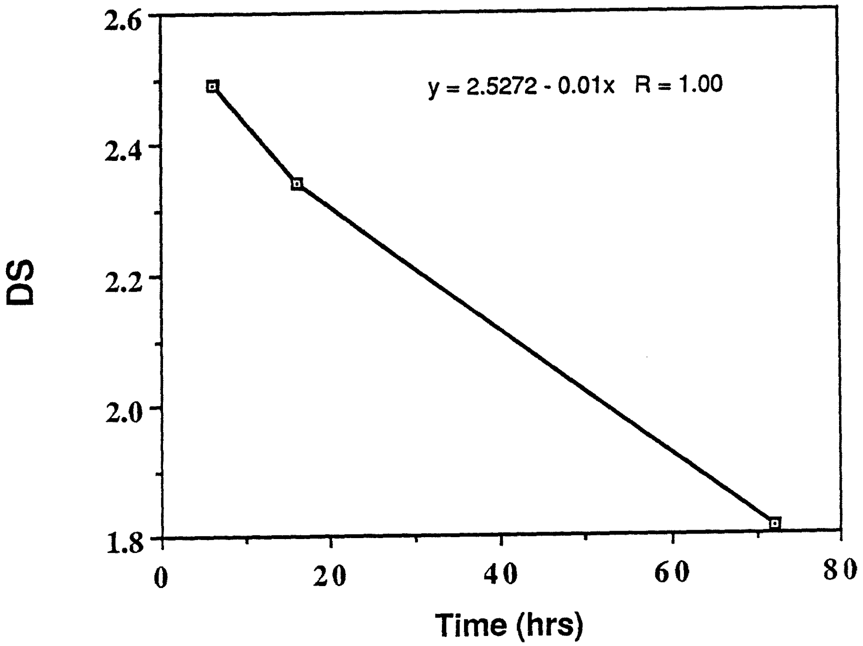


Fig.3 The relationship of DS and hydrolytic time

Table 11 Characteristics of cellulose acetate

Source	Cell-OH / HAc (w / v)	Cell-OH / Ac$_2$0 (w / v)	Catalyst / Cell-OH %	Time (hrs) esterifying	Time (hrs) hydrolysis	DS	Intrnsic viscosity	D.P.	MW (x 10^4)	Pre-treatment
sawdust	1:8.0	1:5.0	23	5	-	2.50				SC*- 3 **
〃	1:6.0	1:4.0	18	5	3	2.46				
〃	〃	〃	3	8	16	2.44				
〃	〃	〃	7	6	6	2.47				
〃	1:10.5	1:2.5	7	10	12	2.13				
〃	1:7.2	1:4.8	10	8	12	2.53				
〃	1:12	1:3.0	10	8	15	2.07				
〃	〃	〃	〃	〃	65	1.59				
〃	1:10	1:4.0	7	2	16	2.23	1.871	311.7	7.97	
〃	〃	〃	〃	8	6	2.49	1.402	220.5	5.88	
〃	〃	〃	〃	〃	16	2.34	1.589	256.3	6.67	
〃	〃	〃	〃	〃	72	1.81	1.683	274.5	5.13	
〃	〃	〃	〃	12	16	2.38	1.699	277.7	7.27	
〃	〃	〃	〃	36	〃	2.47	1.362	213.0	5.66	
〃	1:10	1:2.5	7	2	16	2.13				
〃	〃	〃	〃	8	〃	2.24				
〃	1:20	1:4.0	7	8	16	2.10	1.894	316.4	7.92	
〃	1:10	1:4.0	7	8	16	2.24	1.555	249.7	6.39	
〃	〃	〃	〃	8	16	2.17	1.796	296.8	7.51	
〃 (T) ***	1:10	1:4.0	7	8	16	2.14	1.307	202.7	5.11	
〃 (B) ***	〃	〃	〃	〃	16	2.07	1.186	180.4	4.49	
Poplar	1:10	1:8	7	24	16	1.79	-	-	-	untreated
〃	1:10	1:4	7	11	15	2.26	1.496	238.4	6.12	SC- 3
〃	〃	〃	〃	〃	〃	2.28	1.378	216.0	5.57	@1, SC-3
〃	〃	〃	〃	10	12	2.34	1.120	168.4	4.38	@2, SC-3
〃	〃	〃	〃	〃	〃	2.31	0.976	134.0	3.47	@3 ,SC-3
〃	1:8	1:4	〃	4	2	2.40	0.827	117.0	3.07	@3 ,SC-3
〃	〃	〃	〃	〃	〃	2.46	0.747	103.6	2.75	〃
〃	〃	〃	〃	〃	〃	2.59	0.960	140.0	3.79	〃
〃	〃	〃	〃	〃	〃	2.45	1.036	153.4	4.06	@3,SC-2**
〃	〃	〃	〃	〃	〃	2.46	1.290	199.6	5.30	@3 ,SC-3

* SC means sodilum chlorite ($NaClO_2$).

** The number means used $NaClO_2$ twice and three timesduring bleaching processes.

*** T or B means top or buttom products after centrifugation,respectively.

@1 means H_2O autoclaved befoer treated with $NaClO_2$.

@2 means 1N H_2SO_4 autoclaved before treated with $NaClO_2$.

@3 means 3%H_2O_2 -15%NaOH(1:20) autoclaved before treated with $NaClO_2$.

Table 12 Characteristics of cellulose acetate butyrate and cellulose acetate propionate

Species	Source	HAc	Cell-OH / HBt (HPr)	(w/v) BtO$_2$(Pr$_2$O)	Time(hrs) esterifying	acetyl	Content butyryl	(%) propionyl	Intrinsic viscosity	D.P.	MW ($\times 10^4$)	Pre-treatment
Cellulose acetate butyrate (CAB)	Sawdust	1:3.0	-	1:11.5	20.0	19.62	33.97		0.505	45.5	1.59	SC *-3**
	Poplar	1:3.5	-	1:10.0	7.5	20.59	29.40		0.835	82.4	2.77	@3,SC-3
	〃	1:1.5	1:5.5	1: 5.0	6.0	24.72	14.21		0.796	77.9	2.40	〃
	〃	1:2.5	1:4.5	1: 5.5	9.0	15.51	32.18		0.793	77.6	2.42	〃
	〃	1:2.5	1:4.5	1: 5.5	7.0	18.36	26.32		1.089	112.8	3.52	@3,SC-2
	〃	1:1.5	1:5.0	1: 5.0	8.0	13.41	33.51		0.631	59.2	1.88	〃
	〃	1:1.5	1:6.0	1: 5.5	8.0	8.92	37.56					〃
	〃	〃	〃	〃	12.0	5.63	44.14					〃
	〃	〃	〃	〃	24.0	6.63	44.84					〃
Cellulose acetate propionat (CAP)	sawdust	1:2.0	-	1:12	10.0				1.079	111.5	3.52	SC-3
	〃	1:3.0	-	1:11	6.0				2.434	281.7	8.90	〃
	〃	1:3.0	-	1:11	6.0	20.16		21.73	1.384	148.0	4.25	〃
	poplar	1:1.5	1:5.5	1:5.0	6.0	15.41		30.09	0.965	98.1	2.96	@3,SC-3
	〃	〃	〃	〃	6.0	16.61		26.38	0.886	89.0	2.60	@3,SC-2
	〃	1:1.5	1:6.0	1:5.0	9.0	12.34		31.34	0.862	86.3	2.55	〃
	〃	1:1.5	1:6.0	1:5.0	8.0	1.92		42.60				〃
	〃	〃	〃	〃	12.0	2.65		42.86				〃
	〃	〃	〃	〃	24.0	1.56		44.77				〃

* SC means sodilum chlorite ($NaClO_2$).

** The number means used $NaClO_2$ twice and three times during bleaching processes.

@3 means 3%H $_2O_2$-15%NaOH (1:20) autoclaved beforetreated with $NaClO_2$.

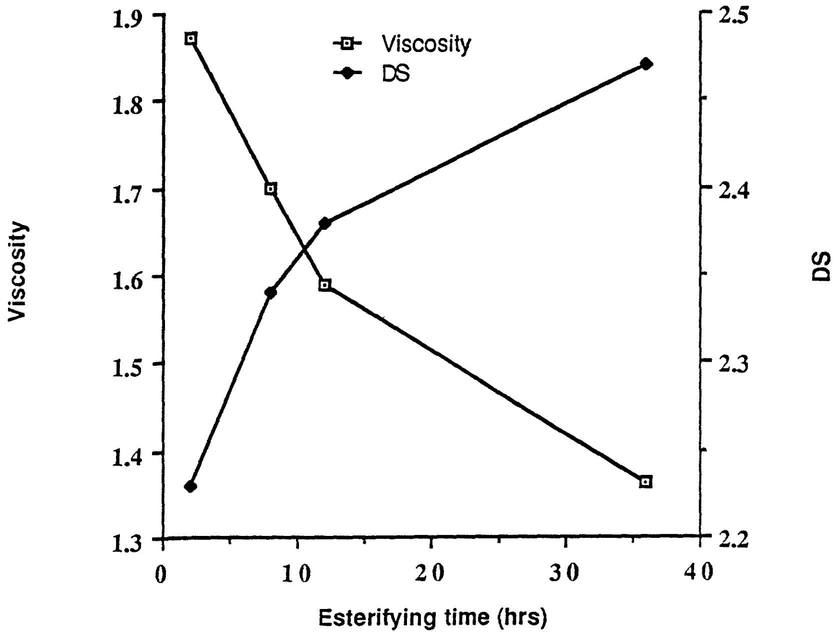


Fig.4 The relationship of intrinsic viscosity, esterifying time and DS

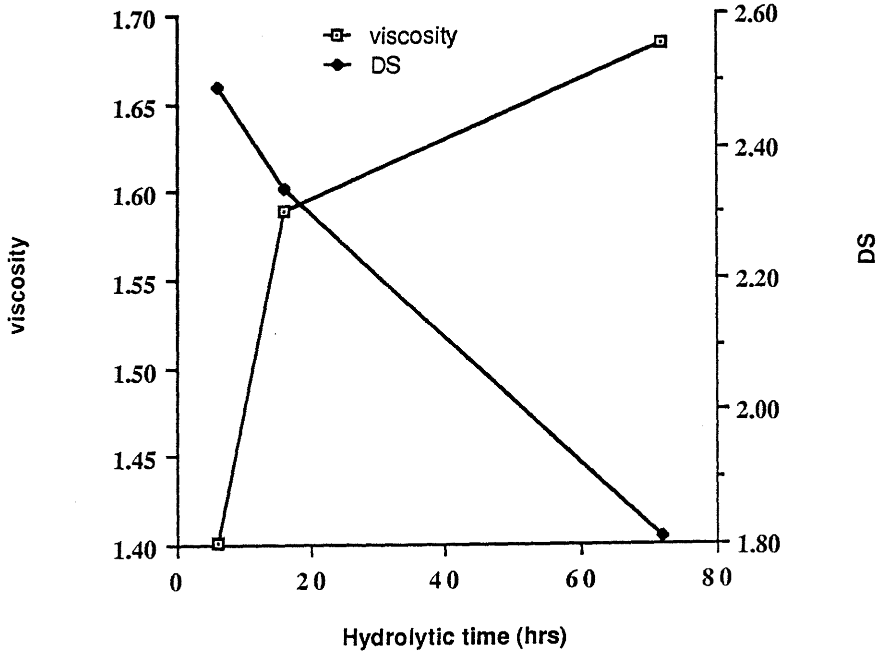


Fig.5 The relationship of intrinsic viscosity, hydrolytic time and DS

Table 13 **Flexibility and stability of plasticizers in CAB and CAP film**

plasticizer		Dietyl phthalate (b.p= 298^{o}C)					Acetyl triethyl citrate (b.p= 294^{o}C)				
by esters	%(w/w)	10	20	30	40	50	10	20	30	40	50
CAB	flexibility	MS	S	S	VS	ES	MS	S	S	VS	ES
	stability	-	-	-	-	+	-	-	-	+	++
CAP	flexibility	MS	MS	S	S	VS	MS	MS	S	S	VS
	stability	-	-	-	-	-	-	-	-	-	+

MS, S, VS & ES means flexibility from medium soft to extremely soft.
MS = medium soft.
S = soft.
VS = very soft.
ES = extremely soft.
\+ means plasticizer has volatilized slightly.
++ means plasticizer has volatilized intermediately.

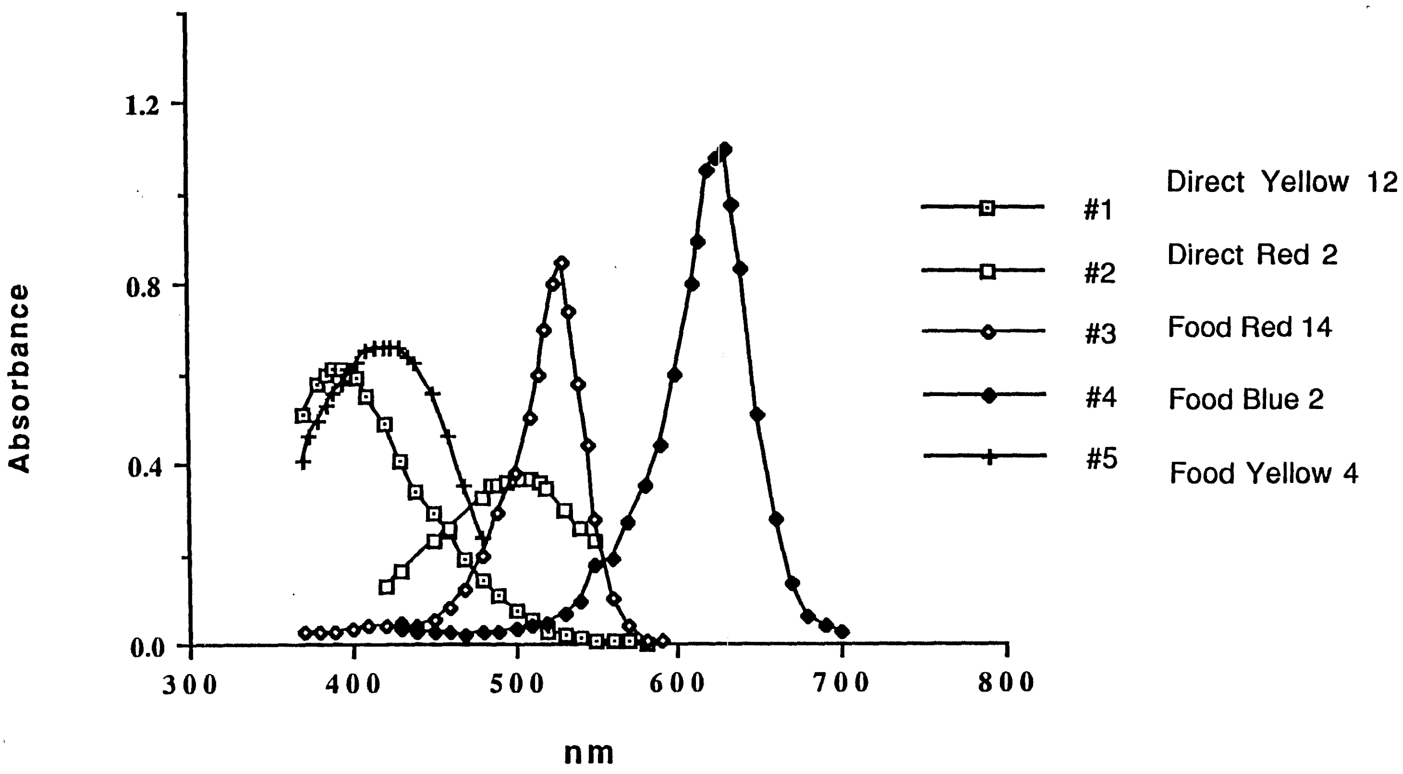


Fig.28 Absorption Curve of Five Kinds of Colorant

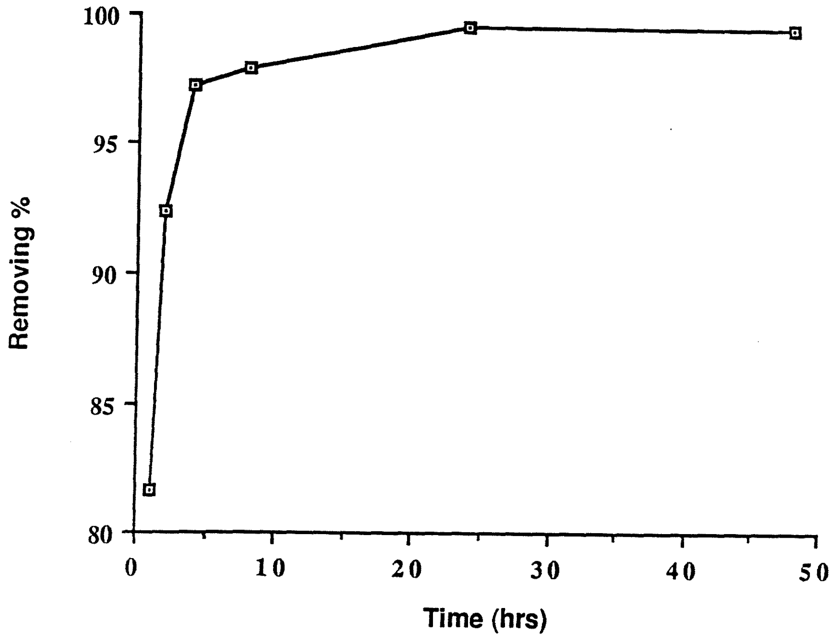
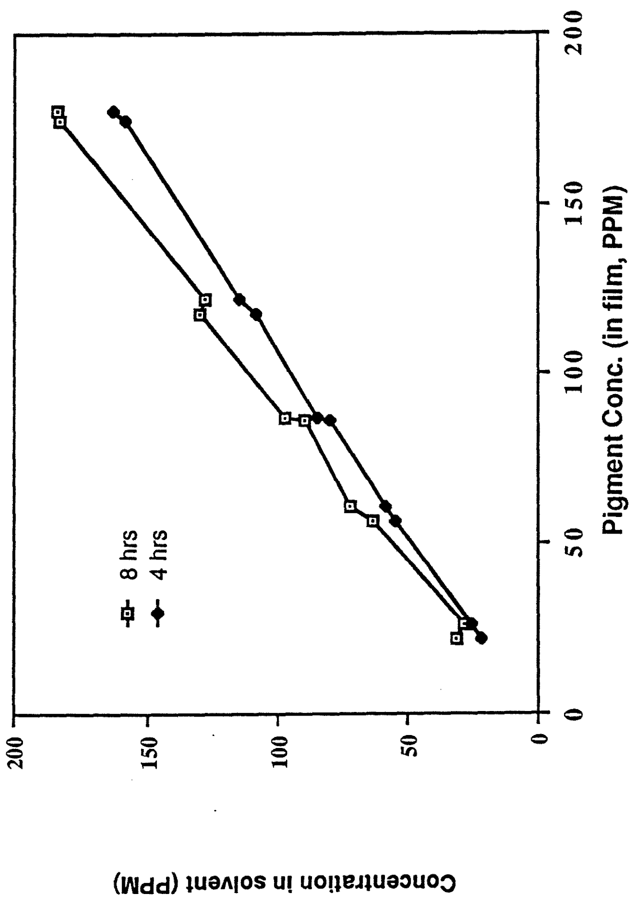


Fig.6 The Removing Rate of Erythrosin B From CA Film



y=2.7298+0.9025x R=1.00 (4 hrs) y=2.7960+0.9232x R=1.00 (8 hrs)

Fig.7 Extractability of pigment(in the film) in solvent(methanol)

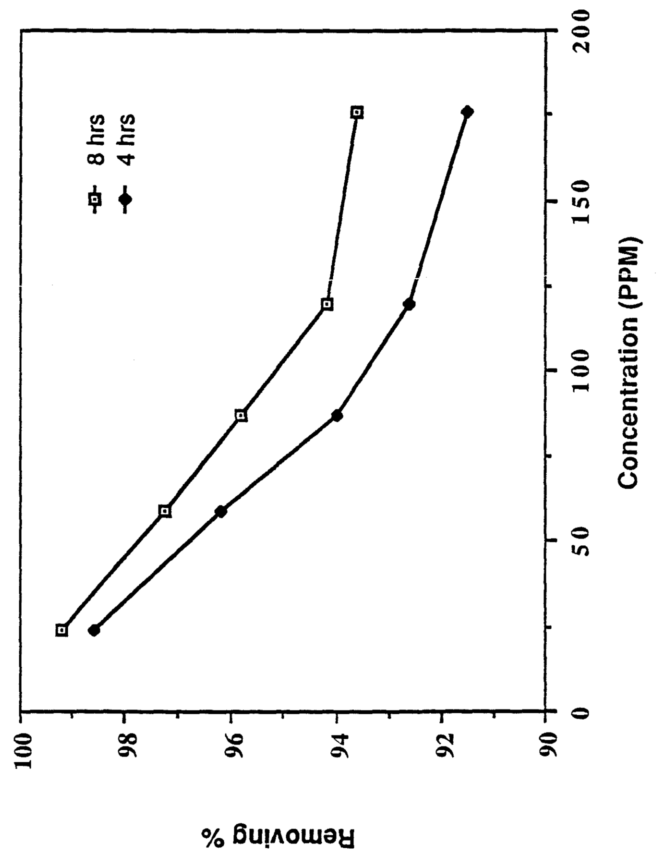


Fig.8 The Removing Rate of Erythrosin B from CA Film at various pigment Concentrations

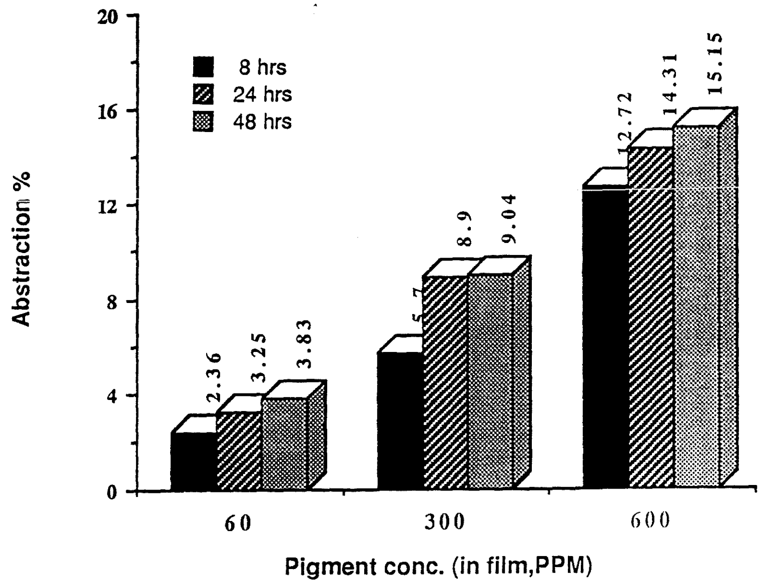


Fig.9 The Abstraction Rate of Erythrosin B in Water

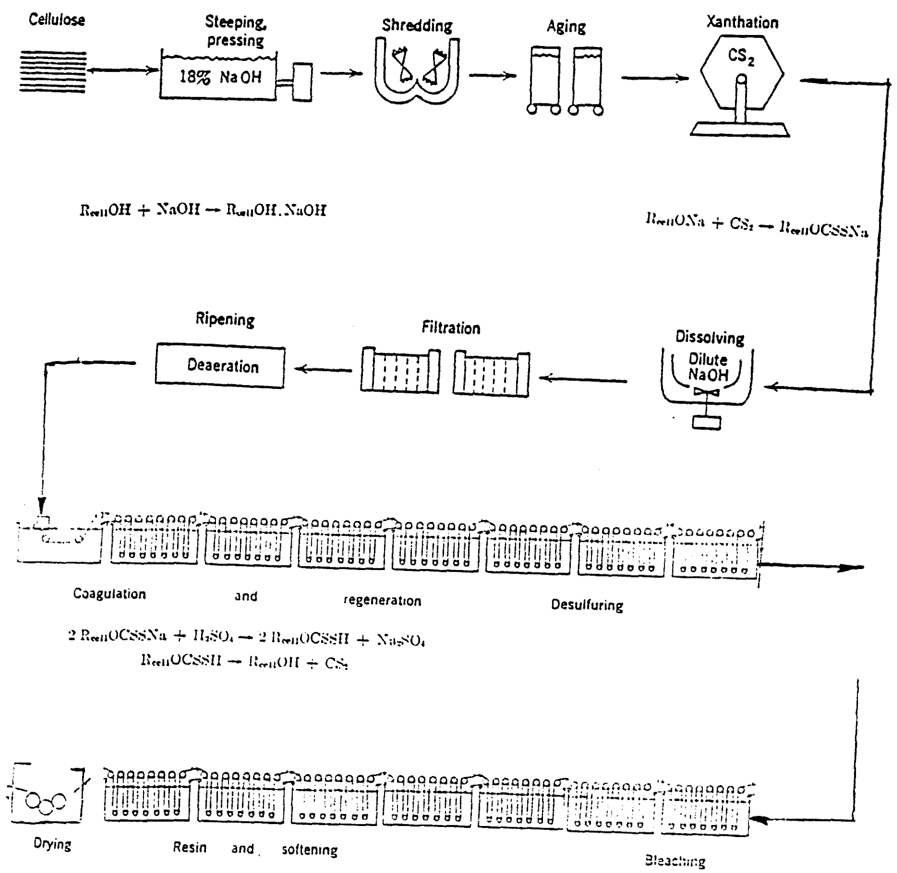


Fig.11 Viscose Process Flow Diagrame for Cellophane Production

Table 14. Grafting methyl aerylate on holocellulose at 40°C using 3.0 mmol of Ce(IV).

Cellulose Source	Monomer Concentration (mmol/g cellulose)	Conversion (%)	Homopolymer Fomed (%)	Efficiency of grafting (%)
Paper towel	21.74	79.12	5.49	90.84
Sawdust	23.01	68.40	10.96	81.03
Poplar	20.97	81.25	16.63	72.15

Table 18 Tensile Strength of Cellulosic and Commercial Plastic Films

(N / mm^2)

Film Material	CA	CAB	CAP	MA/CAP	Cellophane Thickness	Cellophane Vertically	Cellophane Horizontally	SB	GB	FB
Poplar	27.6	10.8	16.0	39.0	Thin	164.8	130.7	20.0 Vertically	12.4 Vertically	25.0 Vertically
Sawdust	38.2	22.4	5.8	25.5	Madium	104.8	55.8			
Paper Towel	34.8	16.7	19.4	23.0	Thick	64.9	46.0	26.5 Horizontally	18.8 Horizontally	39.0 Horizontally
Range*	49.2 ~ 115.3	35.2 ~ 63.3	28.1 ~ 35.2*		49.2 ~ 126.6			10.5 ~ 42.9		

CA : Cellulose acetate

CAB : Cellulose acetate butyrate.

CAP : Cellulose acetate propionate.

MA/CAP : Graft with methyl acrylate + Cellulose acetate propionate.

SB : Sandwich bag (polyethelene).

GB : Garbage bag (30% recycled polyolefins and polyethelenes).

FB : Food storage bag (polyethelene).

* referred from "GUIDE TO PLASTICS" pp. 175.

Table 19 Tearing Strength & Elongation of Cellulosic and Commercial Plastic Film

	MA/CAP			Cellophane	SB		GB		FB	
	Poplar	Sawdust	Paper Towel		V	H	V	H	V	H
Tearinh Strength (g / mil)	1.22	0.65	1.04	1.43~2.0	92.5	55.0	70.6	63.5	110	70.0
Elongation (%)	30.0	13.3	35.0	18.3~31.7	675	250	613	563	1400	550

MA/CAP : Graft with methyl acrylate + Cellulose acetate propionate

SB : Sandwich bag (polyethelene)

GB : Garbage bag (30% recycled polyolefins and polyethelenes).

FB : Food Storage bag (polyethelene)

V : Vertically

H : Horizontally

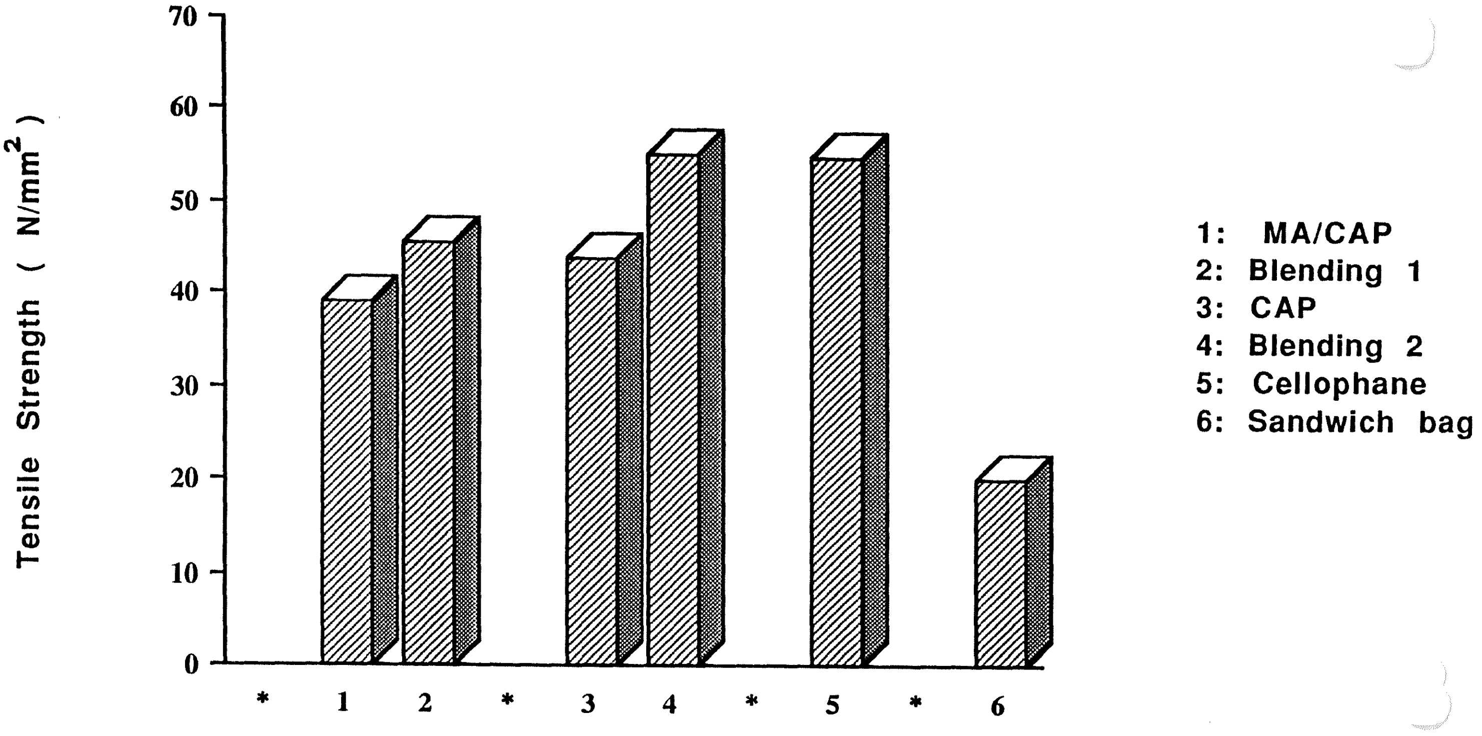


Fig.29 Comparison of Tensile Strength of Some Films

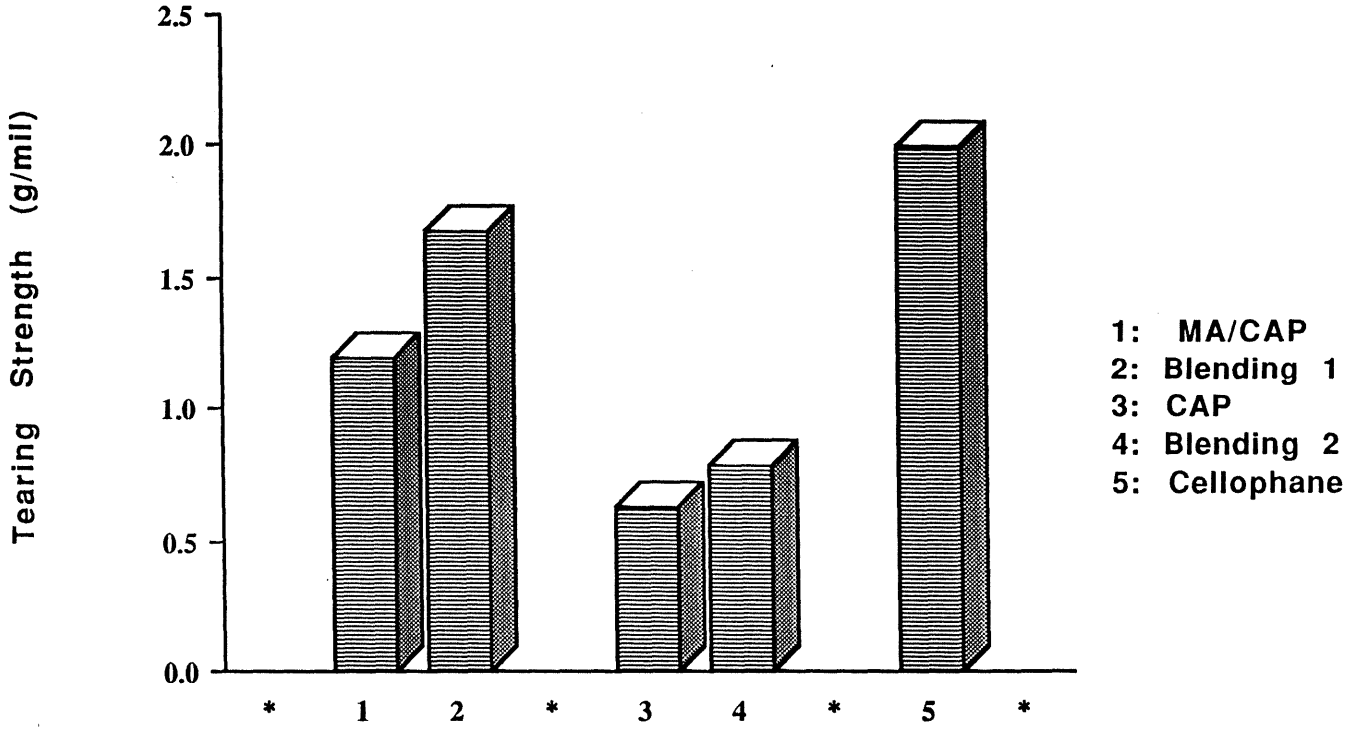


Fig.30 Comparison of Tearing Strength of Cellulosic Films

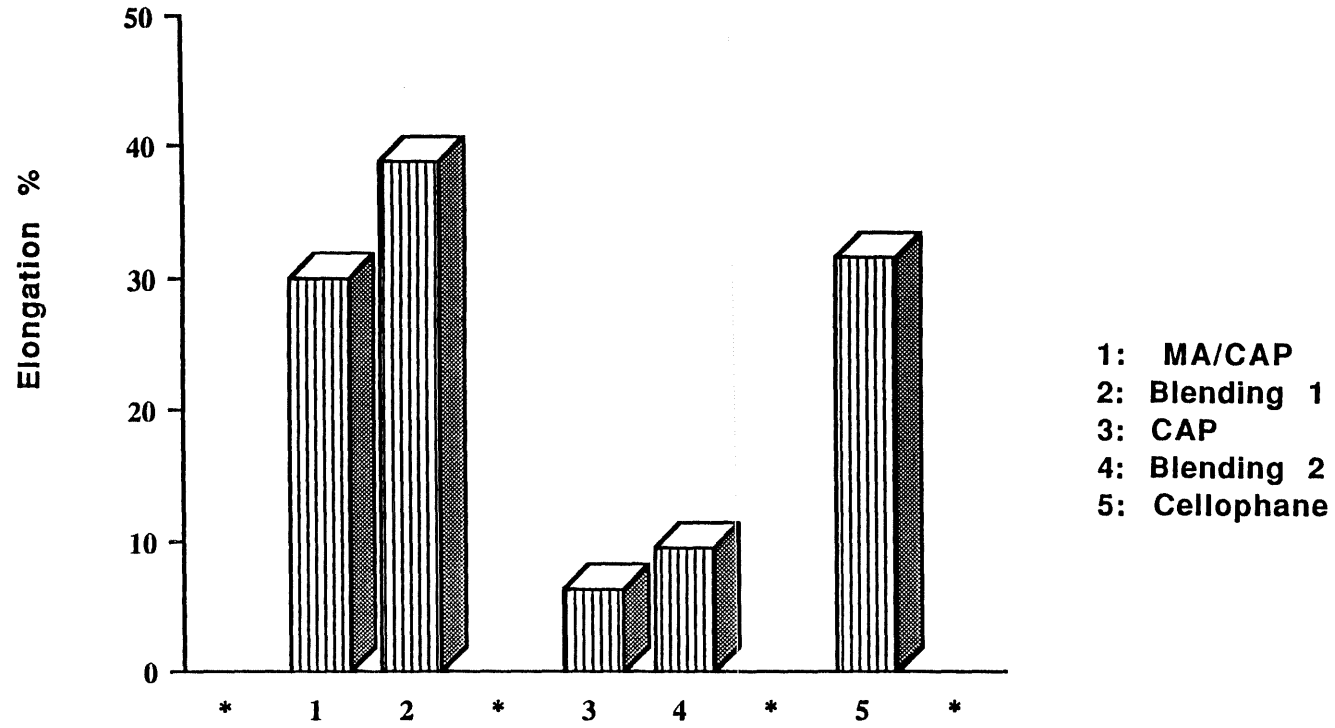


Fig.31 Comparison of Elongation of Cellulosic Films

Table 20 The Effect of Some Environmental Factors on Viscosity of MA/CAP Film (Sawdust)

	CK	A		B		C		D		E		F	G
		4 h	24 h	4 h	24 h	4 h	24 h	4 h	24 h	3 min.	10min.	15min.	2 h
Viscosity	1.1301	1.0741	0.9819	1.1279	1.1307	1.1541	1.1320	1.1357	1.1568	1.1433	1.1829	1.2096	1.1618
LSD		0.0560	0.1482**	0.0022	0.0060	0.0240	0.0019	0.0056	0.0267	0.0132	0.0528	0.7950*	0.0317
LSR (0.05)	AB	B	C	AB	AB	AB	AB	AB	A	AB	A	A	A
LSR (0.01)	AB	BC	C	AB	AB	AB	AB	AB	AB	AB	A	A	AB

A: Uv Exposed.
B: Freezen.
C: Immersied in water (20 °C).
D: Oven dried (50 °C).
E: Microwave oven.
F: Autoclaved.
G: Boiling water.

** means a very significant difference at 99% confidence interval.

* means a significant difference at 95% confidence interval.

Table 21 Variance Analysis of Viscosity Affected by Environmental Factors

Source	df	SS	MS	F	F 0.05	F 0.01
Within	3	0.0060	0.0020	0.856	2.86	4.38
Among	12	0.1466	0.0122	5.230	2.03	2.72
Error	36	0.0841	0.0023			
Total	51	0.2367				

df: The degree of freedom.

SS: Sum of squares or numerator of the variability.

MS: Mean Squares.

F: F Statistic.

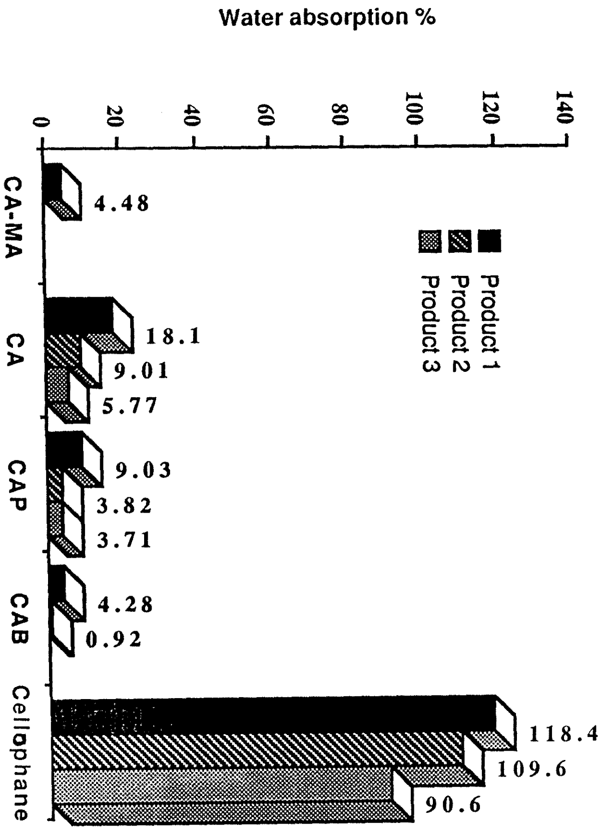


Fig.10 Water absorption capacity

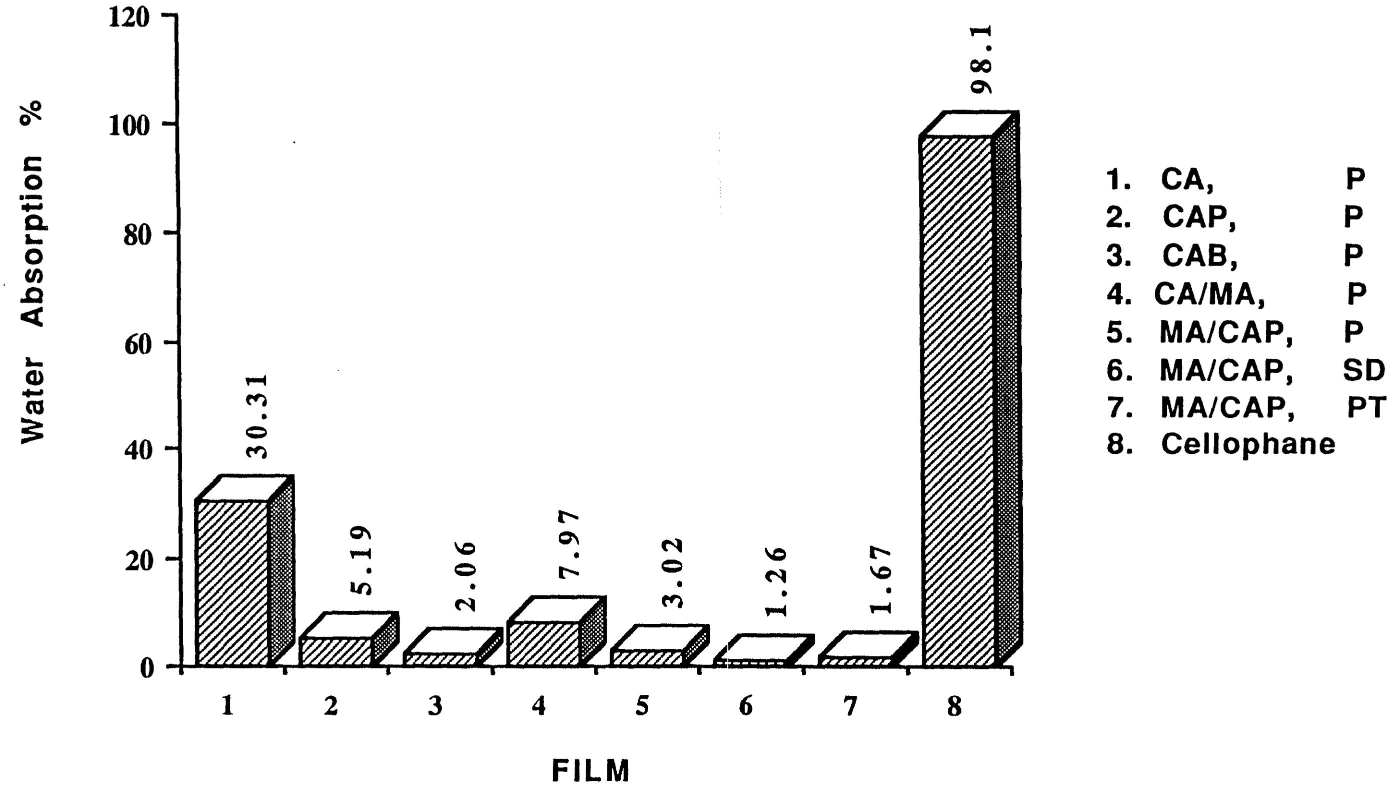


Fig.32 Water Absorption Capacity of Cellulosic Films
(24h, 50℃)

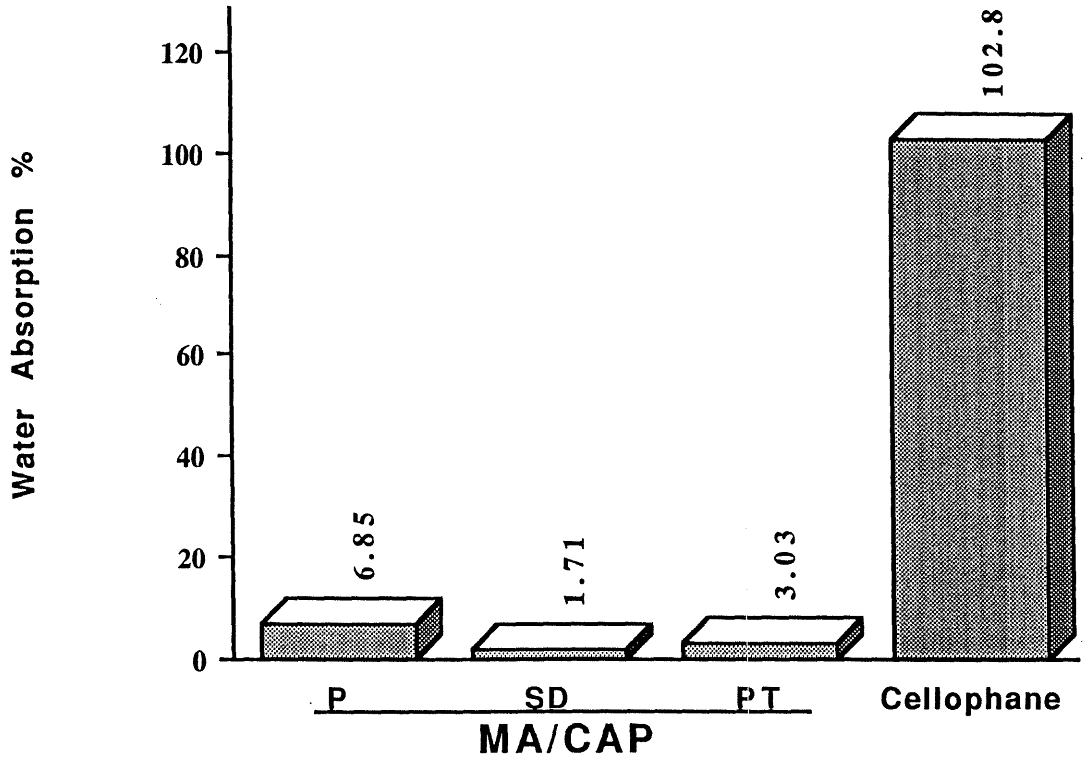


Fig.33 Water Absorption Capacity of Cellulosic Films

(2h, boiling water)

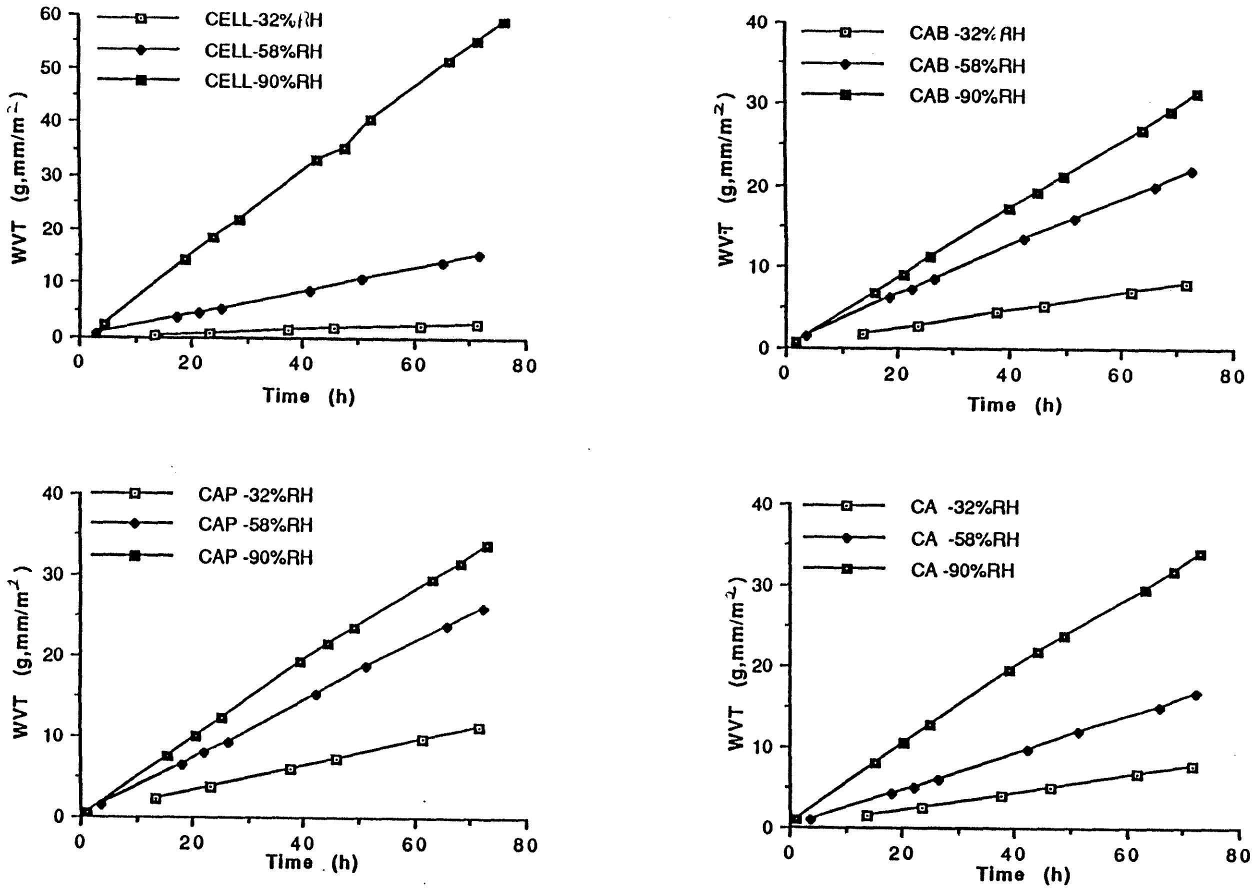


Fig.12 Water vapour transmission through cellulosic (Poplar) films at different humidities

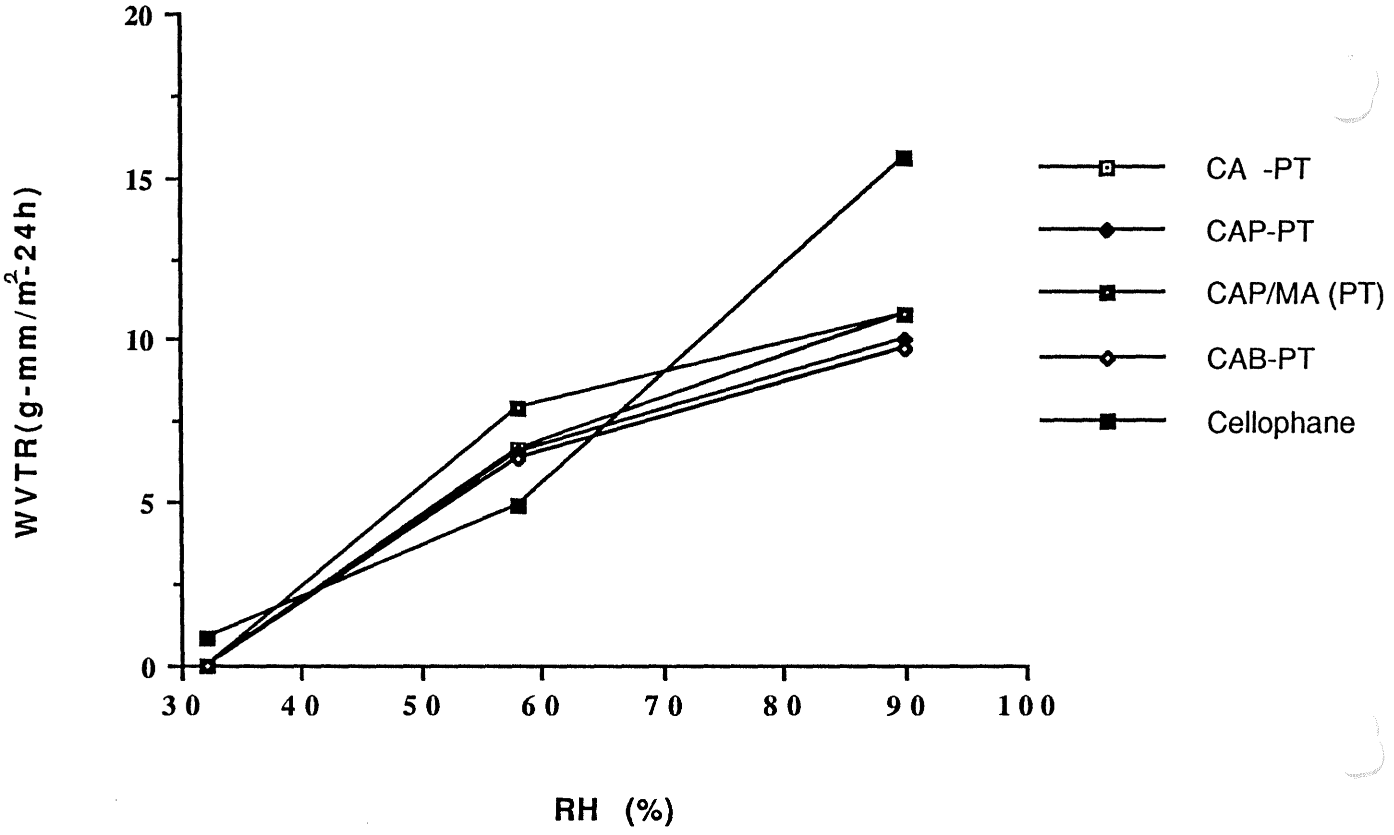


Fig.13 The Relationship of WVTR (Paper Towel) with Relative Humidities (RH,%)

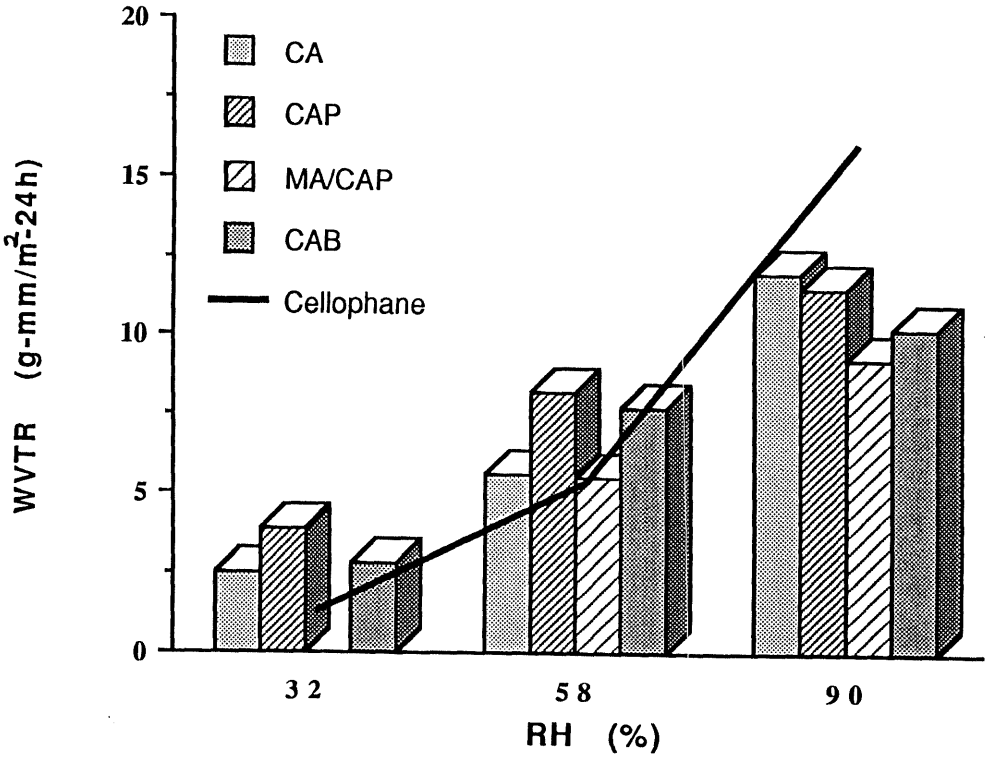


Fig.14 Water Vapour Transmission Rate of Cellulosic Film (Poplar) at Three Relative Humidities

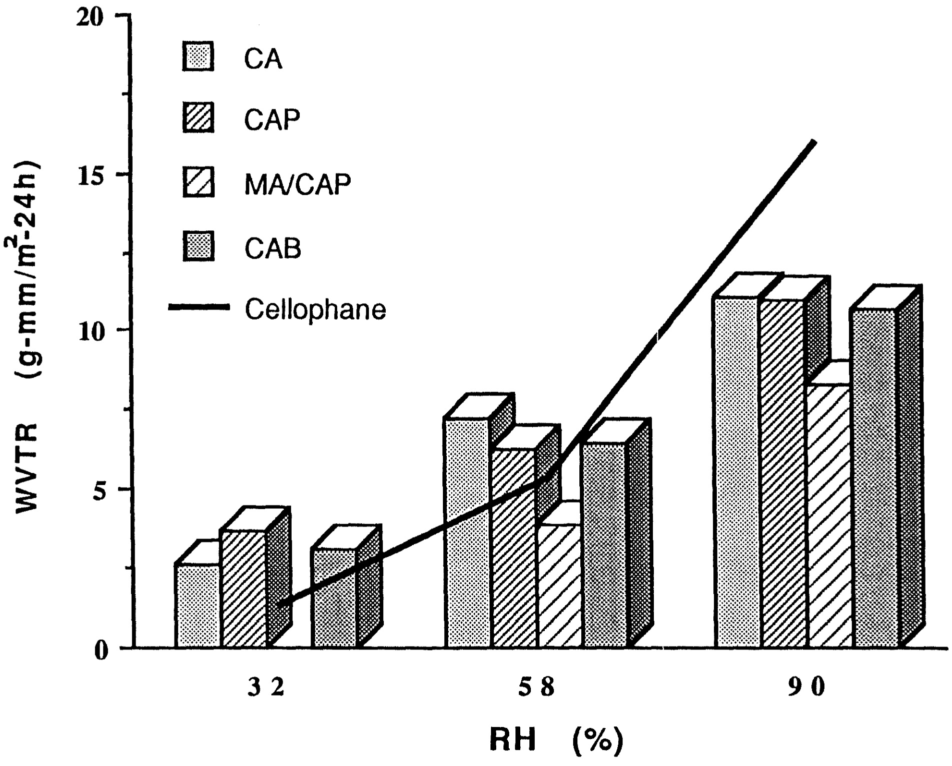


Fig.15 Water Vapour Transmission Rate of Cellulosic Film (Sawdust) at Three Relative Humidities

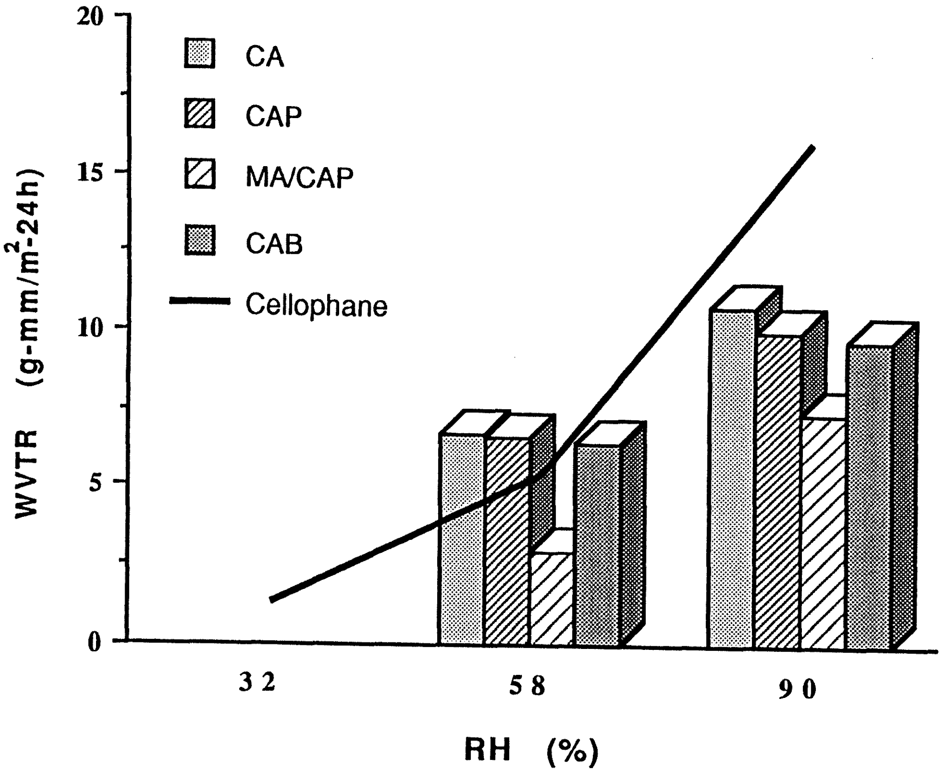


Fig.16 Water Vapour Transmission Rate of Cellulosic Film (Paper Towel) at Three Relative Humidities

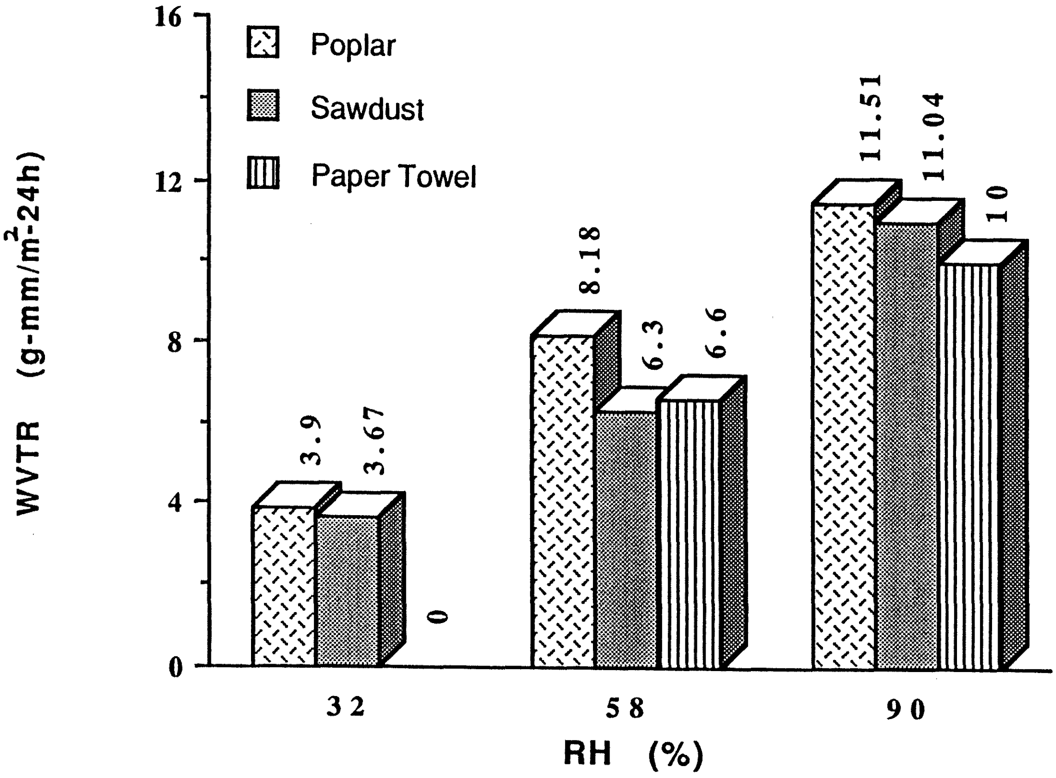


Fig.34 WVTR of CAP Films Made from Three Kinds of Material at Three Relative Humidities

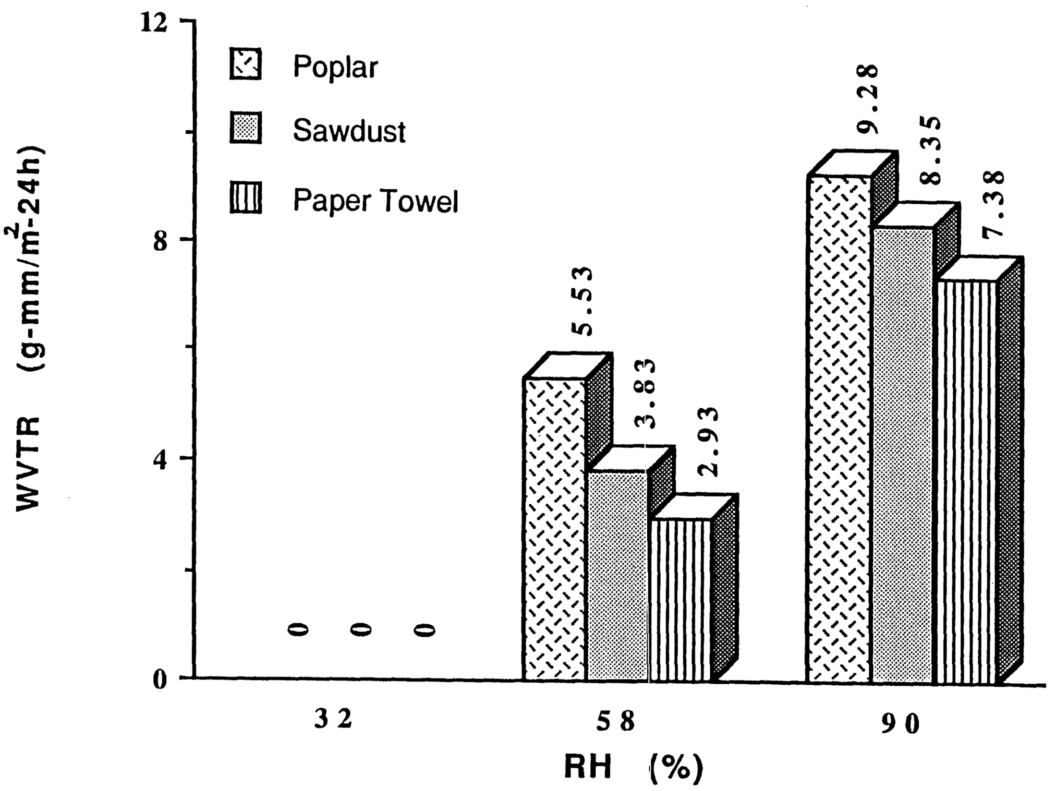


Fig.35 WVTR of MA/CAP Films Made from Three Kinds of Raw Material at Two Relative Humidities

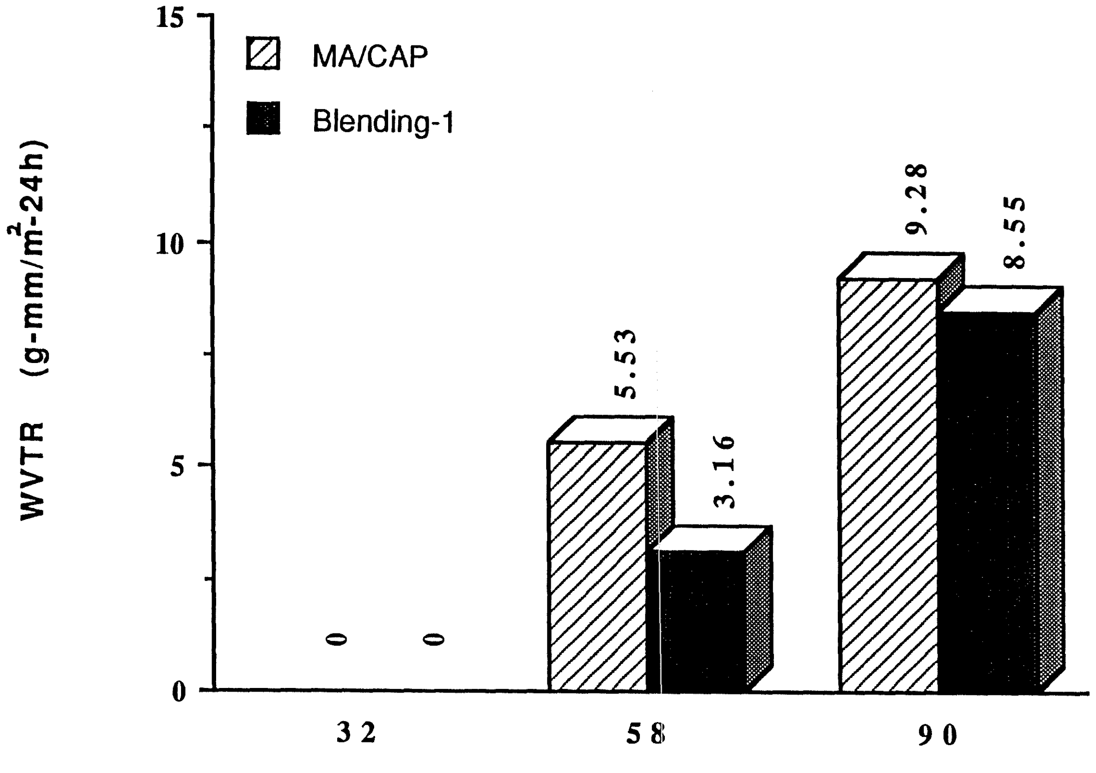


Fig.36 Comparison of WVTR of MA/CAP (Poplar) Film with MA/CAP Blanded Copolymer Film

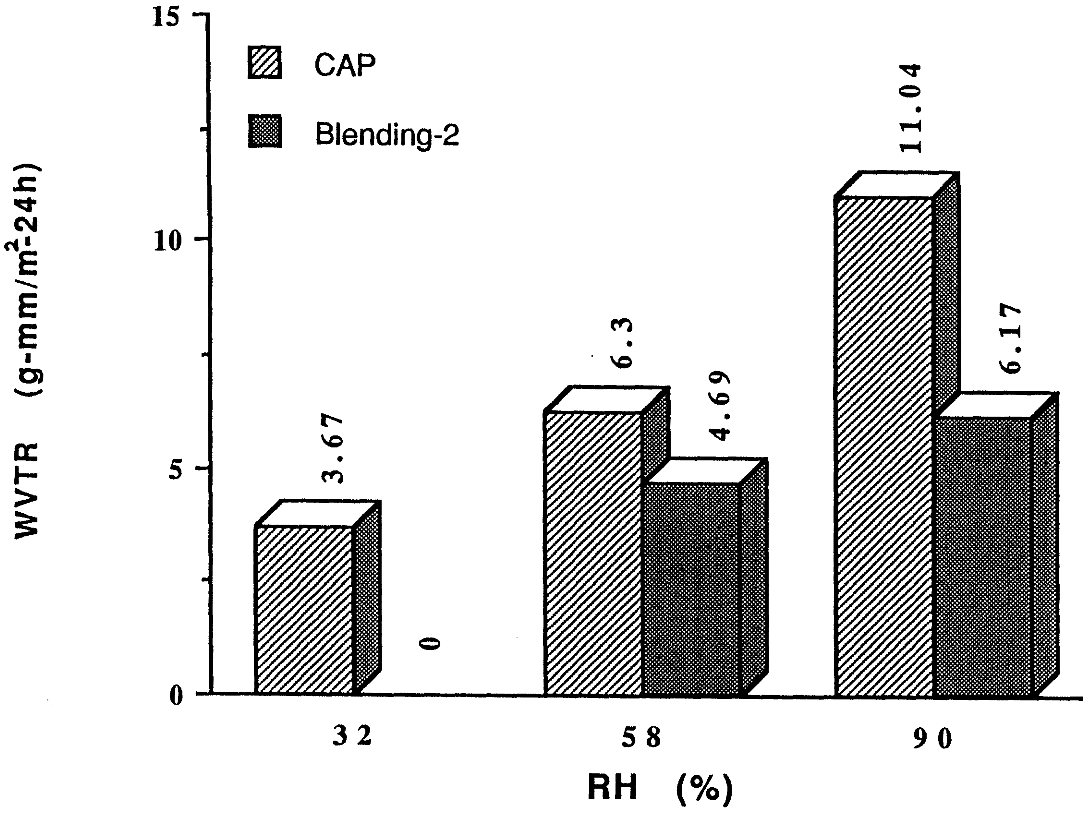


Fig.37 Comparison of WVTR of CAP (Sawdust) Film with CAP Blanded Homopolymer Film

Table 15. Water Retention Capacity of Cellulosic Un- and Grafts (g/g).

	CA	CAP	CAP/MA	CAB
Paper towel	2.24	2.48	1.88	2.56
Sawdust	2.28	2.65	2.47	2.14
Poplar	2.04	2.74	1.70	-----

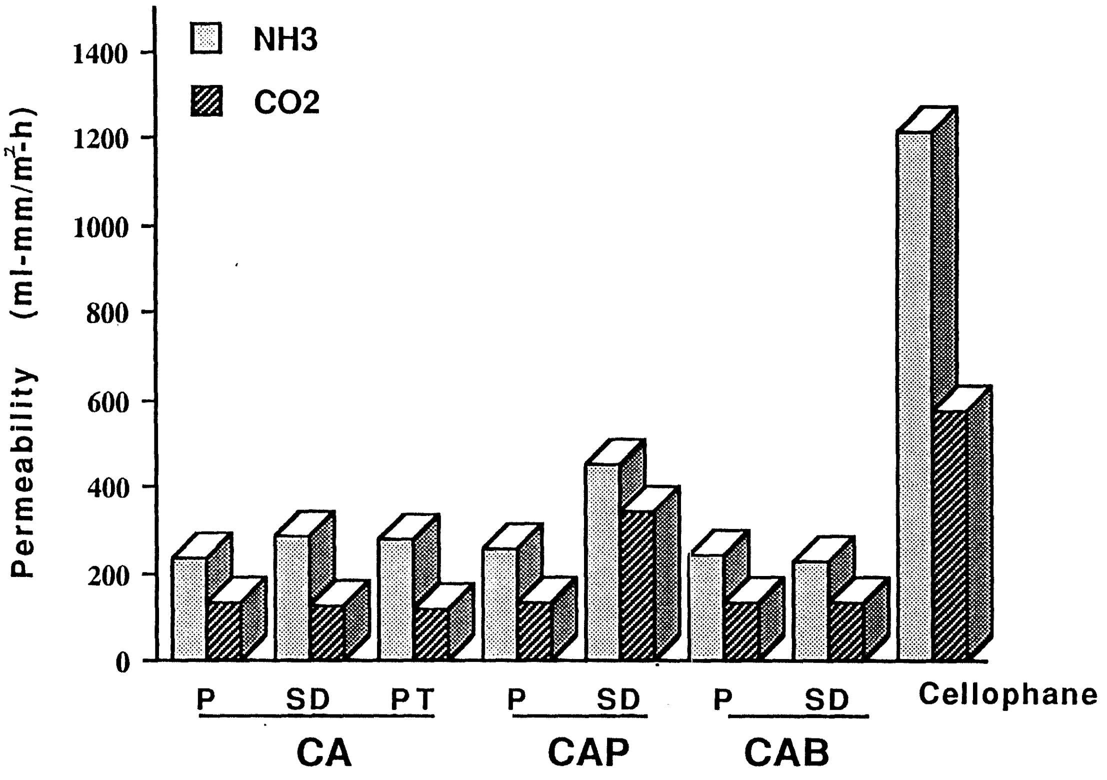


Fig.17 Permeability of Some Cellulosic Films to Gases (P=Poplar, SD=Sawdust, PT=Paper Towel)

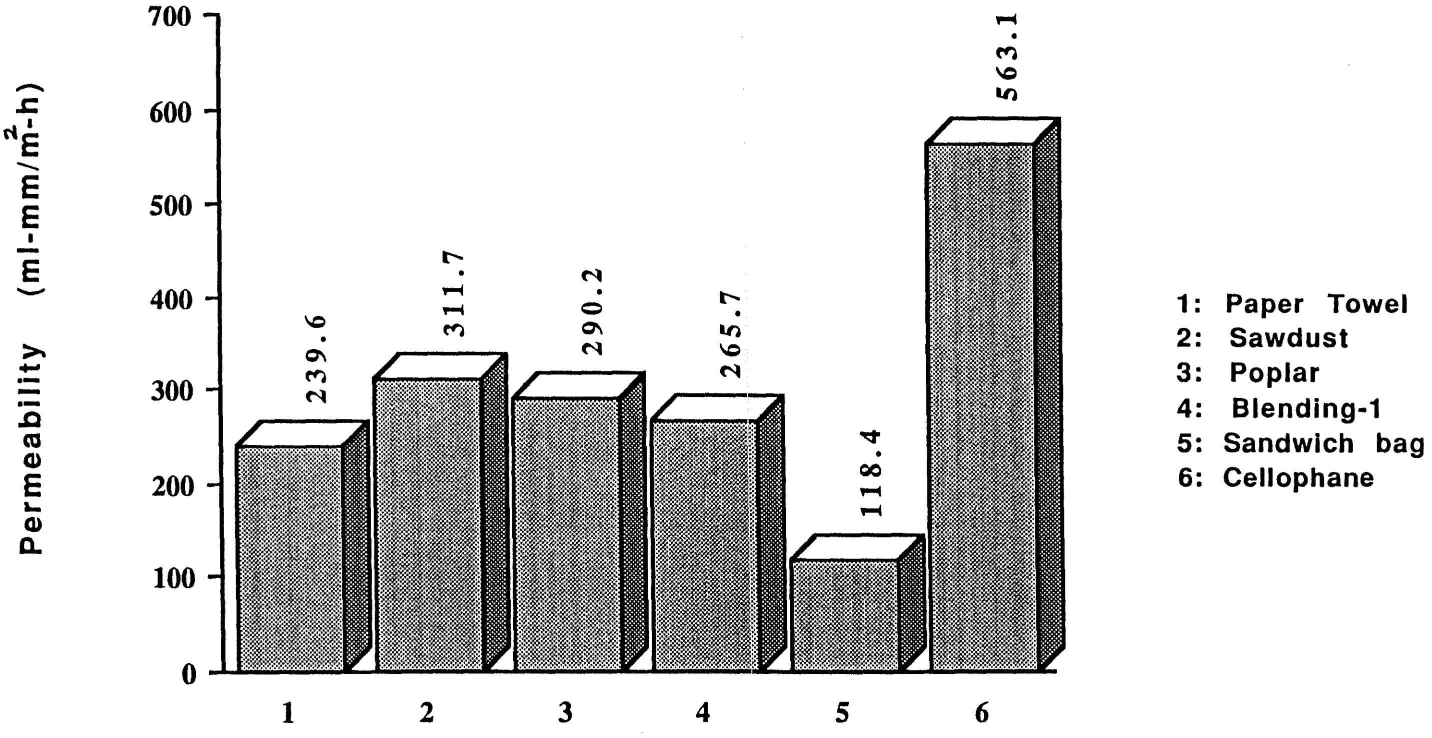


Fig.38 Permeability of MA/CAP Films Compared with Commercial Plastic to Carbon Dioxide

Table 16 Clarity of Some Cellulosic Films

(PPM/thickness)

Source	CA	CAP	CAB	CAP/MA	Cellophane
Poplar	65.0	32.5	46.0	69.5	59.5
Sawdust	114.0	55.8	76.3	54.5	
Paper Towel	60.8	65.8	62.3	67.0	

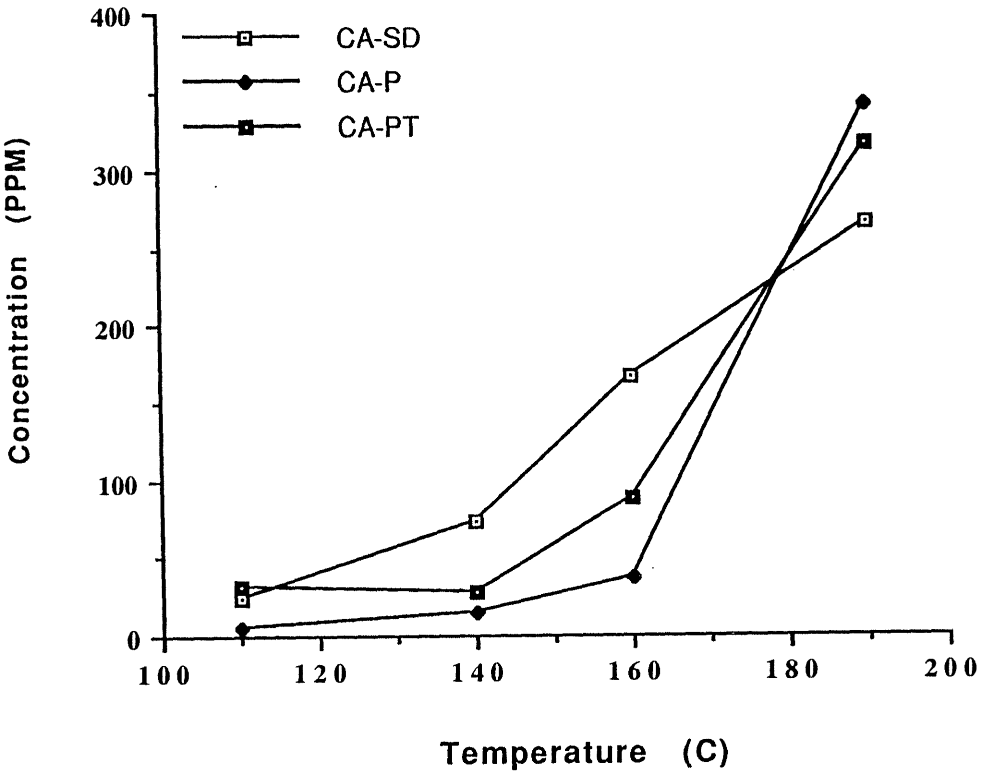


Fig.18 Effect of Temperature on Cellulose Acetate Stability

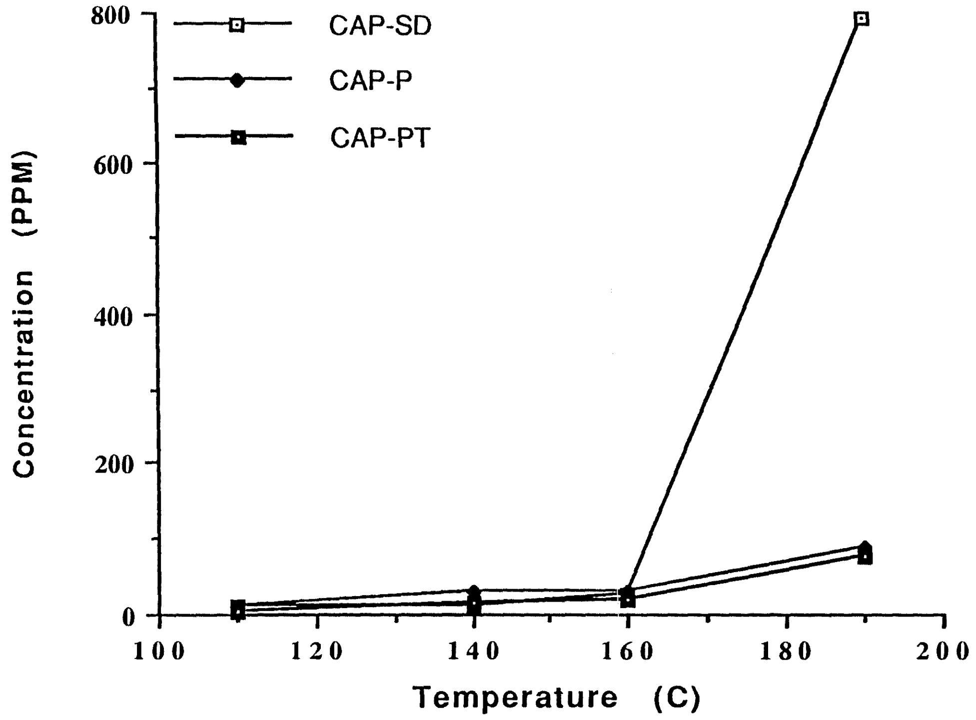


Fig.19 Effect of Temperature on Cellulose Acetate Propionate Stability

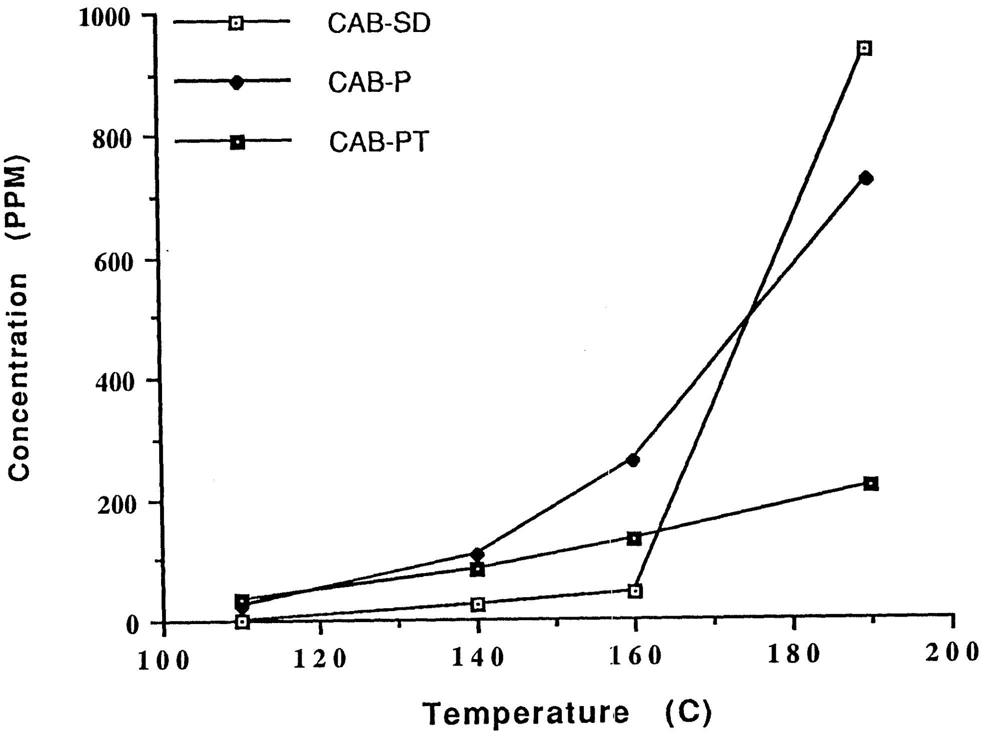


Fig.20 Effect of Temperature on Cellulose Acetate Butyrate Stability

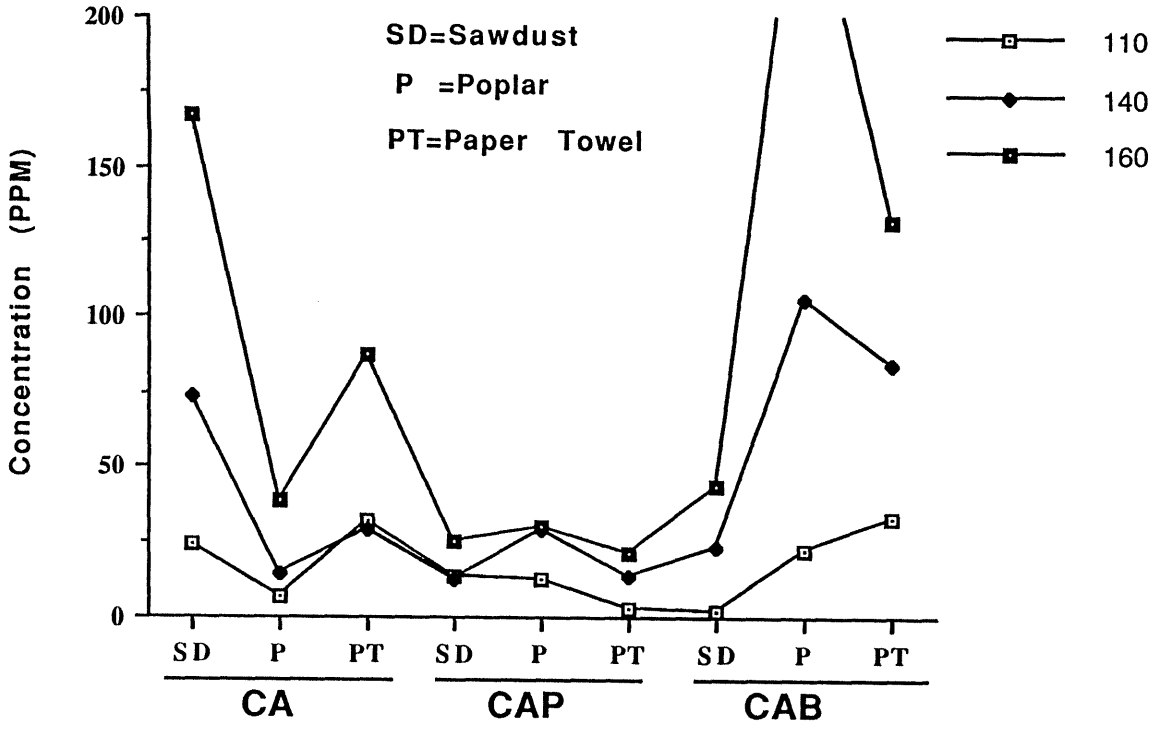


Fig.21 Heat Stability of Cellulosic at three Temperature (°C)

Table17 Temperature of Heat Stability of Cellulosic (°C)

(Clarity=100PPM)

	Sawdust	Poplar	Paper Towel
CA	151.7	172.1	160.9
CAP	166.6	198.4	196.2
CAB	163.4	141.2	152.3

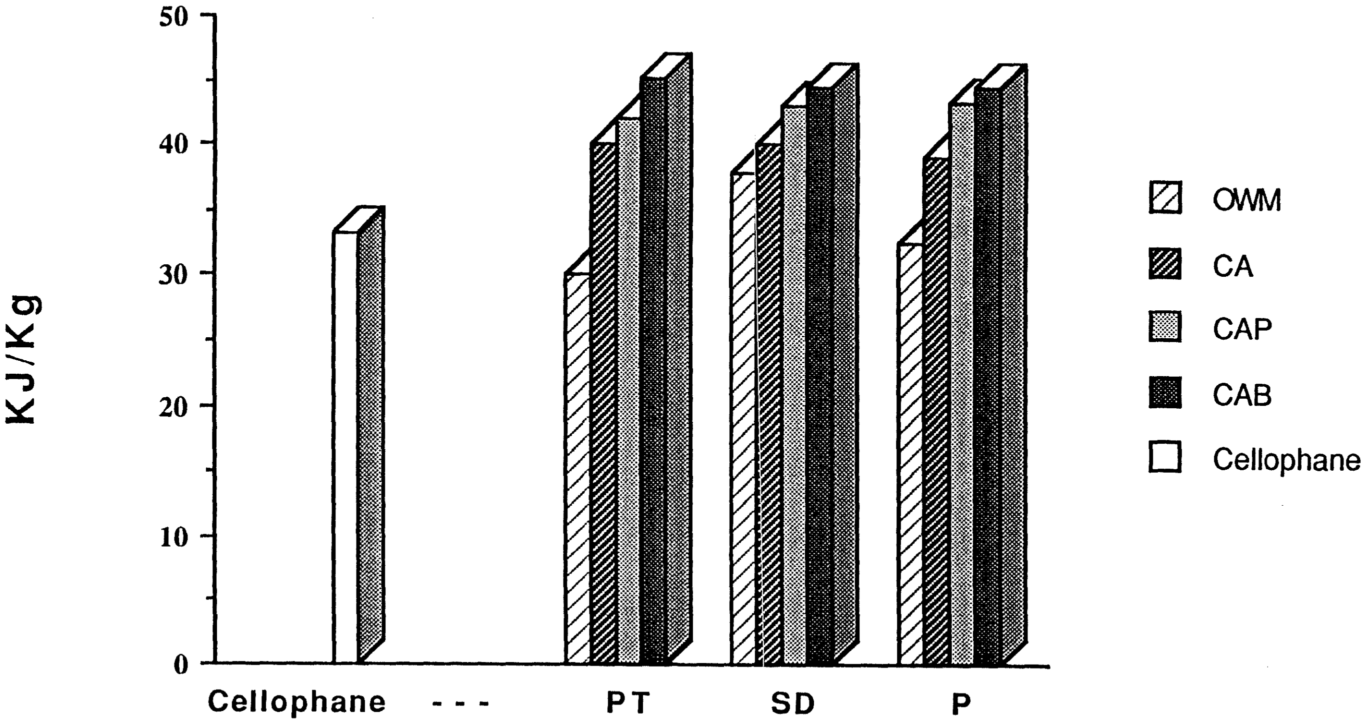


Fig.22 Combustion Energy of Cellulosic Films

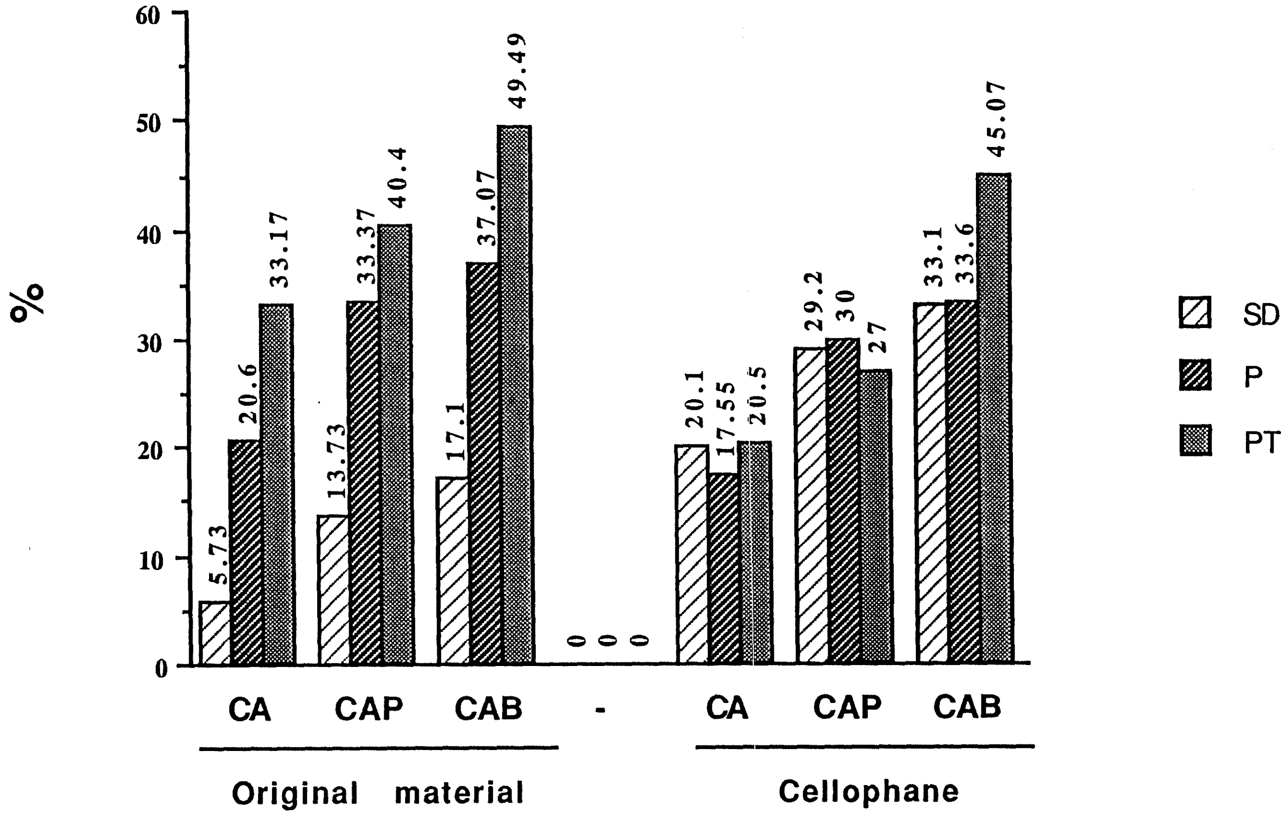


Fig.23 Percentage Increase in Combustion Energy of Three Kinds Cellulosic Film

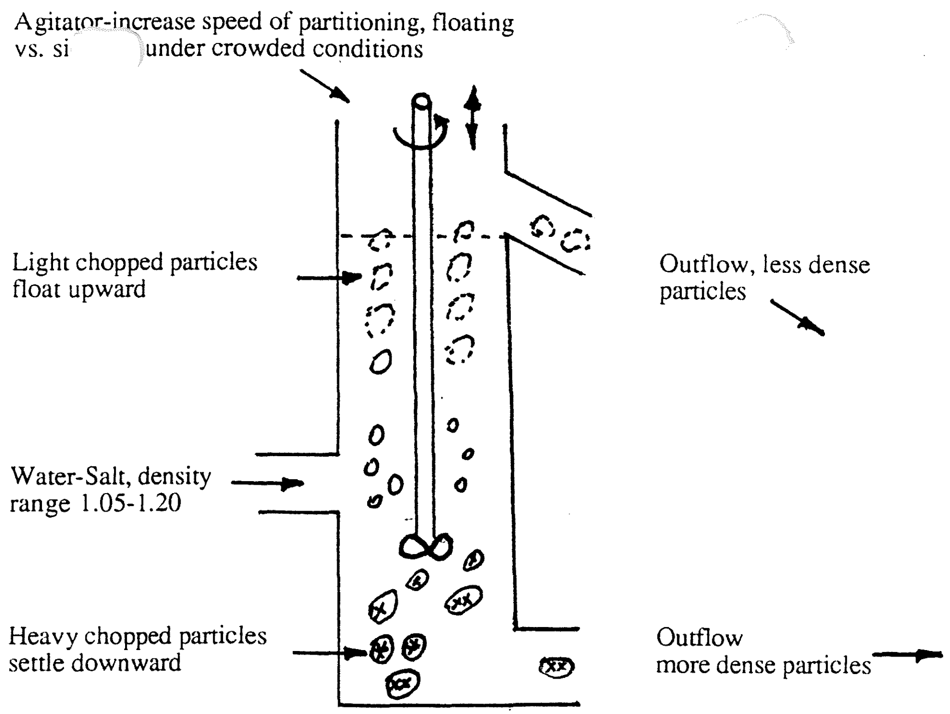


Fig. 46. Apparatus used for the separation of chopped packaging material for recycling

Table 27. Derivatization of recycle cellulosics, characterization in mechanical and thermal properties.

Material	Sample Thickness Range (mils)	Derivatization	Range of Substitution	Softening Temp. (C)	Tensile Strength	Cling*
Green giant Veg. carton cellulose laurinate #1	50-80	Acetylation	10-20%	170-230	1.3-2.0	20%
Green giant laurinate #2	40-80	Acetylation	10-30%	160-250	1.5-2.2	30%
Cardboard box laurinate #1	80-120	Propionate	5-20%	150-220	3.8-4.4	15%
Cardboard box laurinate #2	70-120	Hydroxyprop.	20-30%	190-230	4.6-5.2	30%
Heavy sack Kraft	120	Acetylation	10-20%	240-290	6.2-7.0	10%
Light sack Kraft	70	Butylation	5-15%	180-230	4.3-5.5	20%

*Relative to equivalent thickness of Saran wrap.

Table 28. Physical Characterization of Four Carbons from Packaging Materials, Comparison with a Commercial Sample.

Sample	Particle Size (mm.)	Surface area (m^2/gm)	Pore size(nm)	K_d
Green giant veg. pack	0.5-2.0	320±60	2	14±5
Oatmeal carton	0.4-3.0	480±80	3	18±5
Kraft paper sack (heavy)	0.5-3.4	150±60	5	55±6
Cardboard packing	0.1-0.8	230±80	5	38±8
Commercial activated carbon	2-3	700±100	0.8	180±17

K_d = Molar distribution coefficient of TCA between 50 mL of water solution and 1.0 gm of the carbon.

Pyrolysis conditions: All samples run 350-450°C, 1 hr., nitrogen atmosphere.

Pore size: Approximated by water uptake, apparent surface volume, and particle density factor input to Kelvin-Sing method. (Porous glass particle calibration standard).

Surface area: Approximated by naphthalene-phenanthrene equilibration between standard samples and carbon particles, in monolayer-bilayer coverage region.

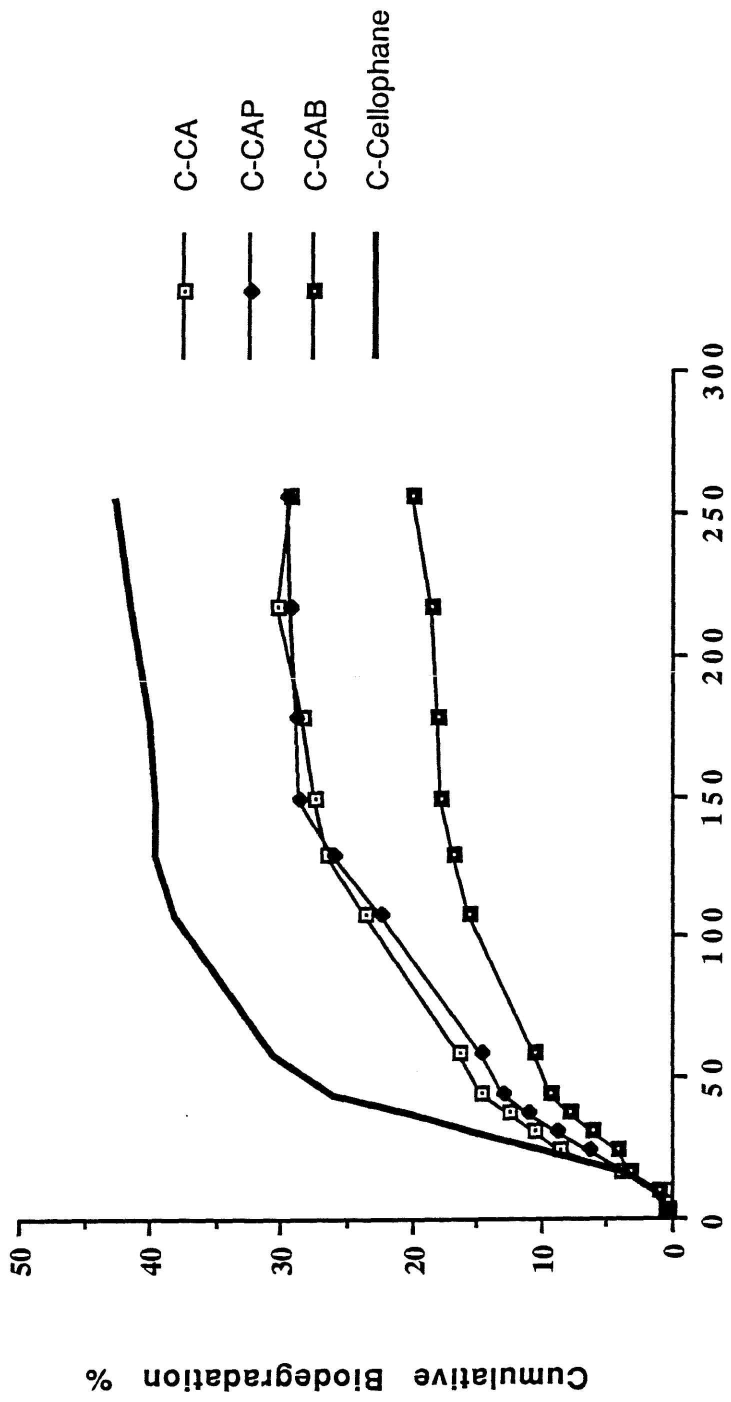


Fig.24 Biodegradation of Cellulosic (Poplar) Films (cut pieces)

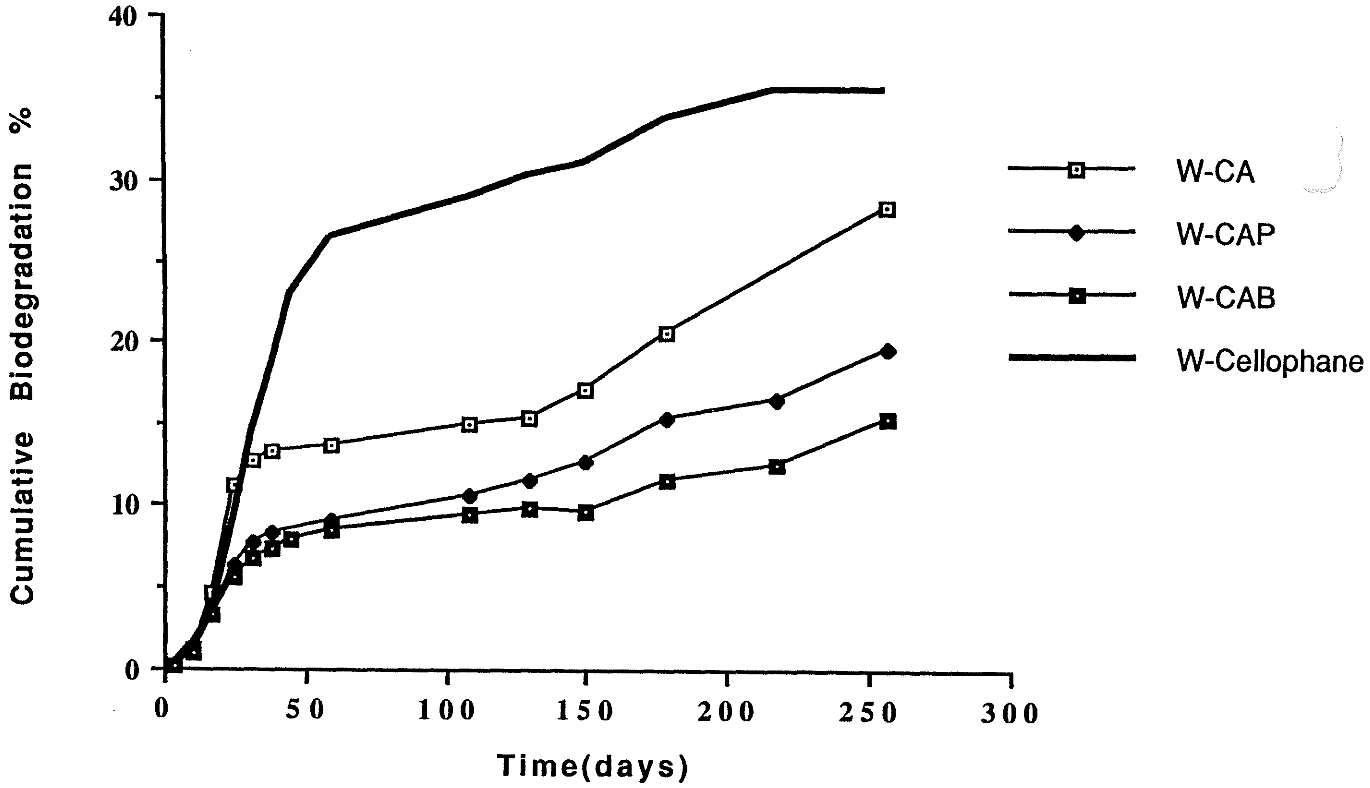


Fig.25 Biodegradation of Cellulosic (Poplar) Films (whole pieces)

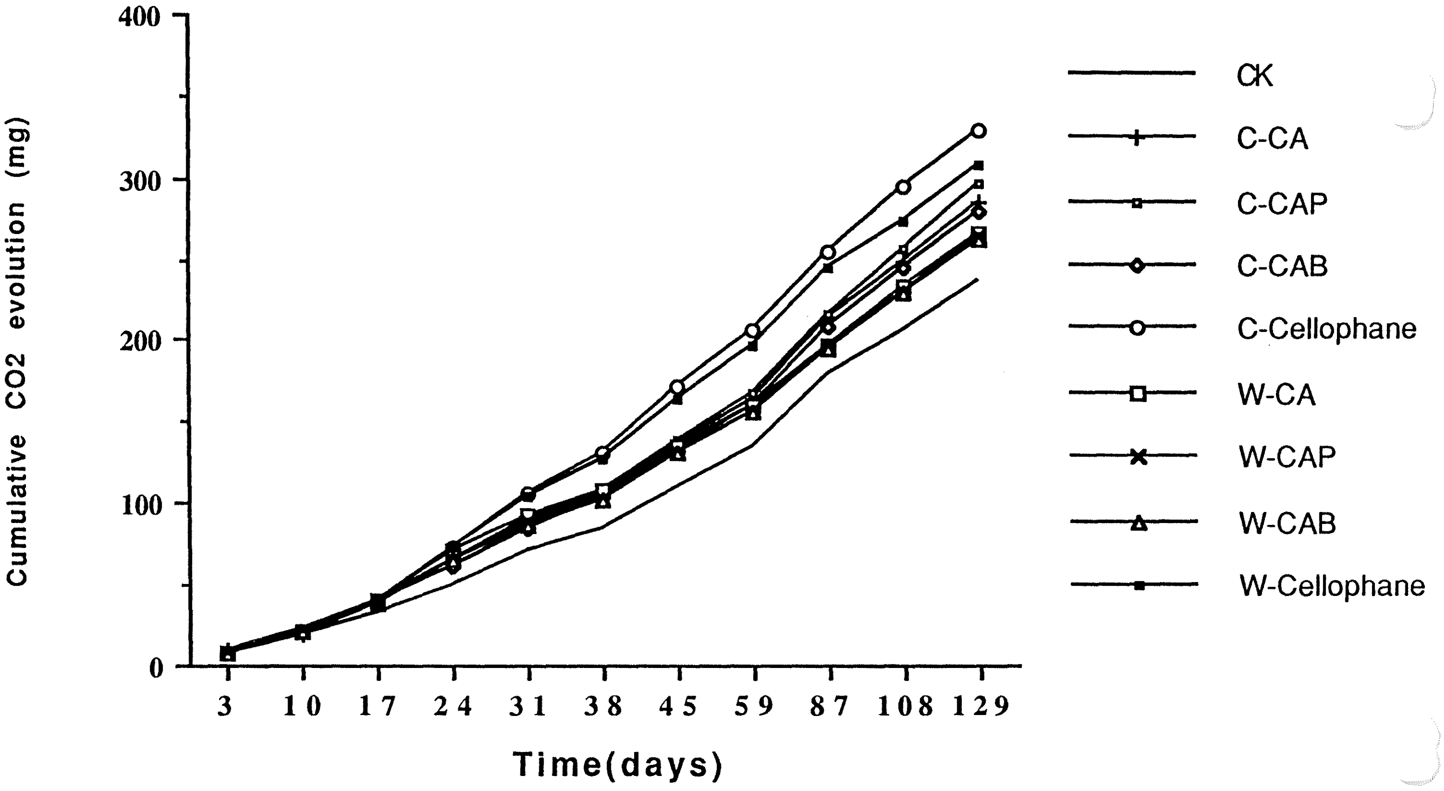


Fig.26 Cumulative Carbon Dioxide Evolution

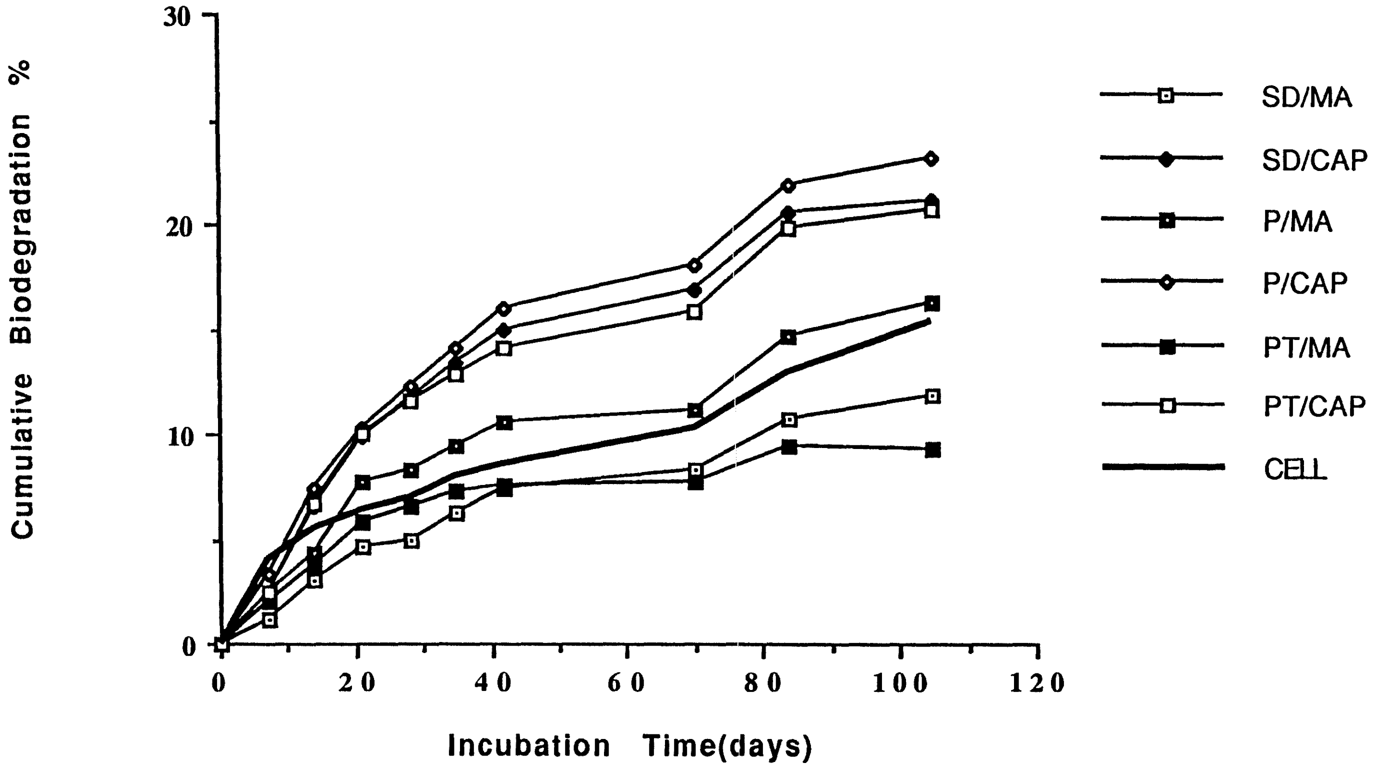


Fig.39 Biodegradation of Cellulosic Films in Sandy Soil (#1)

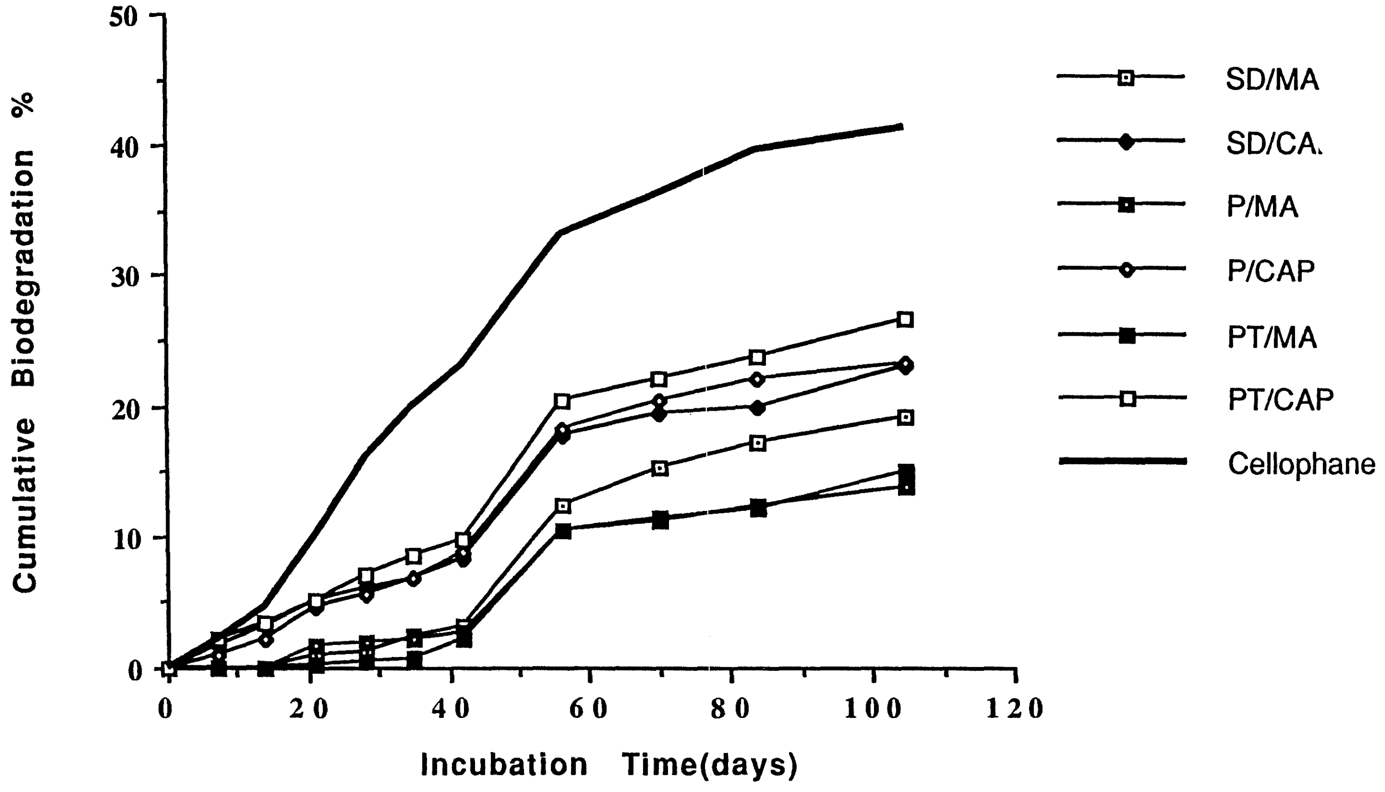


Fig.40 Biodegradation of Cellulosic Films in Organic Rich Clay Soil (#2)

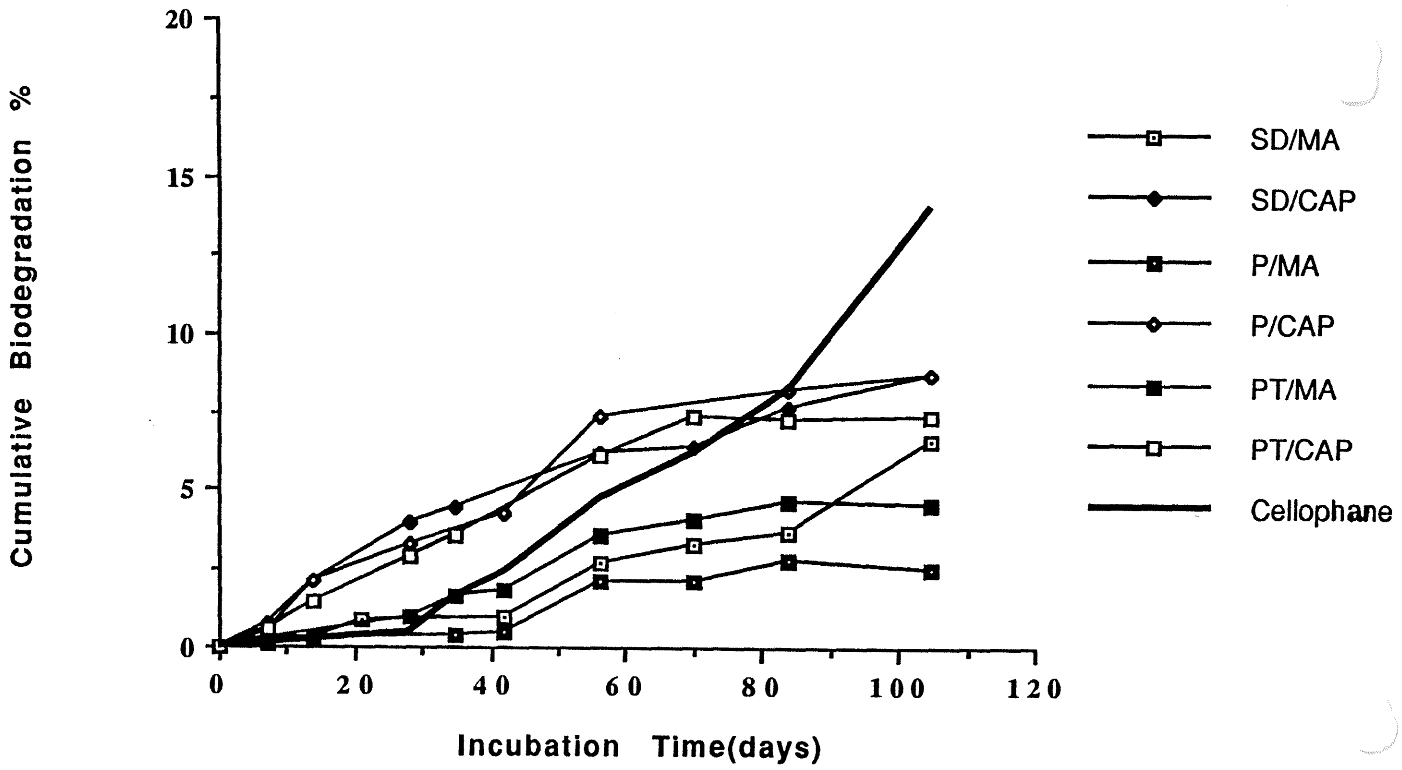


Fig.41 Biodegradation of Cellulosic Films in Clay Soil (#3)

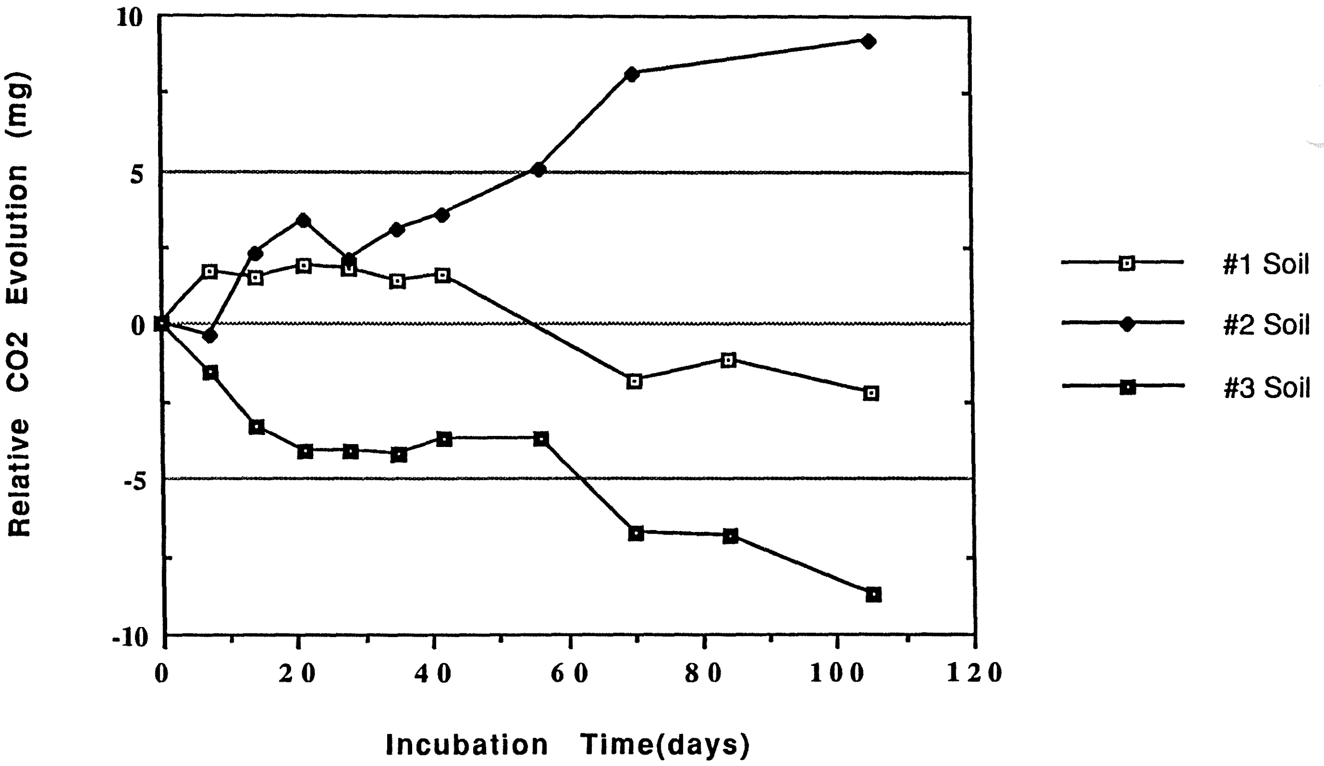


Fig.42 Mineralization of Garbage Bag in Three Soils

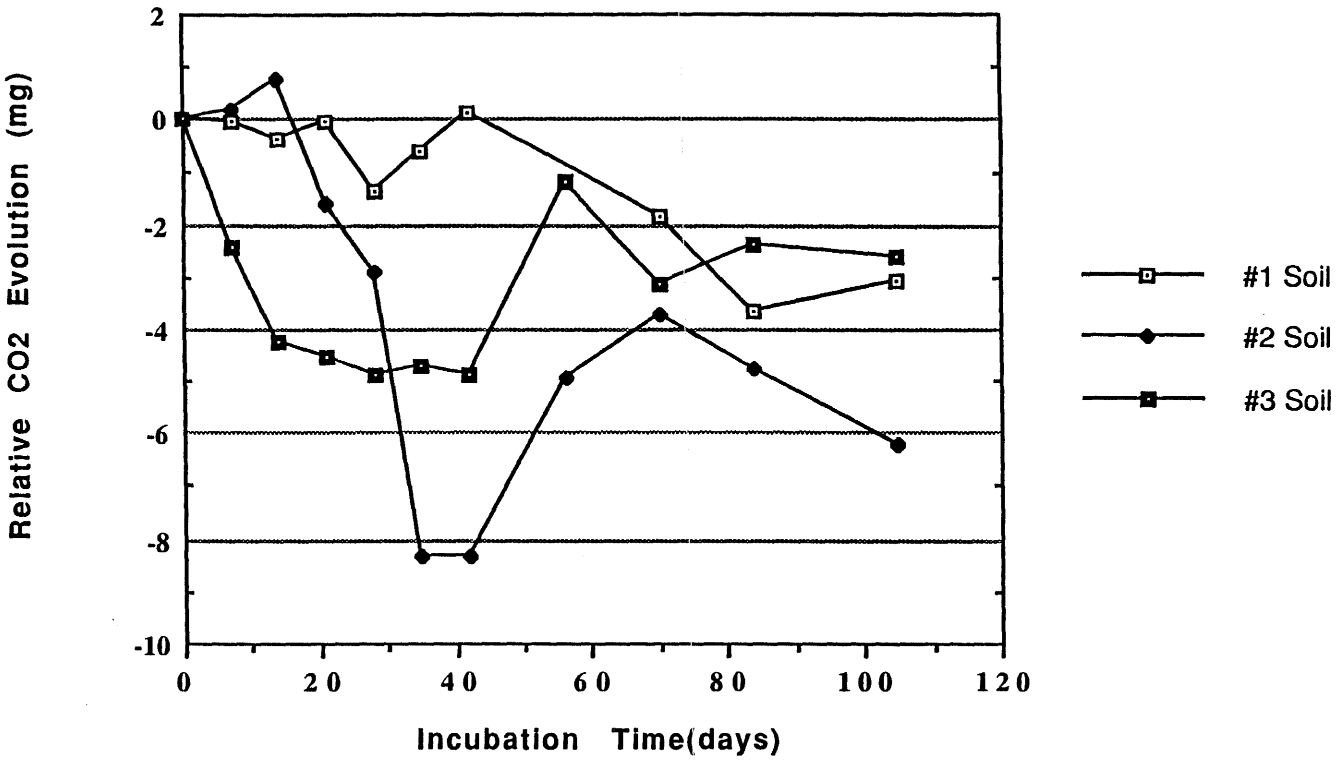


Fig.43 Mineralization of Sandwich Bag in Three Soils

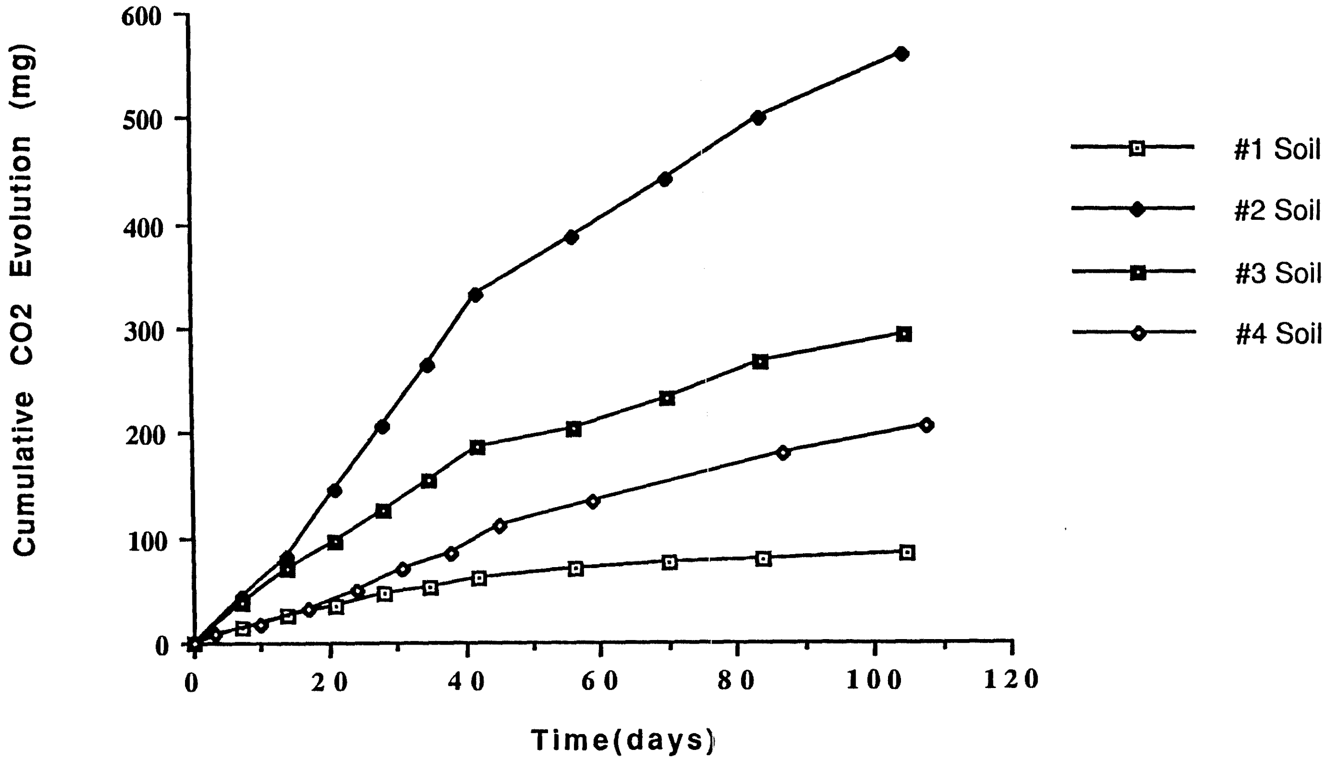


Fig.44 Comparison of Microbial Activity in Four Soils

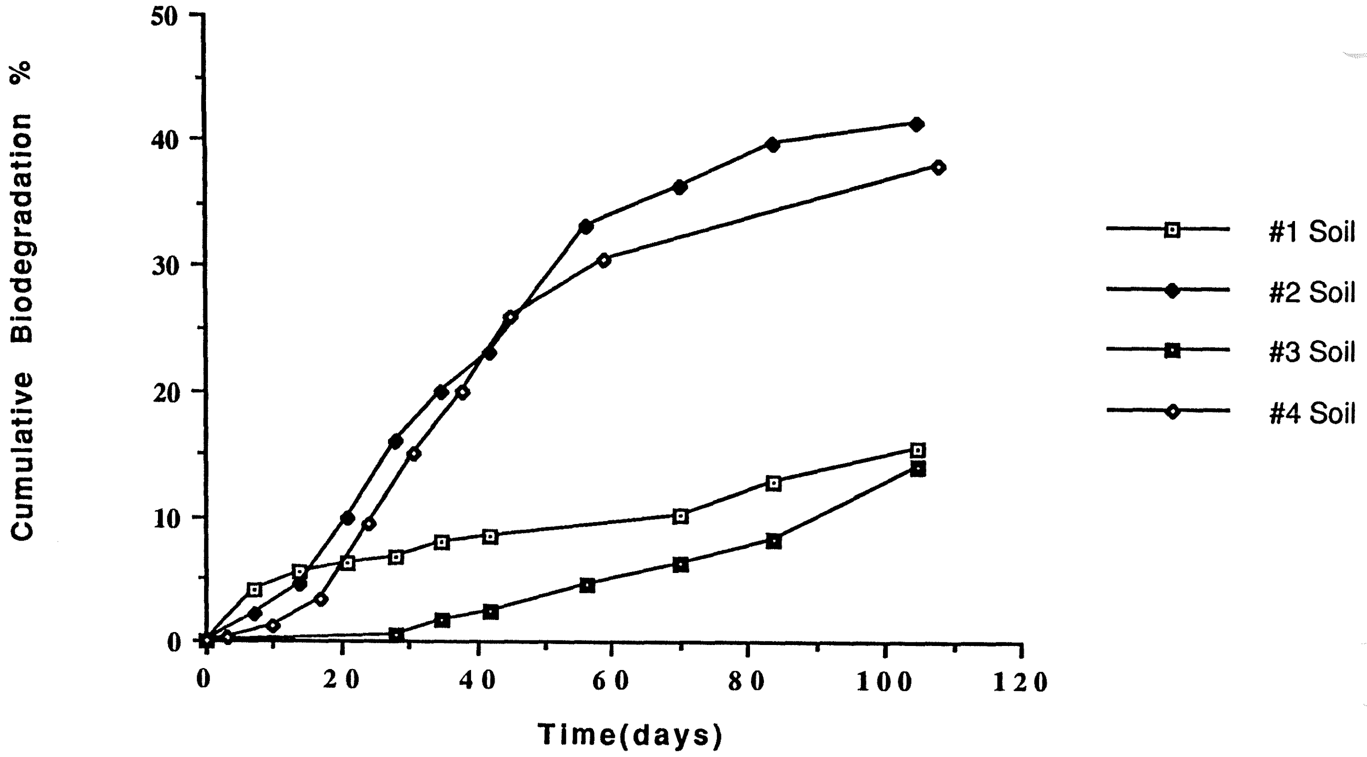


Fig.45 Comparison of Cellophane Biodegrability in Four Soils

Table 23 Chlorine in Various Cellulosic Materials

(mg/Kg)

	Poplar	Sawdust	Paper Towel
Raw materials	68	582	619
Holocellulose	7400	6700	1240
CAP Films	3540	2130	579
MA/CAP Films	1450	780	134
Cellophane		1180	

Table 25 Heavy Metals Content in Some Plastic Materials

(mg/Kg)

	Cu	Zn	Ni	Pb	Cd	Mn
MA/CAP Film (Sawdust)	N.D*	18	N.D	N.D	N.D	4.0
MA/CAP Film (Poplar)	N.D	6	N.D	N.D	N.D	N.D
MA/CAP Film (Paper Towel)	N.D	8	N.D	N.D	N.D	N.D
Cellophane	N.D	N.D	N.D	N.D	N.D	N.D
Sandwich Bag	22	17	N.D	N.D	N.D	N.D
Garbage Bag	31	223	N.D	N.D	N.D	5.5
Black Paper	18	19	N.D	N.D	N.D	N.D
Sawdust Material	208	159	1.6	2.4	1.1	52.

* N.D means not- detectable.

Table 26 Effect of Some Environmental Conditions on Stability of Color Tagging in MA/CAP (Sawdust) Film

(PPM)

Colorant	CK	A		B		C		D		E		F
		4 h	24 h	4 h	24 h	4 h	24 h	4 h	24 h	3 min.	10min.	15min.
2 #	44.45	41.68	37.13	43.53	44.59	42.13	41.30	43.69	43.66	43.99	43.56	35.83
3 #	125.20	112.40	42.75	132.4	153.12	121.20	83.93	124.70	120.20			
4 #	62.55	62.06	62.21	62.08	60.29	62.55	60.98	62.20	62.47	62.55	61.03	65.63

A: Uv exposed
B: Freezen
C: Water immersied (20 ^{o}C)
D: Oven dried (40 ^{0}C)
E: Microwave oven
F: Autoclavod

2# : Direct Red 2	Benzopurpurin 4B
3# : Food Red 14	Erythrosin B
4# : Food Yellow 4	Tartrazine

Planting for Energy Conservation in Minnesota Communities
SUMMARY REPORT FOR 1991-93 LCMR RESEARCH PROJECT
ABSTRACT

The Minnesota ReLeaf "Tree and Shrub Planting for Energy in Minnesota Communities" project consisted of research, publications, implementation plan, and cost-share program. The research component, undertaken by the University of Minnesota, was to evaluate the potential of energy conservation plantings under Minnesota conditions and to develop research-based guidelines.

Results. Measurements of trees in various locations were made to determine typical size, form, growth rate, and foliation periods of Minnesota plants. Similar predicted tree height growth rates and curves were found for most of the deciduous trees. Maples, hackberry, linden, walnut and ash reached a predicted height of 25 feet in 15-20 years and 40 feet in about 30-40 years. Less consistency in predicted height and width was found between the evergreens measured. The evergreens were predicted to reach 25 feet height in 19-25 years and 40 feet height in 30-42 years.

The field observations of foliation period of Minnesota trees yielded information on which tree species and cultivars may be better for strategic shade of buildings. This study suggests that, of the species observed, green ash and Ohio buckeye are most solar friendly, followed closely by black walnut and Kentucky coffeetree.

Energy savings from trees was simulated using the DOE2.1D computer program. The greatest energy savings benefit from trees was found when trees are used collectively to shield homes from the wind. Wind shielding reduces both heating and air-conditioning costs for one and two story homes. In the Fargo-Moorhead area, a 50% tree canopy cover would save $76 to $101 a year. In the Twin Cities, about $4-7 per tree could be saved each year from wind shielding due to tree cover and in Fargo-Moorhead about $7-11 per tree could be saved each year.

The cost benefit analysis focused on the net present value of tree shade <u>only</u> on homes in the Twin Cities and Fargo-Moorhead areas. The present value shading impacts of a tree over a 60-year life time ranged from a best case scenario of $82.80 savings for a deciduous tree due west of Minneapolis home to a worst case scenario of $223.20 loss for an evergreen tree south of a Fargo home. Average present values of cooling savings over the life of a tree were about $50 for a tree planted on the west or east.

Specific guidelines to maximize benefits from planting suggested: 1) shade west and east windows, 2) avoid trees south of windows, 3) create windbreaks, and 4) increase tree canopy cover.

Conclusions. Planting for energy conservation programs can be very valuable because of the multiple benefits provided to the environment and the people involved. The modest and long term nature of the economic benefits of trees to reduce utility bills should be acknowledged. The most cost effective strategies are to plant the smallest size stock that will thrive in a given situation and to preserve existing healthy trees and community forests. The success of programs aimed at conserving energy with trees depends upon the quality of education and implementation efforts. The value of tree canopy cover and community windbreaks needs further exploration and community-scale strategic planting needs to be integrated into community development processes.