Thermal and Biological Properties of Tin-Modified Cellulosic Material Derived from Cotton

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Synopsis

Thermal and biological properties of tin-modified cellulose derived from cotton are described. The inception temperature of degradation for tin-modified cellulosic products is inferior to that of cotton itself, but the heats of degradation in air are less than that of cotton consistent with the modified products being superior in this respect. Degradation of the modified materials in helium as monitored by coupled thermogravimetric analysis–mass spectroscopy shows that degradation occurs through a series of complex steps with the evolution of products characteristic of both the tin-containing and cellulose materials. The tin-modified cellulose was tested against five fungi using disk and protein assays. The fungi tested are typical and widespread, and these tests provide a good indication of the applicability of such products as retarders of fungi-related rot and mildew. Most of the tested samples showed good inhibition of the tested fungi.

INTRODUCTION

Cellulose is a naturally occurring polymeric carbohydrate, hydrolyzable to glucose, consisting of anhydroglucose units and constituting about one-third of all vegetable matter. The structure of cellulose is actually quite complex and varies depending upon the source and method of preparation. Cotton is a relatively pure natural source of cellulose, which contains only 3–15% noncellulosic material and has chain lengths typically 1000–3000 "glucose" units long.

Cotton modification is one of the earliest recorded chemical processes. Even so, research is still in progress to identify new modifications of cellulose which yield materials useful for a wide variety of applications. Most of these modifications are topochemical in nature, involving cellulosic reactive groups which are available in the amorphous regions and on the surfaces of crystalline areas. We chose to attempt a more intimate, homogeneous modification of cellulose in the research associated with that reported herein.

Recently we reported the modification of cellulose derived from cotton through condensation with organotin halides utilizing an interfacial technique.[1] Here, we present some thermal and biological properties of these modified cellulosic materials:

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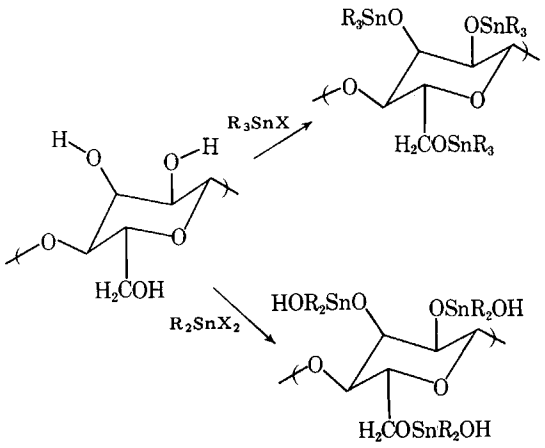

I

II

EXPERIMENTAL

Sample Preparation

Modification of the cellulose was accomplished by addition of cellulose-containing bisethylenediamine copper II hydroxide aqueous solutions to rapidly stirred (20,500 rpm, no load) solutions of organic solvents containing organotin halide. Repeated washings of the product with water were carried out until the blue coloration was no longer visible. Details of the synthesis and characterization (spectral and chemical) of the products have been provided previously.[1] Elemental analyses of the products were accomplished utilizing a Varian Techtron AA6 Atomic Absorption Spectrophotometer. Copper content was found to be less than 10^{-2}%.

Thermal Analysis

Thermal stability of the product was determined utilizing differential scanning calorimetry (DSC), thermal gravimetric analysis (TG), and combined thermal gravimetric–mass spectrometric analysis (TG–MS). A DuPont 990 DSC cell attached to a 990 Thermal Analyzer Console was utilized for the DSC measurements. A DuPont 951 Thermal Gravimetric Analyzer was employed for the TG measurements. DSC was conducted in open aluminum cups allowing volatile materials to leave, simulating the conditions under which TG and TG–MS measurements were obtained. A Mettler H2O T Semimicro Balance was utilized for weighing samples utilized in the DSC studies.

Briefly, the TG–MS combination consists of a double-focusing DuPont 21-491 Mass Spectrometer coupled through a single-stage glass jet separator to a DuPont 951 Thermal Gravimetric Analyzer. The latter is controlled by the DuPont 990 Thermal Analyzer Console. The TG–MS is equipped with a Hewlett-Packard HP-2116C Computer, having a disc-oriented data system specially developed for the DuPont 21-491 MS. The MS system is controlled by the HP computer, which is equipped with 24K of core memory, a dual 2.5M-byte disc drive, a

Hewlett-Packard Cathode Ray Tube terminal, a Tektronix storage scope driven by a dual 12-bit digital-to-analog converter, and a Versatec printer/plotter. Data is acquired using a 14-bit analog-to-digital converter. The system can operate and process data at rates to 8 KHz. The TG quartz furnace tube is attached to the MS using 2.5 in. of 1/4 in. o.d. quartz tubing connected directly to the jet separator. The tubing connecting the TG-quartz tube and the MS is wrapped with heating tape and maintained at 230°C. A thermocouple interfaced with the HP computer and attached to the TG was utilized to monitor the actual sample temperature during each run. An MS scan is completed every 24 s (every 8°C).

The MS is also equipped with a Hall probe which provides voltages indicative of the magnetic field. The mass scale of the MS was calibrated using perfluorokerosene and voltage to mass conversions were performed by a special algorithm written for the HP2116C computer. Using this system, masses are typically identified with a scan-to-scan reproducibility of ±200–500 ppm. The performance of the system was finally checked by using standard calcium oxalate monohydrate.

Biological Analysis

For the disk assays the test organisms, *Aspergillus fumigatus*, *flavus* and *niger*, obtained from the College of American Pathologists were used. Spores of each organism were suspended in sterile water and innoculated (1000 cells) onto Sabouraud's dextrose agar plates. Solid, ground, and modified cellulosic products (0.1 g), added to paper discs were placed at separate locations onto the innoculated medium. Inhibition of growth about the added cellulosic compounds was an indication of the antifungal potential of the particular compound after incubation at room temperature for 24 h.

To assess growth in a liquid medium the following procedure was carried out. *Trichoderma reesei*, strain QM-9414, was obtained from D. Evaleigh and is described in Ref. 2. *Chaetominum globosum* was from our own culture collection.

To prepare cellulose for control media, absorbant cotton was added to concentrated hydrochloric acid and then an equal volume of distilled water was subsequently added. After setting for 48 h at room temperature, the acid solution was removed by filtration, and the cotton mat was washed repeatedly with distilled water. The cellulose mat was dried at 37°C giving a material which could be pulverized to a fine powder with a mortar and pestle.

Each compound was added to a salt medium at a concentration of 1 mg of sample to 1 ml of solution. The salt solution consisted of 0.5 g K_2HPO_4, 3.5 g K_2HPO_4, 0.5 g $(NH_4)_2SO_4$, 0.05 g $CaCl_2$, 0.05 g $MgSO_4 \cdot 7H_2O$, 1.0 g NaCl in 1000 mL distilled water.[3] Homogeneous suspensions of the powdered samples were obtained by homogenizing the mixtures in a Teflon pestle homogenizer. Volumes of 2.5 mL were added to tubes (16 × 125 mm), capped and autoclaved at 15 lb for 15 min. A second series of media containing 1 mg dextrose/mL in addition to the cellulose test compounds and salts were prepared.

Spores of the fungi, grown for 1–2 weeks on Sabouraud's dextrose agar, were harvested in 0.15*N* NaCl. Spores were washed twice with saline by centrifuga-

tion. Approximately 10^3–10^4 spores (0.1 mL) were innoculated into each tube of medium. The tubes were placed in an inclined position on a rotary shaker (125 rpm) and incubated at 20°C for 7 days.

Protein assay was the measure of growth and was done as follows. Cold percloric acid was added to each culture tube after the 7 days of growth to make a concentration of 0.5*M*. Pellets were collected after centrifugation at 2000 rpm in a Sorvall, GLC-2B laboratory centrifuge. The supernatant fluids were discarded; the pellets were then suspended in 2.5 mL 1*N* NaOH. Tubes containing the suspension were capped and autoclaved at 15 lb for 20 min. Resulting solubilized protein in the supernatant fluids was determined as described in Ref. 4 using bovine serum albumin, fraction *V*, as the standard.

Thermal Analysis

One suggested use of the tin-modified cellulose is as an insulation material. Determination of the "burning" properties of the material is therefore appropriate in order to help assess the merits of such modified cellulose for insulating applications. A number of different properties have been indicated as important in describing "burning" characteristics. In the present study we have utilized DSC to derive information associated with the relative energies of "burning" and TG–MS to obtain information concerning the nature and sequence of appearance of evolved degradation products when the material is heated.

The TG, TG–MS, and DSC studies indicate that inception of degradation of the product in air (TG and DSC used), helium, or nitrogen atmospheres typically occurs at about 200–300°C (with the exception of the evolution of small amounts (10^{-1}% by weight) of trapped water), which is lower than the decomposition onset observed for cotton itself (about 310°C). Thus the modified cellulosic products are inferior to cotton in this respect.

A second parameter of interest is the heat given off during combustion of the material. Table I shows heats of combustion of the modified materials relative to that of cotton itself in air and argon. This data was derived utilizing DSC. In air, all of the tin-modified cellulose products listed exhibit heats of combustion

TABLE I
Relative Heats of Combustion for Modified Cellulosic Materials

Cellulose modified with	Relative ΔH^a	Relative ΔH^b	Sample designation (Table VII)
Cotton (itself)	1.00	1.00	
Dibutyltin dichloride	0.97	0.57	6
Dipropyltin dichloride	0.78	0.73	1
Diphenyltin dichloride	0.65	—	—
Triphenyltin chloride	0.77	0.27	2
Dioctyltin dichloride	0.54	0.30	3

[a] Compared to cellulose derived from cotton and determined using a DuPont 990 Differential Scanning Calorimeter in air at a heating rate of 20 C°/min with all energies being exothermic.

[b] As in footnote a, except in argon at a heating rate of 25 C°/min with all energies being endothermic.

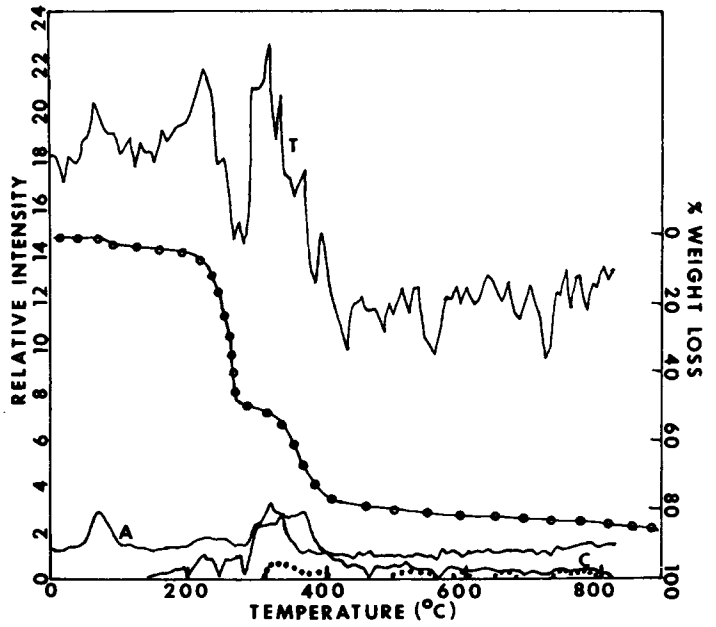

Fig. 1. TG and MS plots for the condensation product from cellulose derived from cotton and triphenyltin chloride at a mass spectrometer ionizing voltage of 70 eV, flow rate of helium at 55 mL/min, and a sample frequency of 41 KC, with a TG heating rate of 20°C/min; T = total ion current, A = plot of m/e = 18, B = plot of m/e = 56 and 57, and C = plot of m/z = 78.

which are less than that for cellulose itself and are therefore superior to cellulose with respect to the contribution of the material to "burning." Degradation in inert atmospheres are all endothermic with the energies associated with the degradation for the modified celluloses all being less than that of the cellulose itself. Under inert conditions, cellulose is superior to the modified celluloses with respect to the contribution of the materials to degradation. Thus the relative merit(s) of the modified celluloses towards continued degradation (with regard to energy contributions) varies with the atmosphere employed for degradation.

It is also important, in describing the thermal behavior of materials, to identify the generated degradation products which are evolved. We recently described an apparatus which couples thermogravimetric analysis with mass spectroscopy, TG–MS, which is ideally suited for essentially continuous monitoring of such thermally generated products.[5] This apparatus is applicable primarily for identification of gaseous degradation species formed in an inert gas atmosphere.

Figure 1 shows both the total ion current and sample weight loss as a function of temperature for a sample of cellulose modified by condensation with triphenyltin chloride. There is a direct correspondence between the temperatures at which the total ion current maximizes and the temperature regions where accelerated weight loss occurs. Tables II and III show the major ions in the mass spectra recorded at several different temperatures corresponding to various maxima in the total ion current. Identification of the degradation product

TABLE II
Major Ions in Mass Spectrum of Cellulosic Material Modified by Condensation with Triphenyltin Chloride at Various Temperatures[a]

		Normalized intensity			
m/e	Parent	70°C	247°C	331°C	842°C
17	H_2O	5.1		10.3	
18	H_2O	24.9		40.0	
117	cel	2.1			
119	cel	2.5			
26	ϕ		1.4	1.9	
38	ϕ			3.2	
39	ϕ		1.4	7.3	
50	ϕ			6.8	
51	ϕ		1.3	7.3	
52	ϕ		1.9	8.0	2.8
74	ϕ			2.1	
76	ϕ			1.9	
77	ϕ		2.4	6.7	
78	ϕ		6.4	34.8	4.5
79	ϕ		1.1	2.4	
27	cel			3.1	
29	cel			9.3	
31	cel			4.2	
37	cel			3.1	
42	cel			2.1	
43	cel			4.6	
57	cel			1.7	
73	cel			2.9	

[a] ϕ = phenyl, Cel = cellulose; only normalized intensities greater than 1 are given. Includes all ions with normalized intensities greater than one.

yielding the ion listed is based on the overall fragmentation pattern and the relative abundances of the spectral ions. Thus the identification of benzene is based on both the appearance of the molecular (parent) ion characteristic of this species and on the observation of other appropriate fragment ions with relative intensities corresponding to those in the standard mass spectrum of benzene (Table IV).

The initial weight loss (3%) occurs at a temperature of about 70°C with the evolution of water (probably trapped water) and small quantities of products exhibiting ions at *m/z* 117 and 119. This is near the mass ions for atomic tin itself

TABLE III
Major Ions in Mass Spectra of Cellulosic Material Modified by Condensation with Triphenyltin Chloride Giving Appearance Temperatures and Intensities

	Parent	Initial appearance		Maximum intensity		Final appearance	
m/e	moiety	Temp (°C)	NI[a]	Temp (°C)	NI[a]	Temp (°C)	NI[a]
18	H_2O	50	11.3	94	24.9	138	11.8
18	H_2O	226	13.3	338	55.5	485	15.7
73	Cellulose	226	0.28	330	2.9	478	1.1
78	Phenyl	138	0.60	380	54.1	790	—

[a] NI = normalized intensity relative to the intensity of *m/e* 28 taken as 100.

TABLE IV
Mass Spectrum Observed for Degradation Product Identified as Benzene Compared with Standard Mass Spectrum of Benzene Listed in McLafferty–Stenhagen[a] Compilation[b]

	Relative intensities			Relative intensities	
m/e	McLafferty–Stenhagen	TG–MS	*m/e*	McLafferty–Stenhagen	TG–MS
78	1000	1000	76	62	55
51	205	209	38	61	91
52	196	229	74	48	60
50	179	195	37	48	28
39	141	230	26	43	14
77	140	192			
79	65	69			

[a] E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Eds., *Atlas of Mass Spectral Data*, Wiley-Interscience, New York, 1969.

[b] Intensities relative to the most abundant ion, in this case *m/e* 78.

(118 and 120); thus it was important to determine if in fact these were due to atomic tin or to other molecular ions. The mass spectrophotometer was again recalibrated, concentrating on the mass range, of 100–150 amu employing pyroprobe mass spectrometry and the pressure of *m/z* 117 and 119, and not *m/z* 118 and 120 was confirmed. While evolution of elemental tin or tin-associated moieties was not observed (but cannot be entirely ruled out), it is worthwhile noting that evolved tin would probably be rapidly converted to tin oxide upon decomposition of the material in an oxygen environment, and the TLV of tin oxide is relatively low, approximately the same as coal dust.[6] In addition, toxic

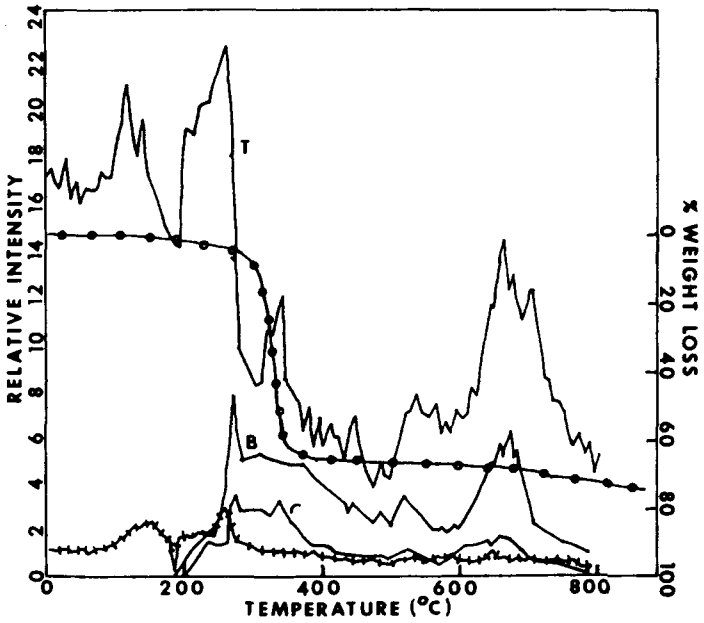

Fig. 2. TG and MS plots for the condensation product from cellulose derived from cotton and dibutyltin dichloride at an accelerating voltage of 70 eV, flow rate of helium at 55 mL/min for a heating rate of 20 C°/min and a sampling frequency of 41 KC, where T = total ion current, A = plot of m/e = 18, B = plot of m/z = 41, and C = plot of m/z = 56.

TABLE V
Major Ions in Mass Spectra of Cellulosic Material Derived from Condensation with Dibutyltin Dichloride at Various Temperatures[a]

		Normalized intensity		
m/e	Parent	149°C	320°C	740°C
17	H_2O	3.0	10.1	7.0
18	H_2O	15.7	39.0	43.2
15	Bu		2.9	13.9
27	Bu		22.0	24.9
29	Bu		15.8	30.3
39	Bu		1.8	20.7
41	Bu		25.5	58.9
43	Bu		17.5	10.6
26	Cel		9.9	9.4
55	Cel		5.4	25.9
56	Cel		10.9	26.0
57	Cel		5.4	26.0
73	Cel		4.1	
147	Cel		1.8	2.6
271	Cel		1.7	9.0

[a] Other significant fragments derived from cellulose at 740°C (*m/e*) normalized intensity: (49) 2.2; (50) 6.0; (51) 4.1; (53) 4.9; (70) 1.7; (85) 1.5; (117) 1.7; (119) 4.2; (121) 4.2; (150) 8.1; (152) 1.8; (153) 3.9; (154) 8.4; (159) 2.6; (173) 2.0; (175) 6.3; (176) 5.4; (177) 12.2; (180) 1.3; (184) 1.9; (211) 5.6; (213) 5.0; (214) 1.9; (217) 3.1; (259) 3.1; (267) 15.3; (317) 2.3; Bu = butyl and Cel = cellulose.

effects of tin oxide are reversible following withdrawal from exposure.[6] Thus even in its worst form, an an airborne mist, the toxicity of tin oxide is apparently not great. On the other hand, the evolution of products possessing aromatic character, such as several derived from the phenyl moiety, could be of major toxicological concern, suggesting that industrial-scale production of tin modified cellulose should emphasize aliphatic organotin modifying agents such as dibutyltin dichloride.

The second maximum in the total ion current occurs at a temperature of about 250°C, and corresponds to a 46% loss in weight of the material. Seven ions (relative intensity >1) are apparent in the mass spectrum at this temperature, all characteristic of benzene. The final maximum in the total ion current occurs at a temperature of about 330°C, and 21 significant ions are observed in the mass spectrum. This is coincident with a 30% weight loss for the sample. The 21 ions

TABLE VI
Major Ions in Mass Spectra of Cellulosic Material Derived from Condensation with Dibutyltin Dichloride Giving Appearance Temperatures and Intensities[a]

		Initial appearance		Maximum intensity		Final appearance	
m/e	Parent	Temp (°C)	NI	Temp (°C)	NI	Temp (°C)	NI
18	H_2O	100	13.7	170	19.7	247	13.7
18	H_2O	296	17.9	338	80.7	597	22.5*
41	Bu	268	2.1	352	96.9	>900	
56	Cel	268	0.45	331	40.6	>900	

[a] Bu = butyl and Cel = cellulose; * = small amounts of water above the background 18 amu remain to 900°C; NI = normalized intensity.

TABLE VII
Samples Tested for Fungal Control

Organotin halide modifying agent	Molar ratio tin:cotton, reactive groups in reaction system	Tin found (%)	Tin (calcd assuming complete reaction); structure I and II	Initial degradation temp air	Sample designation
Dipropyltin dichloride	5:1	21	27	280	1
Triphenyltin chloride	5:1	20	29	210	2
Dioctyltin dichloride	5:1	18	29	210	3
Dioctyltin dichloride	2:1	18	29	210	4
Dibutyltin dichloride	5:1	37	40	270	5
Dibutyltin dichloride	4:1	40	40	270	6
Dibutyltin dichloride	3:1	41	40	270	7
Dibutyltin dichloride	2:1			270	8
Dibutyltin dichloride	1:1			270	9
Dibutyltin dichloride	0.50:1	44	40	270	10
Dibutyltin dichloride	0.30:1	41	40	270	11
Dibutyltin dichloride	(itself)				12
Cotton (itself)				310	13

detected correspond to the evolution of water (two masses), benzene (11 masses), and cellulose (eight masses).

The temperatures at which particular loss associated with the evolution of water, cellulose, and benzene appear are indicated in Figure 1 and Table III. It is seen that the evolution of water occurs at two different temperatures. The initially evolved water (at a temperature of about 70°C) is apparently water trapped during the modification of the cellulose, which involves an aqueous interfacial condensation process. The water evolved at about 330°C is probably derived from actual degradation of cellulose. It seems evident that the trapped water could be removed by heating the sample to about 110°C, without degradation of the modified cellulose itself. Benzene (arising from the phenyl moiety) becomes detectable at about 150°C and is observed at temperatures up to 900°C. Detection of fragment ions derived from cellulose begin at about 225°C and continue to about 500°C.

The second product for which TG–MS data are to be described here is that derived from dibutyltin dichloride. Again there is a correspondence between the maxima in the total ion current and changes in sample weight (Fig. 2). Major ions associated with the products evolved at these maxima in total ion current are given in Tables V and VI.

TABLE VIII
Results of Disc Assays for Several Tin-Modified Cellulose Compounds

	Growth inhibition			Zone of inhibition (mm)					
				A. flavus		*A. niger*		*A. fumagatus*	
Compound[a]	*A. flavus*	*A. niger*	*A. fumagatus*	Par	Comp	Par	Comp	Par	Comp
1	4	4	3	30	25	25	15	30	—
2	4	3	3	20	20	18	—	17	—
3	3	0	0	6	—	—	—	—	—
4	0	0	0	—	—	—	—	—	—
5	4	4	3	38	30	30	25	32	—
6	4	4	3	30	20	14	12	22	—
7	4	4	3	26	16	15	10	8	—
8	3	3	1	12	—	10	—	6	—
9	4	3	2	12	4	12	—	8	—
10	3	3	2	10	—	10	—	6	—
11	4	4	2	16	10	15	15	14	—
12	4	4	4	60	40	35	15	46	14

[a] Designation given in Table VII.
[b] 4 = 100%, 3 = 75%, 2 = 50%, 1 = 25%, 0 = 0%.

Initial weight loss occurs at about 120°C with the evolution of products exhibiting ions at m/z 17 and 18, which are characteristic of water and this accounts for about 3% weight loss. The major weight loss, corresponding to 50% of the original sample weight, occurs in the temperature range between 300°C and 350°C, where mass spectral ions characteristic of both butane (butyl group) and cellulose are evident (Fig. 2 and Table V). Gradual weight loss continues to a temperature of 900°C, accounting for an additional 15% weight loss with continuing observation of ions indicative of both butane and cellulose. The numbers of higher molecular weight fragments originating from cellulose increase as temperature increases (Table V). A minor acceleration in weight loss occurs at about 740°C, and 41 significant (relative intensities of one and greater) ions are observed in the mass spectrum. Most of the fragment ions (33) are derived

TABLE IX
Growth of *Trichoderma reesei* on Tin-Modified Cellulose Compounds

	Growth (μg protein/mL)	
Compounds[a]	With dextrose	Without dextrose
1	70	30
2	140	213
3	170	62
4	280	40
5	30	40
6	30	40
7	30	30
8	30	30
9	30	20
10	30	30
11	30	30
Cellulose	420	250

[a] Designation from Table VII.

TABLE X
Growth of *Chaetomium globosum* on Tin-Modified Cellulose

Compound[a]	Growth (μg protein/mL)	
	With dextrose	Without dextrose
1	20[b]	20
2	120	280
3	120	50
4	130	30
5	20	40
6	44	30
7	40	30
8	44	40
9	40	40
10	60	40
11	80	70
Cellulose	300	240

[a] Designations from Table VII.
[b] All values are an average of results from duplicate cultures.

from cellulose. For instance, the ions in the range from m/e 173 to 180 are derived from one hexose unit with two "ether oxygens."

In summary, trapped water is evolved up to a temperature of about 170°C. Evolution of products indicative of both the butyl group and cellulose begins to be detected at about 270°C and continue to 900°C, with a gradual increase in the evolution of higher molecular weight fragments attributable to cellulose. No ions indicative of tin or tin-containing moieties were deteected throughout the temperature range investigated. The absence of tin-associated fragments is believed to be a characteristic feature of the samples discussed in the following section which describes some biological properties of tin-modified cellulose.

From the above discussion, it is concluded that tin-modified cellulose exhibits thermal properties which are compatible with large-scale industrial use. The inception temperature for degradation is inferior to cotton itself, but the heats of degradation of the modified cellulose in air are less than that of cotton.

Biological Activity

A major reason for utilizing organotin reactants as modifying agents for the synthesis of new cellulose products is to produce materials of this type which have good resistance to mildew and rot. This would be expected to improve the performance of such products for both topical–medical applications and for building material applications (such as insulation or paint additives).

Two approaches were taken to investigate the antifungal activity of the modified products. The first was a disk assay procedure, and the second utilized protein determination as a measure of fungal growth in a liquid medium. Table VII contains a listing of samples tested.

Results of the disk assay studies appear in Table VIII. Inhibition of growth about the added cellulosic compounds is an indication of the antifungal potential of the particular compound. All but the products from dioctyltin dichloride showed good fungal inhibition.

Protein concentration was taken to be a measure of fungal growth in a liquid medium with results reported in Tables IX and X.

Compared to growth of the fungi in solutions not containing tin-modified cellulose, all the compounds tested were observed to inhibit the two fungi, except for the sample derived from triphenyltin chloride. Inhibition was greatest for those compounds derived from dipropyltin dichloride and dibutyltin dichloride. This is essentially the same conclusion which resulted from disk assays. Growth inhibition in the dextrose containing media indicated that inhibition was a result of the toxicity of the modified cellulose compounds on the fungi rather than merely an inability of the fungi to degrade the test compounds.

The fungi tested are typical and widespread, and the results obtained are therefore indicative of the applicability of such modified cellulosic products for retardation of fungi related to rot and mildew. Questions such as duration and mechanism of fungal inhibition by these materials have yet to be answered.

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