

# Thermal Properties of Tritylated and Tosylated Cellulose\*

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## Synopsis

Triphenylchloromethane and *p*-toluenesulfonyl chloride were reacted with chopped or powdered cellulose, with and without premercerization, to form trityl-cellulose ethers or tosyl-cellulose esters. Powdered and premercerized cellulose samples were more readily derivatized. Differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses were performed in nitrogen on these derivatives. DSC and TG thermograms were affected by the particular derivative and the degree of substitution. The decomposition temperatures for both derivatives were lower than for the unmodified cellulose. Trityl cleavage may have been detected by DSC as a broad endothermic area showing no weight loss that preceded the major endothermic decomposition peak. Decomposition temperatures were lowered, but not sufficiently to prevent decomposition products from being combustible. No increase in residue was effected. Thermal decomposition of tosyl-cellulose was substantially different from that of the trityl derivative. As the degree of tosyl substitution increased, decomposition occurred at lower temperatures as an increasing exotherm. Tosyl derivatives all produced high residues. These changes in thermal characteristics were indicative of increased flame resistance. Oxygen index (OI) values relate to flame resistance and show that tritylation was detrimental to the cellulose and that tosylation imparted some degree of flame resistance.

## INTRODUCTION

Under thermal stress, cotton cellulose decomposes into many substances; a portion of these are combustible and contribute to cellulose flammability. Gas chromatography (GC) was used by Schwenker and Beck to identify some pyrolysis products.<sup>1</sup> They found that basically the same products were formed during pyrolysis of cellulose in either air or nitrogen and concluded that the degradation mechanism was nonoxidative. The work supported earlier claims<sup>2</sup> that cellulose depolymerized by scission of the 1,4-glycosidic linkages followed by rearrangement of the monomer to levoglucosan. They suggested that the levoglucosan (1) fragmented further to low molecular weight, volatile products, and (2) polymerized to form char.

With these mechanisms in mind, we recently initiated a program to selectively block the hydroxyl groups of cellulose to determine the effect of the substituent groups on the thermal decomposition of cellulose. Two types of blocking groups were chosen—those that do not contribute to flame resistance

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and those that do. Such basic information on changes in the thermal decomposition of cellulose should assist in the development of lower add-on flame retardant systems.

There were two specific approaches made in this initial portion of the research. The first was to measure the effect of blocking the O(6)H primary hydroxyl group of cellulose on the formation of levoglucosan and thus on the thermal degradation of cellulose. The trityl group was chosen for this portion of the research based on its history<sup>3</sup> of affecting thermal stability and the generally accepted fact that it reacts nearly exclusively at the O(6)H position.<sup>4</sup> The second approach was to employ a substituent group with some flame resistance properties. The tosyl group has some effectiveness as a flame resistance (FR) agent<sup>5</sup> due to the presence of oxidized sulfur in the molecule and was chosen. Another portion of the research project involved the reaction of mesyl chloride with cellulose. The mesyl group has a larger percentage of sulfur in the molecule and was more flame retardant.<sup>6</sup> The thermoanalyses of mesyl derivatives and subsequent preparation of halodeoxy derivatives are the subjects of a future report.<sup>7</sup>

## EXPERIMENTAL

The chemicals employed in this study were all reagent grade materials. They included sodium hydroxide (NaOH) pellets and solutions, pyridine dried over NaOH pellets, commercial triphenylchloromethane (trityl chloride), *p*-toluenesulfonyl chloride (tosyl chloride), and absolute methanol.

A 100% cotton printcloth sample that had been desized, scoured, and bleached was the source of the cellulose. The fabric was chopped in a Wiley mill to pass a 20-mesh screen. Five-gram portions of chopped cellulose were placed for 2 h in a vibratory ball mill of the type developed by Hermans and Weidinger<sup>8</sup> to produce a supply of powdered, decrystallized cellulose with a particle size in the range of 3–10  $\mu\text{m}$ . The celluloses were dried overnight in a vacuum oven or desiccator prior to derivatization.

Selected samples of chopped and powdered cellulose were mercerized with 18% NaOH for 2 h, and rinsed thoroughly with water. If such a sample was to be derivatized, the rinsed cellulose was exchanged with pyridine without drying and subsequently reacted.

Tritylation of cellulose was based on a modified procedure of Hearon et al.<sup>4</sup> Ten grams of cellulose were transferred to a reaction flask and heated with 100 mL dry pyridine at 100°C for several hours. Excess triphenylchloromethane (40 g) was added with an additional 75 mL of pyridine, and the mixture was refluxed at 100°C for 16 h. The approximate molar ratios of cellulose/trityl chloride/pyridine were 1/2.4/36. The fibrous cellulose was filtered, and washed with methanol and then with water. Some tritylation products were totally soluble in the reaction mixture after 16 h. Therefore, the filtrate was poured into cold methanol, and any precipitate was recovered and washed with methanol and water. After drying, duplicate 1-g samples of trityl-cellulose were analyzed for triphenylcarbinol content by a gravimetric procedure.<sup>4</sup> Some recovered precipitate could not be analyzed because there was insufficient sample. The percent trityl was converted to degree of substitution (DS).

TABLE I  
Description of Experimental Samples

Derivative	Cellulose substrate	Reaction time	Product(s)	DS	% Trityl	% S	% Cl
Trityl	Chopped	16 h	FIB + (PPT) <sup>a</sup>	0.04	2.49	—	0.3
Trityl	Chopped-NaOH	16 h	FIB + (PPT) <sup>a</sup>	0.64	38.29	—	0.4
Trityl	Powdered	16 h	PPT	1.12	66.99	—	0.6
Trityl	Powdered-NaOH	16 h	PPT	0.91	54.95	—	0.5
Tosyl	Chopped	1 day	FIB	0.08	—	0.8	0.1
Tosyl	Chopped	2 days	FIB	0.20	—	2.1	0.3
Tosyl	Chopped	3 days	FIB	0.55	—	5.6	0.1
Tosyl	Chopped-NaOH	4 days	FIB	1.21	—	12.1	0.8
Tosyl	Powdered	1 day	FIB	0.30	—	3.0	0.1
Tosyl	Powdered	2 days	FIB	0.38	—	3.9	0.7
Tosyl	Powdered	3 days	FIB	0.67	—	6.8	0.7
Tosyl	Powdered-NaOH	4 days	FIB	1.36	—	13.8	0.2

<sup>a</sup> Insufficient sample to test for degree of substitution (DS).

Tosylation was accomplished by an anhydrous, room temperature reaction with *p*-toluenesulfonyl chloride.<sup>9</sup> The molar ratios were held constant at 1/40/15 for cellulose/tosyl chloride/pyridine. Five grams of cellulose were reacted in a batch process. Samples were presoaked in pyridine and reaction times varied from 1 to 4 days. Reactions were terminated by transferring the reaction mixture to a large volume of water. The product was washed in water and then methanol. After drying, the samples were analyzed for sulfur and residual chlorine by the X-ray fluorescence method of Tripp et al.<sup>10</sup>

A summary of reaction conditions and product compositions is contained in Table I. Differential scanning calorimetric (DSC) and Thermogravimetric (TG) analyses (TGA) were performed with the DuPont 1090 thermal analyzer.\* The instrument was equipped with temperature programming and computerized data acquisition capabilities, software for data analyses, and a printer/plotter. The DSC 910 and TGA 951 modules were employed and thermograms were made using nitrogen as the dynamic purge gas with a flow rate of 300 cc/min. Both DSC and TG curves were obtained at a 15°C/min heating rate. DSC specimens, weighing approximately 5 mg, were sealed into aluminum pans. TG samples were placed directly into a platinum boat; the weight was adjusted to approximately 10 mg. TGA residue values were measured at 575°C. "TGA peak temperature" designates the temperature at which the maximum rate of weightloss occurred. Differential thermogravimetric (DTG) analyses were always recorded. They were used to set the limits to integrate the TG weight-loss regions.

Oxygen index (OI) was determined on pressed discs of the celluloses via a modification<sup>6</sup> of the OI test used for fabrics. Weighed cellulose samples were pressed into circular discs and tested. Generally, three 0.5-g discs were sufficient to measure the OI of a sample.

\* Names of companies or commercial products are given solely for providing scientific information and do not imply endorsement by the U.S. Department of Agriculture over others not mentioned.

## RESULTS AND DISCUSSION

Carbohydrate derivatives from trityl chloride and tosyl chloride have been known for 50 years.<sup>11</sup> Those same derivatives of cotton cellulose have been studied since the 1940s.<sup>4,9</sup> Studies of the effects of thermal stress on cellulose and cellulose derivatives began with pyrolysis techniques and evolved to the more sophisticated techniques of differential thermal analyses (DTA), TG, and differential thermogravimetry. Gradually the DTA method has been replaced, at least at lower temperatures, by DSC.

## Cellulose

The thermoanalytical data for the entire study are summarized in Table II. The untreated cellulose data are in the upper third of the table. In Figures 1(a) and 1(b) are shown the DSC and TG thermograms of unmodified chopped

TABLE II  
Thermal Analyses and Oxygen Index Data Summary

Sample Description	DS	DSC			TGA		
		Peak temps (°C)	$\Delta H$ (kJ/mol) Endo	Exo	Peak temps (°C)	% Residue	OI
<u>Untreated cellulose</u>							
Chopped							
Native	0	356	39.0	—	371	7.9	19.1
NaOH	0	361	41.0	—	377	6.5	20.6
Powdered							
Native	0	332	10.7	—	344	14.1	20.9
NaOH	0	345	15.0	—	351	15.5	20.4
<u>Tritylated cellulose</u>							
Chopped							
Native, FIB	0.04	305, 365	1.3, 24.4	—	304, 380	7.3	17.3
NaOH, FIB	0.64	305, 332	4.0, 33.3	—	341	5.3	18.8
Native, PPT	?	280, <sup>a</sup> 315	—, 15.7	—	320	13.6	—
NaOH, PPT	?	313, <sup>a</sup> 328	—, 20.0	—	330	9.9	—
Powdered							
Native, PPT	1.12	309, <sup>a</sup> 327	—, 18.8	—	331	9.3	18.2
NaOH, PPT	0.91	290, <sup>a</sup> 323	—, 27.5	—	334	8.8	18.4
<u>Tosylated cellulose—all products are fibrous<sup>b</sup></u>							
Chopped							
Native	0.08	226, 305	18.2	1.9	246, s	30.8	24.6
Native	0.20	216, 230	9.4	1.4	221, s	30.2	24.8
Native	0.55	197, 215	10.0	22.7	203, s	30.5	25.1
Native-NaOH	1.20	—, 211	—	86.4	213, s	30.0	21.9
Powdered							
Native	0.30	209, 227	20.6	6.3	213, s	31.1	27.9
Native	0.38	206, 224	10.1	16.6	213, s	31.6	27.2
Native	0.67	203, 224	5.9	51.7	215, s	30.3	24.3
Native-NaOH	1.40	—, 213	—	111.0	210, s	30.0	22.1

<sup>a</sup>Broad endothermic area—no  $\Delta H$  measured.

<sup>b</sup>Only major endothermic and exothermic peak data are tabulated; s = shoulder, i.e., continued gradual weight loss.

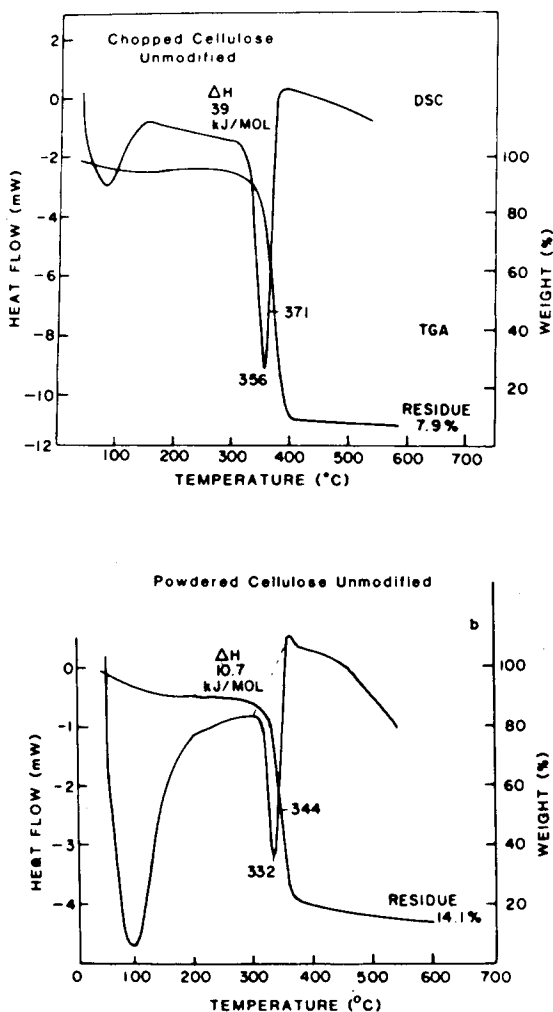


Fig. 1. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of unmodified, chopped (a), and powdered (b) cellulose.

and powdered celluloses respectively. The DSC thermogram revealed that chopped cellulose decomposed as two, distinct endothermic peaks. The first peak represented loss of water, and the major peak at 356°C was cellulose decomposition. The  $\Delta H$  of the decomposition peak measured 39 kJ/mol. By comparison, the DSC thermogram of powdered cellulose had a larger, water-loss endotherm, and the decomposition endotherm itself occurred at a slightly lower temperature with a smaller heat of transition (10.7 kJ/mol).

Superimposed upon the DSC curves in Figure 1 are the TG, weight-loss curves. For both chopped and powdered cellulose samples, the weight-loss regions occurred over the same temperature ranges as the DSC decomposition peaks. The actual temperature at which the maximum rate of weight-loss occurred was slightly higher than the matching DSC peak temperature for both chopped and powdered celluloses. The percent residue at 575°C was higher for powdered cellulose (14.1) than for chopped cellulose (7.9).

Differences in thermal characteristics between chopped and powdered celluloses were related to the decrease in crystallinity produced by ball milling for 2 h. Powdered cellulose was more amorphous, had substantially higher moisture regain, and was expected to be more easily derivatized.

Mercerization with NaOH was also expected to make the cellulose more accessible to derivatization by altering the crystallinity. While lower crystallinity occurred, the samples were less amorphous than ball-milled cellulose. Therefore, the effects of mercerizing on thermal characteristics (Table II) were smaller than those produced by ball milling.

### Trytlylated Cellulose

Trytlylation of chopped cellulose resulted in two products. The major one was insoluble and fibrous. The minor product was recoverable from the pyridine solution by precipitation in methanol as a regenerated cellulose. A single product was obtained when powdered cellulose was tritylated. With or without premercerization, powdered cellulose went into solution and the product had to be recovered by precipitation. The thermoanalytical data for the trityl-celluloses are contained in the central portion of Table II.

In Figure 2, the DSC and TG thermograms of a fibrous, tritylated cellulose with a low DS (0.04) are plotted. The DSC curve was characterized by water desorption, a broad endothermic area, and two endothermic peaks. The small peak at 305°C was new while the remainder of the thermogram resembled unmodified cellulose with a decomposition peak at 365°C. The  $\Delta H$  of the major peak (24.4) was less than that of unmodified chopped cellulose.

The TG curve was superimposed upon the DSC curve and showed two weight-loss regions that corresponded to the decomposition peaks. There was no significant weight loss associated with the endothermic area that preceded

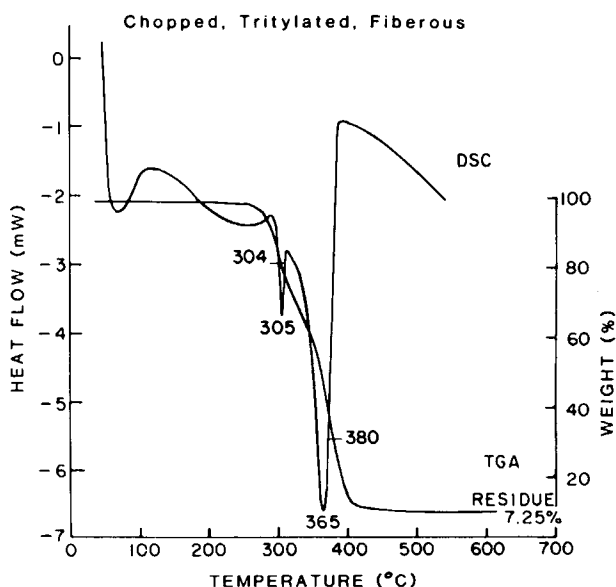


Fig. 2. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of a fibrous trityl-cellulose (DS 0.04) prepared from chopped cellulose.

the decomposition peaks. The residue that remained at 575°C was low and essentially the same as that of the unmodified cellulose.

Similar thermal characteristics (not shown) were measured on the other fibrous trityl-cellulose prepared from sodium hydroxide mercerized, chopped cellulose (DS 0.64). The sample was characterized with a small first peak (305°C) and a second, sharper decomposition peak that occurred at a lower temperature (332°C) than the trityl-cellulose in Figure 2.

The DSC and TG thermograms of a derivative prepared from powdered cellulose are plotted in Figure 3. It is illustrative of regenerated trityl-cellulose products, whether they occurred as the small amount recovered from chopped cellulose or the major product produced from powdered cellulose. In the DSC curve, water desorption preceded a broad endothermic area that ended near 309°C. The curve's major feature was a single, narrow endotherm that peaked at 327°C. The  $\Delta H$  of the decomposition peak was small. There was only a single weight-loss region for the TG curve whose peak temperature matched well with the DSC peak decomposition temperature. The percent residue value was small. Similar thermograms were also obtained whether the samples were tritylated with or without premercerization. All the DSC thermograms of a regenerated product showed a single sharp endothermic peak at low decomposition temperatures and small  $\Delta H$  values. Trityl-cellulose residues at 575°C were all < 10%.

In Figure 3 and some of the later thermograms, the DSC curves exhibited indications that a sharp endotherm might have been superimposed over a broad exothermic area. The DTG thermograms, however, showed only a single weight-loss region instead of multiple peaks. In all instances, the DSC curves were more complex than the DTG thermograms, and the simpler interpretation was supported.

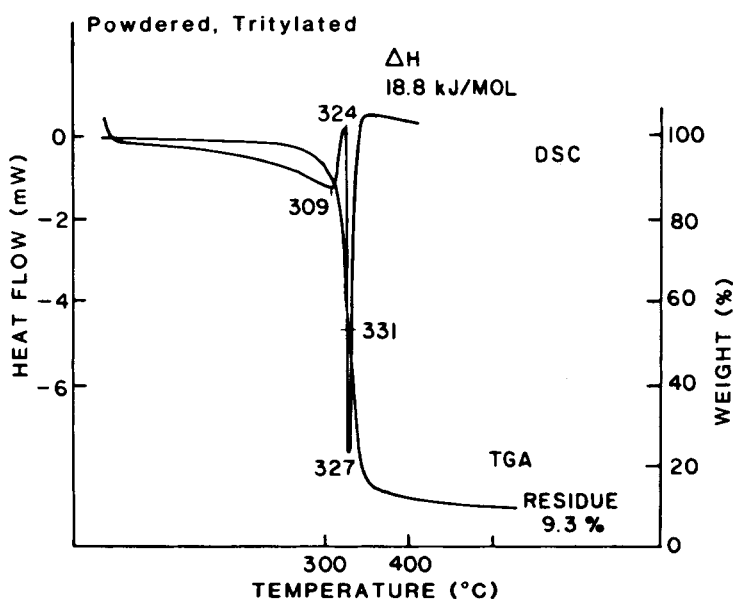


Fig. 3. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of a regenerated trityl-cellulose (DS 1.12) prepared from powdered cellulose.

Initial choice of the trityl group for this study was based upon trityl's ability to act as a blocking agent and the fact that it was not expected to materially aid flame resistance. The large size of the trityl molecule with its three phenyl groups causes the overwhelming majority of reaction to occur at the O(6)H position of the cellulose molecule.<sup>4</sup> The presence of the trityl group on the primary hydroxyl leaves only the two secondary hydroxyl groups available for subsequent reactions.

While the trityl group itself was not expected to aid flame resistance *per se*, it was known to affect the thermal stability of cellulose.<sup>5</sup> Previously Russian scientists studied trityl-cellulose films under thermal stress and detected triphenylmethane in dry nitrogen atmospheres.<sup>12</sup> Hydrocarbon and triphenylcarbinol were detected in moist nitrogen. The presence of the trityl group on cellulose lowered the degradation rate; the lower rate was attributed to possible inhibition by the degradation products themselves, to their structural properties, and perhaps to the steric hindrance by the bulky tertiary carbon group.

King and Stanonis<sup>3</sup> ran a pyrolysis and GC study of cellulose derivatives which included trityl-cellulose. They showed that under thermal stress, triphenylmethane was formed below a column temperature of 220°C. However, when Conrad et al.<sup>13,14</sup> studied the rate of weight loss of trityl-cellulose yarns, they found that the maximum rate of loss was considerably higher than 220°C and concluded that scission of the trityl group was strongly restricted by its attachment to the cellulose molecule. Our thermoanalytical data agreed with Conrad's findings. Trityl-cellulose did not decompose until the temperature was above 300°C. Conrad also suggested a free radical mechanism for both initial scission of the trityl group and subsequent production of levoglucosan. If that proposal is correct, the trityl group's presence on the O(6)H would do nothing to assist flame resistance because it would not prevent levoglucosan from forming.

In the current research, reaction of trityl chloride and cellulose to form an ether linkage occurred to a greater or lesser degree depending on the starting material. While the yield of trityl-cellulose precipitate from chopped cellulose was too small to analyze for DS, the DS probably approached 1.0 as DSC curves for all such trityl products were similar.

The presence of the trityl group on cellulose lowered the thermal stability of the molecule. A broad, endothermic area preceded the major peaks of the samples. There was no significant weight loss associated with these areas. The major peak decomposition temperatures shifted from a high range of 365–370°C to a low range of 313–327°C, and weight loss occurred in the same temperature ranges. The lower decomposition temperatures were accompanied by lower heats of decomposition; the  $\Delta H$  values fell from approximately 40 kJ/mol for unmodified cellulose to 11–28 for trityl-celluloses. Endothermic decomposition temperatures were lowered but not sufficiently to prevent the decomposition products from undergoing combustion. Instead of trityl not effecting flame resistance, its presence may have made the FR situation worse.

### Tosylated Cellulose

Tosylation of cellulose was carried out on the same starting materials used for tritylation. A range in the degree of substitution values was achieved by



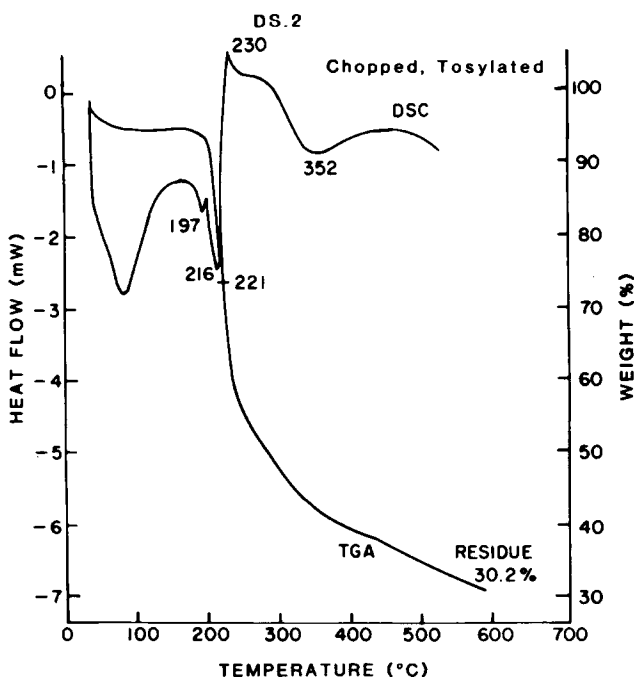


Fig. 4. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of a tosyl-cellulose (DS 0.20) prepared from chopped cellulose.

adjusting the reaction time from 1 to 4 days at ambient temperature. The DS values varied from 0.08 to 1.4. Only fibrous products were produced. Eight tosyl-cellulose samples were included in this report, and the results are tabulated in the lower portion of Table II. Only the major peaks are listed.

Three samples of tosyl-cellulose were chosen to illustrate the results. In Figure 4 are plotted the DSC and TG thermograms of a tosyl-cellulose with a low DS of 0.2. The sample was prepared from chopped cellulose. The DSC curve had a water desorption endotherm similar to unmodified cellulose; however, the remaining major characteristics of the thermogram shifted to lower temperatures. There was a minor endotherm at 197°C, and a major endotherm peaking at 216°C that changed to a small exotherm peaking at 230°C. Finally, evidence of unreacted cellulose was visible as an endotherm at 352°C. The corresponding TG curve showed a region of rapid weight loss peaking at 221°C with a slower rate of weight loss continuing until at 575°C there was 30.2% residue remaining.

In Figure 5 are displayed the DSC and TG thermograms of a tosyl-cellulose with a DS of 0.38. This derivative was produced from powdered cellulose. Water desorption was visible, and there was still a sign of unmodified cellulose decomposition around 350°C in the DSC curve. The thermogram was dominated, however, by an endotherm at 206°C and an equally distinct exotherm that peaked at 224°C. Both peaks were present at slightly lower temperatures than those recorded for the tosyl-cellulose in Figure 4. The TG curve had a major weight-loss region peaking at 213°C and a steep shoulder with a maximum rate of weight loss occurring at 310°C. Loss of sample weight continued gradually until 31.6% residue remained at 575°C.

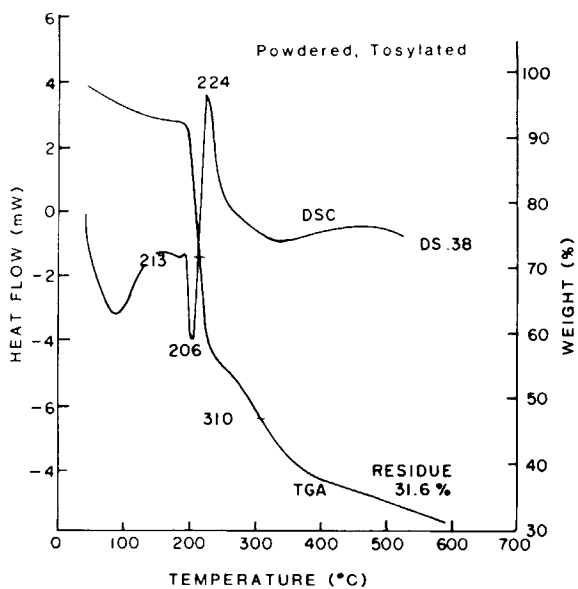


Fig. 5. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of a tosyl-cellulose (DS 0.38) prepared from powdered cellulose.

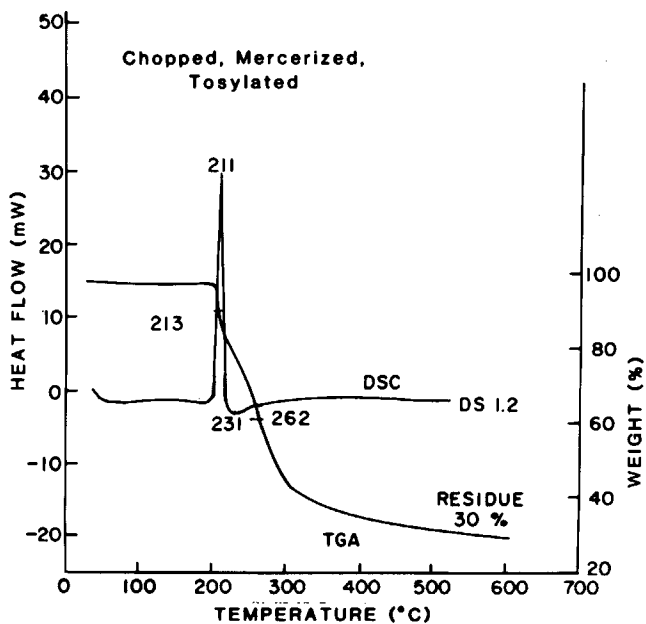


Fig. 6. Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of a tosyl-cellulose (DS 1.2) prepared from mercerized, chopped cellulose.

The DSC and TG curves of tosyl cellulose with a DS of 1.2 appear in Figure 6. The cellulose was chopped and mercerized before esterification. The DSC thermogram was dominated by a single exotherm peaking at 211°C. The corresponding TG curve had a matching peak at 213°C. Substantial weight loss continued as a shoulder with the maximum rate of loss occurring at 231°C. Residue was 30% at 575°C for this sample.

In Table II are data from the DSC and TG thermograms of the tosyl-cellulose samples. Only the data from the major endothermic and exothermic peaks are given in the DSC portion of the table. TG thermograms indicated a single weight-loss region that reflected the combination of both the endothermic and exothermic peaks, and a continued, gradual weight-loss region that appeared as a shoulder. In general we observed that, as the DS of tosyl-cellulose increased, the size of the major endothermic peak progressively diminished and finally disappeared. The endotherms also occurred at progressively lower temperatures. Each endotherm was immediately followed by an exotherm that got progressively larger as sample DS increased. Regardless of starting product, the endotherm associated with tosylation was largest (had the largest  $\Delta H$ ) after 1-day reaction time and began to decline thereafter. Under our reaction conditions, the formation of the exotherm simply increased with increasing degree of substitution and did not level off. These peaks also formed at progressively lower temperatures. The TGA residues remaining at 575°C of all tosyl derivatives were similar and large.

Tosyl-cellulose contains sulfur which has some limited effectiveness as a flame-resistant element. Klein and Snowden<sup>5</sup> tosylated cotton cellulose yarns with FR as their objective and studied them with IR. These same scientists found sodium hydroxide to be the most effective pretreatment for tosylation.

Whereas the trityl group with its three phenyl groups has been shown to react almost exclusively at the primary hydroxyl group of cellulose, the smaller size of the tosyl group with only a single phenyl group can react at all three hydroxyls. In this research tosylation DS increased when the starting material was less crystalline. Tosylation occurred on more than one reaction site as measured by the DS values greater than 1.0. Sodium hydroxide pretreatment increased the DS of tosyl-cellulose also.

Thermoanalytical research with flame-retardant fabrics treated with phosphorus/nitrogen finishes showed the presence of an exotherm associated with flame-retardant finishes.<sup>15,16</sup> The presence of an exotherm recorded for these tosylated celluloses indicated some degree of flame resistance was present. The large amount of residue measured after thermoanalyses was another indicator of flame resistance. Increasing the production of char is one means to achieve improvements in flame resistance.

### Oxygen Index

Pyrolysis and thermal analyses data are basic tools for studying thermal decomposition of materials. When a scientist moves toward practical tests that measure flammability, one of the most versatile and reliable tests available is oxygen index (OI). Van Krevelen<sup>17</sup> stated that scientifically interpretable and reproducible pyrolysis data required that substances be studied in an oxygen-free atmosphere—nitrogen or argon. He also believed the OI test

was an excellent tool to study polymers, and showed that, for pure polymers, OI correlated with pyrolysis residue if no halogen was present.

The initial step in the current program to study the thermal characteristics of cellulose derivatives was the development of the technique to measure the OI of fibrous and powdered cellulose and cellulose derivatives.<sup>6</sup> Data from this test serves as the bridge between basic thermal analyses and practical flame resistance. In general, an OI value of 26–28 represents borderline flame resistance in fabrics.

Because the addition of a mole of trityl/anhydroglucose unit adds more weight than the addition of a mole of tosyl/anhydroglucose unit, the weight percent substituent values were calculated for the derivatives. These data are plotted against OI values in Figure 7. Discs of unmodified cellulose had OI values in the range of 19–21. Tritylation of cellulose reduced the OIs slightly; tosylation caused some improvement in OI values to a weight percent range of 20–30% and then the values began to drop off. Although not shown in this figure, the same data for the mesyl-cellulose derivatives showed an increase in OI as weight percent increased—OI values did not drop off. The addition of approximately three phenyl groups per trityl unit to each anhydroglucose unit was detrimental to the flame resistance by contributing more fuel. The minimal flame resistance of the tosyl derivatives was attributed to the presence of oxidized sulfur in the molecule. The presence of sulfur and/or the appearance of an exotherm upon DSC analyses are not sufficient evidence of flame resistance per se. While both sulfur content and the size of the exotherm continued to increase with the tosylated samples, their flame resistance, as measured by OI, peaked and fell off. The additional weight of the single phenyl group at higher substitution levels may have begun to overcome

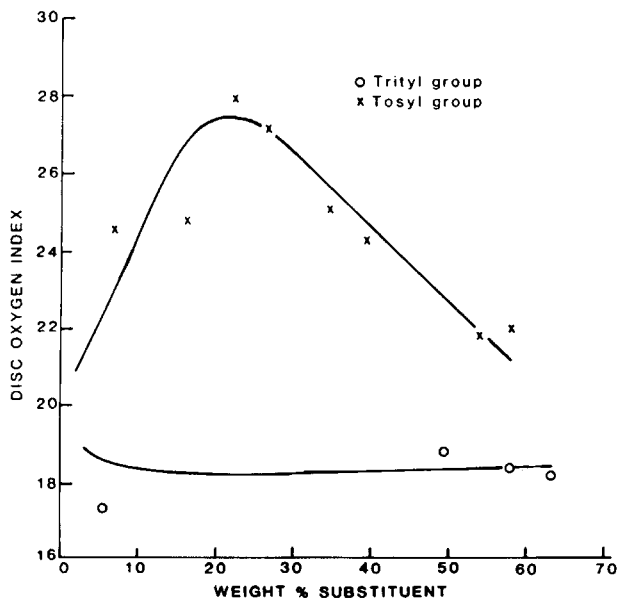


Fig. 7. Comparison of percent weight substituent vs. oxygen index (OI) values for trityl-cellulose (O) and tosyl-cellulose (x) derivatives.

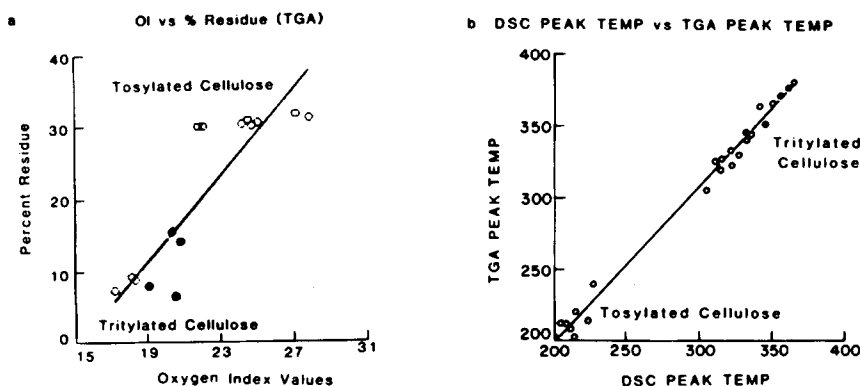


Fig. 8. Correlation of: (a) oxygen index (OI) data with percent residue data from thermogravimetric analyses (TGA)—data from both derivatives and unmodified cellulose (●) are included. Regression equation  $Y = -45.88 + 3.00(x)$ ; Pearson correlation coefficient  $R = 0.884$ . (b) differential scanning calorimetric (DSC) peak temperatures with thermogravimetric analysis (TGA) temperatures of maximum rate of weight loss—data from both derivatives and unmodified cellulose (●) are included. Regression equation  $Y = -12.62 + 1.06(x)$ ; Pearson correlation coefficient  $R = 0.994$ .

sulfur's limited contribution to flame resistance. The extraneous fuel from the mesyl group was so small that it had no deleterious effect on the FR properties contributed by the sulfur.

### Correlations

A comparison of two sets of parameters were made and are contained in the final figure. Because Van Krevelen<sup>17</sup> stated that OI of a polymer is related to percent residue, these same parameters were examined using the cellulose derivative results. The least squares line for these data is contained in Figure 8(a). The OI vs. residue data had a correlation coefficient of 0.88. The data for unmodified and tritylated celluloses are in the lower left portion of the figure, and the tosylated samples are at the top. The relationship is clearly present. The presence of chloride residues may have reduced the correlation in this work just as Van Krevelen reported halogens did with pure polymers.

In Figure 8(b) are plotted the DSC peak temperatures vs. the corresponding TG temperature at which the maximum rate of weight loss occurred. For the tosyl cellulose samples, the TGA peak temperature was matched with the peak temperature of the larger of the DSC endothermic/exothermic pair. These data had a correlation coefficient of 0.99. The decomposition data for the unmodified and tritylated cellulose samples appeared above 300°C. The data for tosylated cellulose samples occurred between 200 and 230°C. The excellent correlation showed that, under these analyses conditions, all the major cellulose decompositions whether endothermic or exothermic were accompanied by weight loss.

### SUMMARY AND CONCLUSIONS

Samples of chopped and powdered cellulose, with and without sodium hydroxide mercerization, were used to make trityl- and tosyl-cellulose

derivatives. These modified celluloses were examined with differential scanning calorimetric and thermogravimetric analyses as well as with the oxygen index flame resistance test.

Tryl capping of cellulose's primary hydroxyl group lowered the thermal stability of the molecule. This decrease in thermal stability was accompanied by a reduction in flame resistance as measured by OI values. The OI's of trityl-cellulose were slightly lower than those of unmodified cellulose. Tritylation did not effect increased residue production after thermal decomposition.

While the presence of the trityl groups on the primary hydroxyl of the anhydroglucose unit blocks this position and protects it from reaction with other substituents, trityl's presence apparently does not inhibit the formation of levoglucosan. Earlier research claimed that the trityl group was cleaved at low temperatures by a free radical mechanism and that the decomposition of cellulose reverts to the levoglucosan pathway. When a sample was adequately tritylated, degradation occurred rapidly in one weight-loss region. The trityl group was not lost at one temperature and the cellulose skeleton degraded at another. Trityl cleavage may have been monitored by the DSC as the broad endothermic area that preceded the major decomposition peak. In this region, free radicals may have formed, abstracted hydrogens, dimerized, etc., all without apparent weight loss. When the sample ultimately disintegrated, the temperature was sufficiently high so that the degradation products were still combustible and therefore not flame-resistant. There was no significant increase in residue.

Tosyl-cellulose esters contained oxidized sulfur and had dramatically different thermal characteristics from the trityl ethers. A DSC decomposition exotherm that increased with increasing DS was characteristic of the tosyl derivatives. The tosyl-cellulose derivatives all produced approximately 30% residue in TG analyses. Each derivative prepared for this research had a higher OI value than either trityl-cellulose derivatives or unmodified controls.

The appearance of a low-temperature exotherm was the first sign that the presence of the tosyl group improved flame resistance. Previous research on phosphorus/nitrogen FR finishes for cotton showed that such an exotherm was present when a sample was flame resistant. Additionally, decomposition at such low temperatures, as were produced by the tosyl derivatives, usually indicate that the degradation products formed will be less combustible and lead to the formation of char.<sup>18</sup> High residues indicated these tosyl derivatives would produce flame retardant char. Higher oxygen index values than trityl-cellulose samples substantiated these findings. The exothermic decomposition and high residue associated with tosyl-cellulose indicated that the derivative underwent dehydration and condensation of decomposition products that increased the yield of carbonaceous char. Therefore, the tosyl group performed, modestly, as a solid phase flame retardant for cellulose.

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