

Preparation of Cellulose Sulfate from α -Cellulose Isolated from *Lantana camara* by the Direct Esterification Method

Neetu Bhatt,¹ P. K. Gupta,¹ Sanjay Naithani²

¹Centre for Advanced Studies in Chemistry of Forest Products, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India

²Cellulose and Paper Division, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India

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ABSTRACT: Cellulose, a (1 \rightarrow 4)-linked β -D-glucopyranosyl polysaccharide, is the main plant cell wall constituent and is water insoluble in its native form. Sodium cellulose sulfate possesses excellent water solubility at degree of substitution (DS) levels as low as 0.25. Cellulose sulfate was prepared from α -cellulose isolated from *Lantana camara* by sulfation in a heterogeneous medium. The variables studied were reaction time, reaction temperature, normality of sulfuric acid, and quantity of sulfuric acid. A water-soluble cellulose sulfate ester with a DS of 0.392 was obtained at a reaction time of 60 min, a temperature 0°C, a

normality of 34.2N aqueous sulfuric acid, and a quantity of aqueous sulfuric acid of 40 mL/g of α -cellulose. The optimized product exhibited cold-water solubility and a clear solution in an aqueous medium, which suggested interesting rheological properties. The optimized product was further evaluated with IR spectroscopy, scanning electron microscopy, thermogravimetric analysis/differential thermal analysis, and wide-angle X-ray diffraction. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2895–2901, 2008

Key words: additives; cellulose; esterification

INTRODUCTION

Cellulose, a (1 \rightarrow 4)-linked β -D-glucopyranosyl polysaccharide, is the main plant cell wall constituent and gives plants their structural support. Cellulose is water insoluble in its native form and is used to prepare different materials, such as paper, filtration membranes, and food additives. Cellulose derivatives are prepared by the replacement of hydrogen atoms of the primary and secondary hydroxyl groups of its β -D-glucopyranosyl units with reactive groups such as methyl, ethyl, carboxymethyl, and acetyl.¹ The esterification of cellulose is one important route of cellulose derivatization, and the resulting esters have entirely different physical and chemical properties from the original cellulose and are soluble in a wide range of solvents.² Methods for the manufacture of cellulose sulfate have been reported in the literature.^{3–6} Sodium cellulose sulfate possesses excellent water solubility at degree of substitution (DS) levels as low as 0.25. This is the lowest DS level at which water solubility is attained by any cellulose derivative.⁷ *Lantana camara* (Verbenaceae) is a weed and is rich in lignocellulosic material.⁸ A water-soluble cellulose sulfate ester was prepared by sulfation of α -cellulose isolated from *L. camara* stems

with sulfuric acid in a heterogeneous medium. Conditions were optimized for reaction time, reaction temperature, normality of sulfuric acid, and quantity of sulfuric acid with respect to DS. The optimized product was examined for solubility in aqueous media, and rheological studies were carried out. The optimized product was further evaluated with IR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA)/differential thermal analysis (DTA), and wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

Materials

The *L. camara* used in the study was collected from the field of the Forest Research Institute's campus. All of the chemicals used were analytical grade.

Isolation of α -cellulose

α -Cellulose was isolated from the stems of *L. camara* by an optimized method.⁸

Preparation of cellulose sulfuric acid ester

An azeotrope of 20–60 mL of 19.8–34.2N sulfuric acid and 33% 1-butanol containing 1.65% ammonium sulfate was cooled to 0°C. The azeotrope was added slowly to cellulose powder (1 g) and was stirred,

Correspondence to: P. K. Gupta (guptapk@icfre.org).

with the temperature maintained from -10 to 10°C for 30–120 min, to form a clear viscous solution. The solution was then poured slowly and with vigorous agitation into 3 volumes of acetone to precipitate cellulose sulfuric acid ester, and then, it was repeatedly washed with acetone.

Preparation of sodium cellulose sulfate ester

Cellulose sulfuric acid ester was neutralized with 5% sodium hydroxide solution at 0°C to form a viscous solution of sodium cellulose sulfate ester. It was precipitated, washed, and dried with acetone at room temperature (yield = 110–125%).

Analysis and measurement: determination of DS⁹

The DS was calculated as follows:

$$\text{DS} = [1.62 \times S (\% \text{ in the sample}) / \{32 - [1.02 \times S (\% \text{ in the sample})]\}]$$

The sulfur content of the cellulose sulfate ester was determined as follows. The cellulose sulfate ester (0.5 g) was refluxed in 250 mL of a 10% hydrogen chloride acid solution overnight, and the sulfate was precipitated by the addition of 25 mL of a 10% barium chloride solution. The precipitate was quantitatively transferred to a weighed Gooch crucible, heated 1 h at 300°C , and ignited 1 h at 600°C .⁹

$$S (\%) = [0.13737 \times \text{Weight of barium sulfate (g)}] / [\text{Sample weight (g)}]$$

Determination of the apparent viscosity (η)

η of the optimized product was determined at a shear rate of 9.3 s^{-1} with a Brookfield (Stoughton, MA) model RVT digital viscometer. The measurement was made at a temperature of $25 \pm 1^{\circ}\text{C}$.

IR spectra

IR spectra of the cellulose sulfate and extracted cellulose were recorded on a Josco FTIR 5300 spectrophotometer with KBr disk pellets from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} with five scans per sample.

SEM

SEM was recorded on a Leo model 435 VP instrument (Carl Zeiss SMT, Oberkochen, Germany). The samples were coated with a thin film of gold to make the surface conductive, prevent surface changing, and protect the surface material from thermal damage by the electron beam.

Thermal studies (TGA/DTA)

TGA of the samples were carried out with a Perkin-Elmer (Pyris Diamond) instrument (Waltham, MA) in nitrogen at a rate of $10^{\circ}\text{C}/\text{min}$.

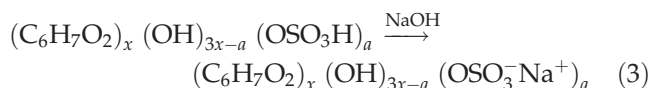
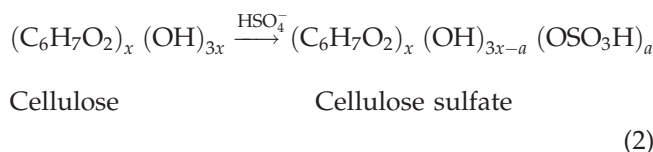
WAXD

WAXD of solid samples was performed with a Bruker AXS D8 Advance X-ray powder diffractometer (Karlsruhe, Germany) with a $\text{Cu K}\alpha$ target.

RESULTS AND DISCUSSION

Cellulose is an alcohol, it undergoes esterification reactions with acids in the presence of a dehydrating agent or by reaction with acid chlorides. The resulting esters have entirely different physical and chemical properties from the original cellulose and are soluble in a wide range of solvents. Cellulose can be esterified with inorganic sulfuric acid in the presence of 1-butanol because, if the sulfation mixture contains an alcohol such as isopropyl or 1-butanol, the degrading action of the sulfuric acid is moderated and the product does not dissolve in the reaction liquor.

The sulfation of cellulose with sulfuric acid to form sodium cellulose sulfate is an example of a typical esterification reaction.¹⁰ In sulfation, the hydrogen sulfate ion, HSO_3^- , is the sulfating species. This ion is produced according to reaction (1). A sufficient amount of water in the reaction mixture is needed for the production of sulfate ions and thus to carry out out sulfation:



Sulfation of α -cellulose isolated from *L. camara* (Av DP 430) was optimized by variation of the process parameters, as shown in Table I. We varied each of the parameters one by one keeping the remaining parameters constant in the reaction. DS was determined, and its dependence on each of the variables was investigated.

The effect of sulfuric acid content on DS was studied. The sulfation of α -cellulose was carried out by variation of the sulfuric acid content, and the DS was determined for all of the conditions. With a reaction time of 60 min, a reaction temperature of

TABLE I
Reaction Parameters Used in the Sulfation of α -Cellulose from *L. camara*

Figure	Experiment	Sulfuric acid concentration (N)	Time (min)	Temperature ($^{\circ}$ C)	Sulfuric acid (mL)	Sulfur (%)	DS
1	a	34.2	60	-10	20	4.15	0.241
	b				30	5.27	0.320
	c				40	6.04	0.378
	d				50	6.04	0.378
	e				60	6.04	0.378
2	a	34.2	60	-10	40	6.04	0.378
	b			-5		6.10	0.384
	c			0		6.22	0.392
	d			+5		6.22	0.392
	e			+10		—	—
3	a	34.2	30	0	40	5.20	0.315
	b		60			6.22	0.392
	c		90			6.01	0.376
	d		120			5.88	0.366
4	a	19.5	60	0	40	2.34	0.128
	b	23.4				2.75	0.152
	c	27.0				5.09	0.308
	d	30.6				5.77	0.357
	e	34.2				6.22	0.392

In all experiments, 1 g of *L. camara* α -cellulose was used.

-10 $^{\circ}$ C, and a sulfuric acid concentration of 34.2N, as shown in Figure 1, with the increase in the amount of sulfuric acid from 20 to 40 mL, the DS increased from 0.241 to 0.378 and then became constant thereafter. Thus, 40 mL of sulfuric acid showed the maximum DS for the sulfation of α -cellulose.

With a sulfuric acid content of 40 mL, the sulfation of α -cellulose was performed at different temperatures, that is, -10 to 10 $^{\circ}$ C. The dependence of DS on the reaction temperature is shown in Figure 2. At a sulfuric acid concentration of 34.2N and a reaction time of 60 min, DS increased from 0.372 to 0.392 prominently as the reaction temperature increased to 0 $^{\circ}$ C and then became constant; finally, at temperatures greater than 10 $^{\circ}$ C, the reaction failed to proceed further because of excessive degradation; the product turned black.

With a sulfuric acid content of 40 mL and a constant temperature of 0 $^{\circ}$ C, the effect of reaction time of sulfation was studied on DS with a sulfuric acid

concentration of 34.2N. The DS increased with the increase in reaction time and reached a maximum in 60 min, and a significant decrease was observed with increasing time thereafter, as shown in Figure 3. The enhancement of DS by the prolonging of the duration of the reaction from 30 to 60 min was a direct consequence of the favorable effect of time on the swelling of *Lantana* cellulose. Similar observations were made earlier by different workers.^{1,10}

With the reaction at a temperature 0 $^{\circ}$ C with a sulfuric acid content of 40 mL and a reaction time of 60 min, the effect of sulfuric acid concentration on DS was investigated, and the results are illustrated in Figure 4. With increasing concentration from 19.8–34.2N, the DS increased significantly as the concentration of sulfuric acid increased up to 34.2N. However, further increases in concentration were not possible because a sufficient amount of water in the reaction was very important.¹¹

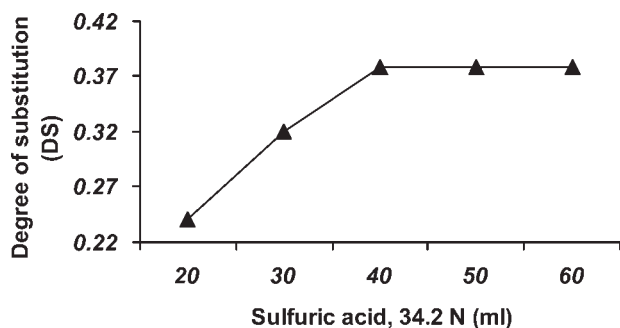


Figure 1 Dependence of DS on the sulfuric acid content. The reaction conditions are shown in Table I.

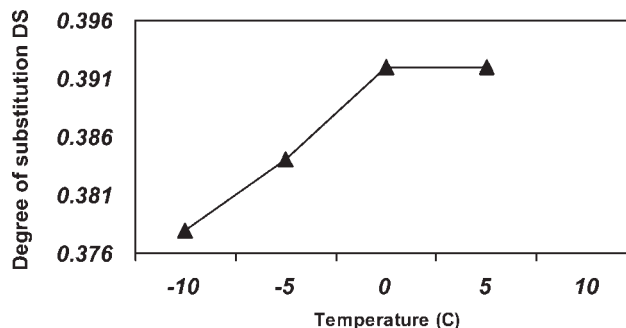


Figure 2 Dependence of DS on the reaction temperature. The reaction conditions are shown in Table I.

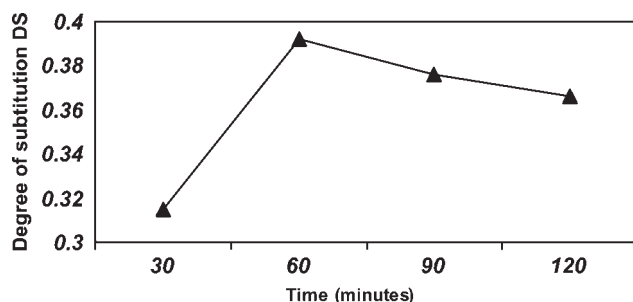


Figure 3 Dependence of DS on the reaction time. The reaction conditions are shown in Table I.

The IR spectra of sodium cellulose sulfate [Fig. 5(b)] displayed prominent bands at 2900, 1066, 638, and 1131 cm^{-1} , which were assigned to $-\text{OH}$ stretching, hydrated $-\text{HSO}_3$ stretching, $\text{S}-\text{O}$ stretching, and $-\text{SO}_2$ symmetric stretching, respectively, which were absent in the α -cellulose [Fig. 5(a)], which thereby indicated the formation of sodium cellulose sulfate.

Figure 6(a,b) shows the scanning electron micrographs of the pure α -cellulose and sodium cellulose sulfate fiber, respectively. The surface topology of raw α -cellulose was found to be even, whereas the modified α -cellulose revealed that the fiber surface had deposits of sulfate molecules, and the evenness of the fiber surface was not present.

As shown by the WAXD studies, the degree of crystallinity of the extracted cellulose [Fig. 7(a)] was 53%. On sulfation [Fig. 7(b)], this was further reduced to 35% because of fewer intermolecular chain interactions. Such a decrease in crystallinity was desirable in the direction of the maximum homogenization of the linear chain of cellulose sulfate for network formation, and the surface-active nature of cellulose sulfate should have further contributed to facilitate uniform network formation.

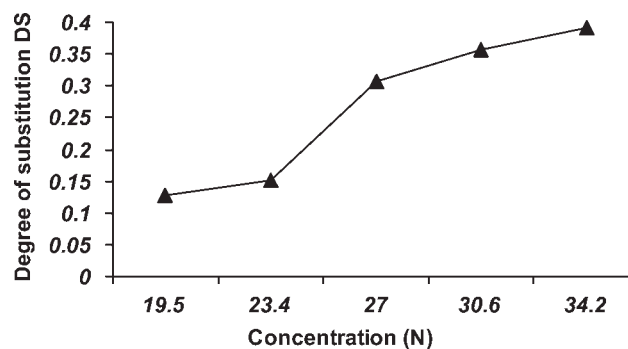
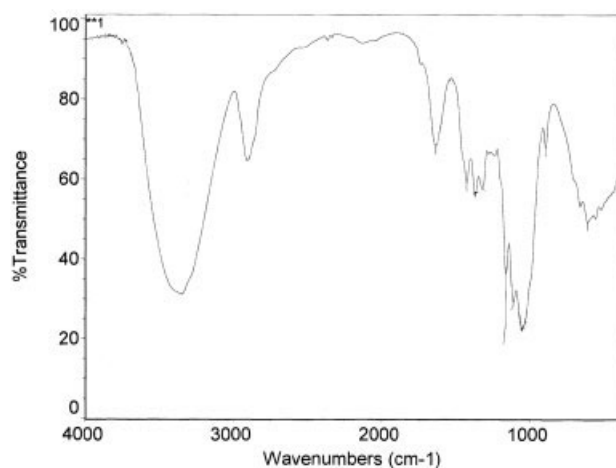


Figure 4 Dependence of DS on the sulfuric acid concentration. The reaction conditions are shown in Table I.

DTA curves for the parent cellulose and optimized cellulose sulfate samples are shown in Figure 8(a,b), respectively. In the case of cellulose, only one endothermic peak was observed, whereas for the cellulose sulfate derivative, many endothermic peaks were observed at various temperatures. Endothermic peaks occurred at 346°C in cellulose and at 47°C, 200, 263, 444, and 713°C in the case of cellulose sulfate. These endothermic peaks were formed because of decomposition, which occurred in the cellulose and cellulose sulfate. In cellulose sulfate, these endothermic peaks were due to the semimelting and decomposition of the sulfate molecule. The TGA curve for the parent cellulose sample showed that after an initial loss of moisture at 100°C, a loss of weight in the cellulose occurred. For cellulose, this loss was attributed to the actual pyrolysis by a minor decomposition reaction at about 250 and 324°C, and major decomposition proceeded at 349 and 375°C. The TGA curve for cellulose sulfate revealed that after the initial loss of moisture at 100°C, decomposition took place due to pyrolysis and the volatilization of the sulfate group at various successive temperatures, namely, 200°C

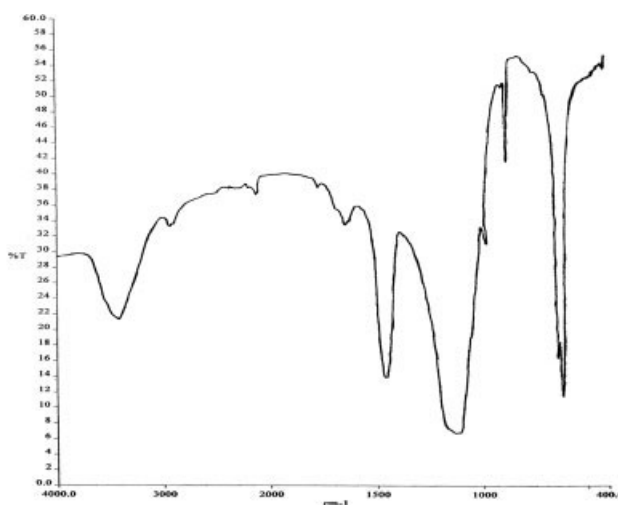


Figure 5 Fourier transform infrared spectra of (a) α -cellulose isolated from *L. camara* and (b) cellulose sulfate.

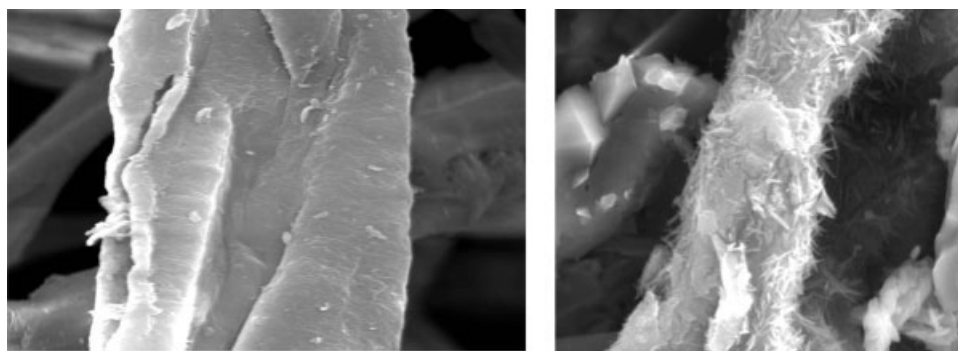


Figure 6 SEM images of (a) α -cellulose isolated from *L. camara* and (b) cellulose sulfate (3000 \times).

(94.30%), 275 $^{\circ}$ C (86.39%), 499 $^{\circ}$ C (81.98%), 699 $^{\circ}$ C (76.16%), and 758 $^{\circ}$ C (69.32%), and when 31.05% of the residue was left, this remaining amount of the product was stable at 800 $^{\circ}$ C. The decomposition temperature of the cellulose sulfate derivative compared to that of crude cellulose could be attributed to the swelling of cellulose chains due to the decrease in its crystallinity on sulfation.

The water solubility of cellulose sulfate was linked to the presence of sulfate groups. Cellulose sulfate with DSs as low as 0.25 have been reported to possess excellent water solubility. This is the lowest DS at which water solubility is attained by any cellulose derivative.⁶ A DS of 0.392 was obtained for the optimized cellulose sulfate ester, and the product exhibited cold-water solubility and a clear solution in an aqueous medium. η of the optimized product in an aqueous medium at a 2.0% solution concentration was 625 cps at a shear rate of 9.3 s $^{-1}$ and temperature of 25 \pm 1 $^{\circ}$ C.

CONCLUSIONS

A water-soluble sodium cellulose sulfate ester was prepared by the sulfation of α -cellulose isolated

from stems of *L. camara* with sulfuric acid in a heterogeneous medium. The conditions optimized were sulfuric acid content, reaction time, temperature, and concentration of sulfuric acid, and a water-soluble cellulose sulfate ester was prepared. With an optimized set of conditions, namely, an aqueous sulfuric acid content of 40 mL/g of α -cellulose, a reaction time of 60 min, a temperature of 0 $^{\circ}$ C, and a concentration of aqueous sulfuric acid of 34.2N, a sodium cellulose sulfate ester with a DS of 0.392 was obtained. The sodium cellulose sulfate prepared showed IR absorption bands at 2900, 1066, 638, and 1131 cm $^{-1}$, which confirmed the sodium cellulose sulfate substitution of the α -cellulose molecule. In the scanning electron micrographs, the surface topology of raw α -cellulose was found to be even, whereas in the sulfated α -cellulose, evenness of the fiber surface was not present. The degree of crystallinity of the extracted cellulose was 53%, which, on sulfation, was reduced to 35% because of fewer intermolecular chain interactions. In case of cellulose in the DTA curves, only one endothermic peak was observed at 346 $^{\circ}$ C, whereas for the cellulose sulfate derivative, many endothermic peaks were observed at various temperatures, namely, 47, 200, 263, 444,

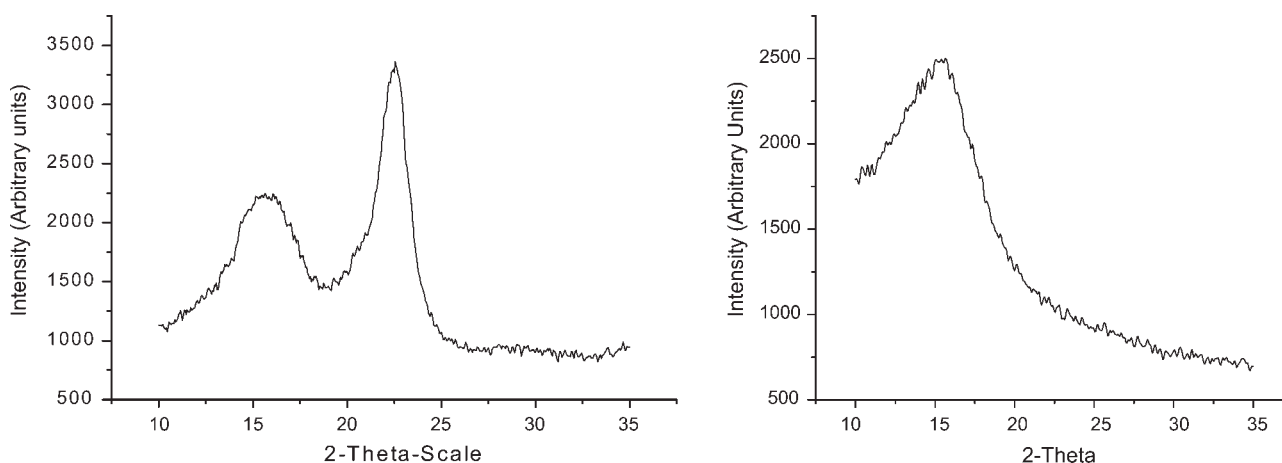


Figure 7 WAXD of (a) α -cellulose isolated from *L. camara* and (b) cellulose sulfate.

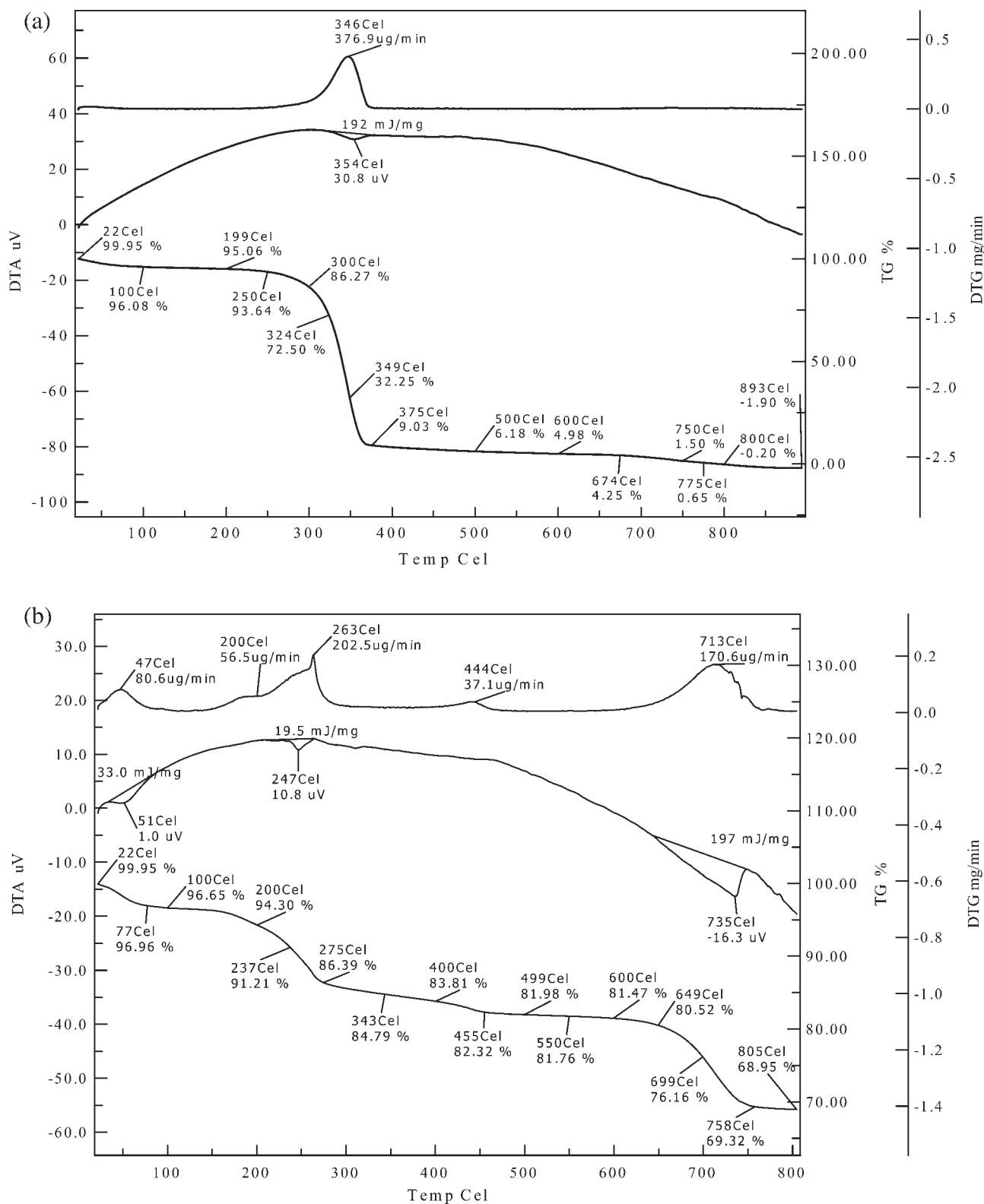


Figure 8 TGA/DTA of (a) α -cellulose isolated from *L. camara* and (b) cellulose sulfate.

and 713°C. These endothermic peaks were formed because of decomposition, which occurred in the cellulose and cellulose sulfate. In cellulose sulfate, these

endothermic peaks were due to the semimelting and decomposition of the sulfate molecule. TGA curves for the parent cellulose showed that after an initial

loss of moisture at 100°C, a loss of weight of cellulose occurred at about 250 and 324°C, and major decomposition proceeded at 340 and 374°C, but in the case of cellulose sulfate, after the initial loss of moisture at 100°C, decomposition took place due to pyrolysis and volatilization of the sulfate group at various successive temperatures, namely, 200°C (94.30%), 275°C (86.39%), 499°C (81.98%), 699°C (76.16%), and 758°C (69.32%), and when 31.05% of the residue was left, this amount was shown to be stable at 800°C. The decomposition temperature of the cellulose sulfate derivative compared to that of the crude cellulose was attributed to the swelling of cellulose chains due to the decrease in its crystallinity on sulfation. The optimized product exhibited cold-water solubility and gave a clear solution in an aqueous medium. η of the optimized product in an aqueous medium at 2.0% solution concentration was 625 cps at a shear rate of 9.3 s^{-1} and a temperature of $25 \pm 1^\circ\text{C}$.

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