# Cellulose Furoate. II. Characterization

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**ABSTRACT:** The chemical structure of furoate moiety in cellulose furoate was confirmed by FTIR, UV spectroscopy, and NMR and X-ray spectroscopy. Thermal property was studied by TGA and DSC. TGA results showed cellulose furoate has a very similar thermal property to cellulose. Thermograms revealed its decomposition started at about 300°C, and had a maximum rate of weight loss at about 360°C. DSC studies revealed the glass transition temperatures for cellulose furoates ranged from 207 to 230°C, depending upon the DS. *Myrothecium verrucaria, Cheatomium globosum,* and *Aspergillus terreus* were used to determine the biodegradability of cellulose furoate. Biodegradation tests showed that each glucose unit in cellulose required as least one substitution to significantly improve the antibiodegradation property. Solubility tests revealed that cellulose furoates with DS ranged from 1.09 and 2.66, prepared from the homogeneous system, are dissolvable in dioxane, DMSO, DMF, and DMAc. Specimens prepared from the heterogeneous system; only those with DS ranging from 1.09 and 1.98 are dissolvable in DMSO. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 243–252, 2001

**Key words:** cellulose furoate; FITR; TGA; DSC; degree of substitution; biodegradation; solubility; hydrogen bonding; crystallinity; *Myrothecium verrucaria; Cheatomium globosum; Spergillus terreus*

## INTRODUCTION

Cellulose is a wonder material. Its many derivatives also display unique properties for important applications in many industries. Cellulose esters, such as cellulose acetate, cellulose heteroesters, and fatty acid esters, have been widely studied for their structures, reactivities, and thermal behaviors.[1–5] Cellulose furoate, a cellulose derivative with aromatic esters, was a relatively unknown cellulose derivative. The approach to identify cellulose furoate's application dates back to the late 1960s. It was initially studied for its rot resistance[6–8] and membrane use.[9] Only heterogeneous reaction was used to prepare cellulose furoate at that time.

In a previous study,[10] we synthesized cellulose furoate in both heterogeneous and homogeneous reactions. Cotton cellulose and wood cellulose were used. Lithium chloride/dimethylacetamide (LiCI/DMAc) cosolvents were used to dissolve cellulose for the homogeneous reaction. The esterification reaction between cellulose and 2-furoyl chloride was systematically investigated.

In this study, characterization of cellulose furoates with various degrees of substitution (DS) prepeared from both heterogeneous and homogeneous reactions was made. Structure of cellulose furoate was elucidated by means of Fourier transform infrared (FTIR) spectroscopy, ultraviolet (UV) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Its thermal properties were evaluated by thermogravimetry analysis

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(TGA) and differential scanning calorimetry (DSC). Bioresistance of cellulose furoate against fungal degradation *in vitro* was also investigated.

## EXPERIMENTAL

### Materials

Cellulose furoates with various DS were synthesized either in a homogeneous or heterogeneous system. Cotton pulp cellulose and wood pulp cellulose from Hercules, Inc., and commercial cotton cellulose powder from the Aldrich Chemical Company were used. In the homogeneous system, LiCl/DMAc was used as the solvent. Detail of the synthesis procedures was reported in an earlier article.[10]

### Characterization

#### *Furior Transform Infrared (FTIR) Spectroscopy*

Cellulose furoate specimens were ground with KBr and pressed to make transparent pellets. IR spectra were obtained from a FTIR spectrophotometer (Nicolet, Magna-IR 560).

#### *Ultraviolet (UV) Spectroscopy*

Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 3A UV/VIS spectrophotometer. Solutions of cellulose furoates were prepared by dissolving the specimens in 5% LiCl/DMAc cosolvents.

#### *Nuclear Magnetic Resonance (NMR) Spectroscopy*

Proton NMR spectra were recorded at 200 MHZ on a Bruker 300 NMR spectrometer at room temperature. The specimen concentration was 10 mg/mL. DMSO-$d_6$ was used as the solvent.

#### *Thermogravimetry Analysis (TGA)*

A Perkin-Elmer 7 series thermal analysis system was used to study thermal behavior of cellulose furoates. The specimen weight was about 3 mg. The thermograms of specimens were obtained by using a heating rate of 20°C/min under nitrogen purge.

#### *Differential Scanning Calorimetry (DSC)*

A Perkin-Elmer DSC-4 was used to obtain the DSC thermograms. Measurements were carried out under a nitrogen purge with a heating rate of 40°C/min and a cooling rate of 320°C/min. Because the cellulose furoate specimens were a loose powder, they were pressed into small pellets to increase the heat transport rate. Each specimen was run twice. When the temperature reached 260°C, the specimen was quenched to 60°C at a cooling rate of 320°C/min and tested again.

#### *X-Ray Spectroscopy*

An XDS-200 wide-angle X-ray diffractometer from Scintag, Inc. was used to study the changes in supramolecular structures of cellulose and its furoate derivatives. The equatorial diffraction patterns were measured from $2\theta = 10°$ to 35° using Cu radiation ($K_{\alpha 1} = 1.54056$ angstroms) at 45 kV and 40 mA.

#### *Biodegradation Test*

To test the resistance of cellulose furoate against fungal degradation, a simple *in vitro* culture method was used.[11] The test was originally designed to evaluate effectiveness of preservatives for cellulosic materials. It was modified to utilize cellulose furoate as the sole organic carbon source in a mineral salts medium. This medium contained all the necessary growth nutrients for fungal growth except a carbon source. If the test fungi can grow in this medium with cellulose furoate as the carbon source, it suggests that cellulose furoate is decomposed by the fungi.

In these tests, *Myrothecium verrucaria* and *Cheatomium globosum* are employed as the standard test fungi. In addition, another standard fungus (*Aspergillus terreus*), often used for testing durability of fiber boards in the soil, was also included in this evaluation. *Myrothecium verrucaria* #9095, *Cheatomium globosum* #6205, and *Aspergillus terreus* #10690 were purchased from the American Type Culture Collection (Rockville, MA).

The mineral salts medium was composed of 3.0 g ammonium nitrate, 2.5 g monobasic potassium phosphate, 2.0 g dibasic potassium phosphate, 2.0 g magnesium sulfate with $7H_2O$, 20 g BBL purified agar (Becton Dickinson Microbiology Systems, Cockeysville, MD), and 1.0 L deionized water. Each salt was dissolved separately and added together. Agar was finally added to the medium. The medium was stirred and heated until the agar was dissolved. Cellulose furoate (0.5 g) or cellulose powder (60 mesh, 0.5 g) was mixed with 450 mL hot mineral salts medium and auto-

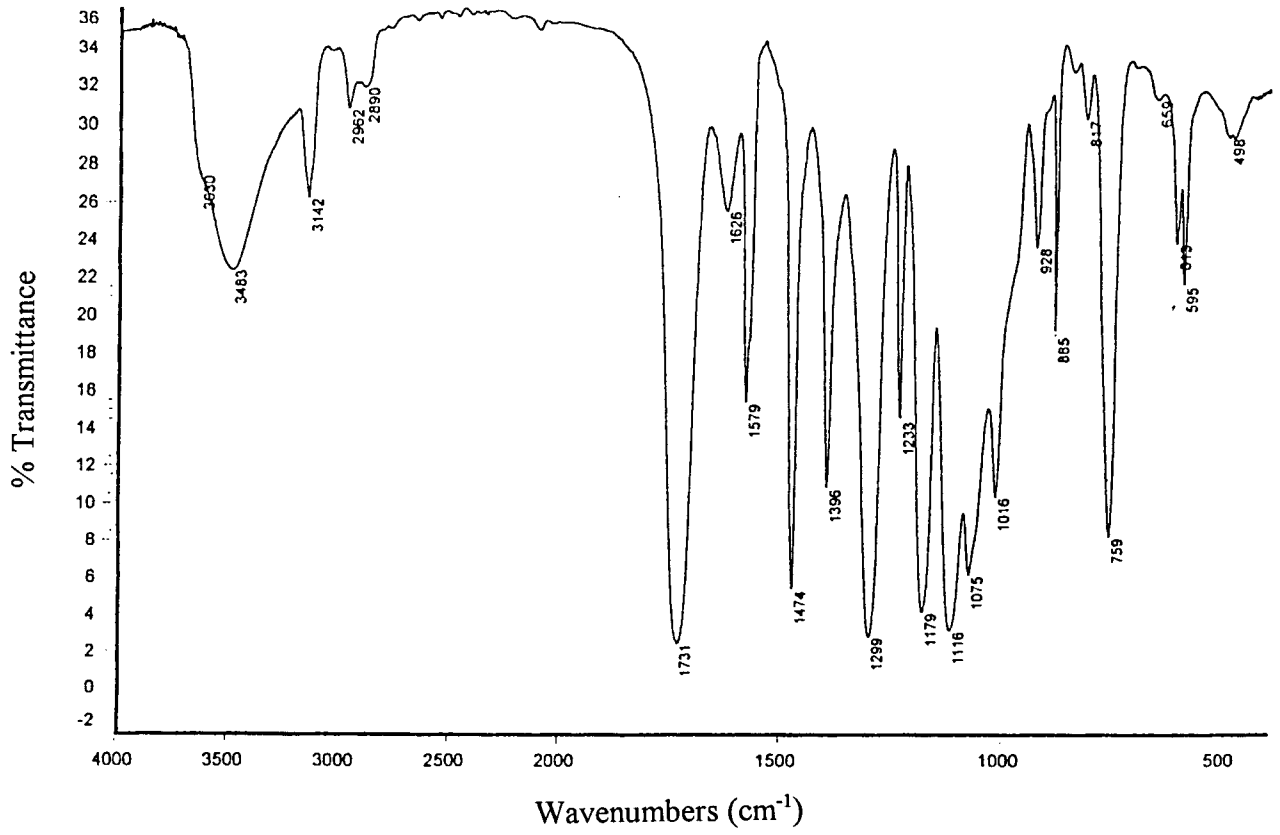


**Figure 1** The IR spectrum of cellulose furoate (DS = 2.84) prepared from a homogeneous reaction.

claved at 120 to 125°C under 15 psi. After sterilization the medium was stirred to suspend the cellulose furoate until the temperature dropped to 45°C. The medium was then quickly transferred to sterile Petri dishes, 25 to 30 mL per plate. Each of the three fungi was inoculated at the center of the plates, five plates for each fungus. There were to controls—one with cellulose and another without any organic carbon source. The plates were sealed with parafilm and incubated at room temperature under office illumination for 30 days. The growth of the fungi was recorded daily in the first 7 days. The so-called "biodegradable" specimen with the highest DS and "highly resistant" specimen with the lowest DS were tested again. The rate of biodegradation was evaluated by observing fungal growth on the agar surface.

### *Solubility Test*

Several reagent-grade solvents were used to study solubility of cellulose furoates with different DS. They are dioxane, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAc), LiCl/DMAc, and ethanol/$CH_2Cl_2$.

## RESULTS AND DISCUSSION

### Analysis of FTIR Spectra

A typical FTIR spectrum of cellulose furoate prepared from a homogeneous solution with a DS of 2.84 is shown in Figure 1. The spectrum displayed hydroxyl group absorption at 3488 $cm^{-1}$, aromatic C—H absorption at 3142 $cm^{-1}$, carbonyl group C═O absorption at 1731 $cm^{-1}$, and aromatic furan ring absorption at 1579 $cm^{-1}$. Moreover, Figure 2 showed the spectra of cellulose furoates prepared from a homogeneous reaction with various DS. As the DS increased, the absorption strength at about 3142, 1728, and 1579 $cm^{-1}$ increased, and both peaks of $\nu_{OH}$ and $\nu_{C=O}$ shifted to higher frequencies. The FTIR spectra of cellulose furoates prepared from a heterogeneous reaction with various DS are shown in Figure 3. For the cellulose furoate made from homogeneous re-

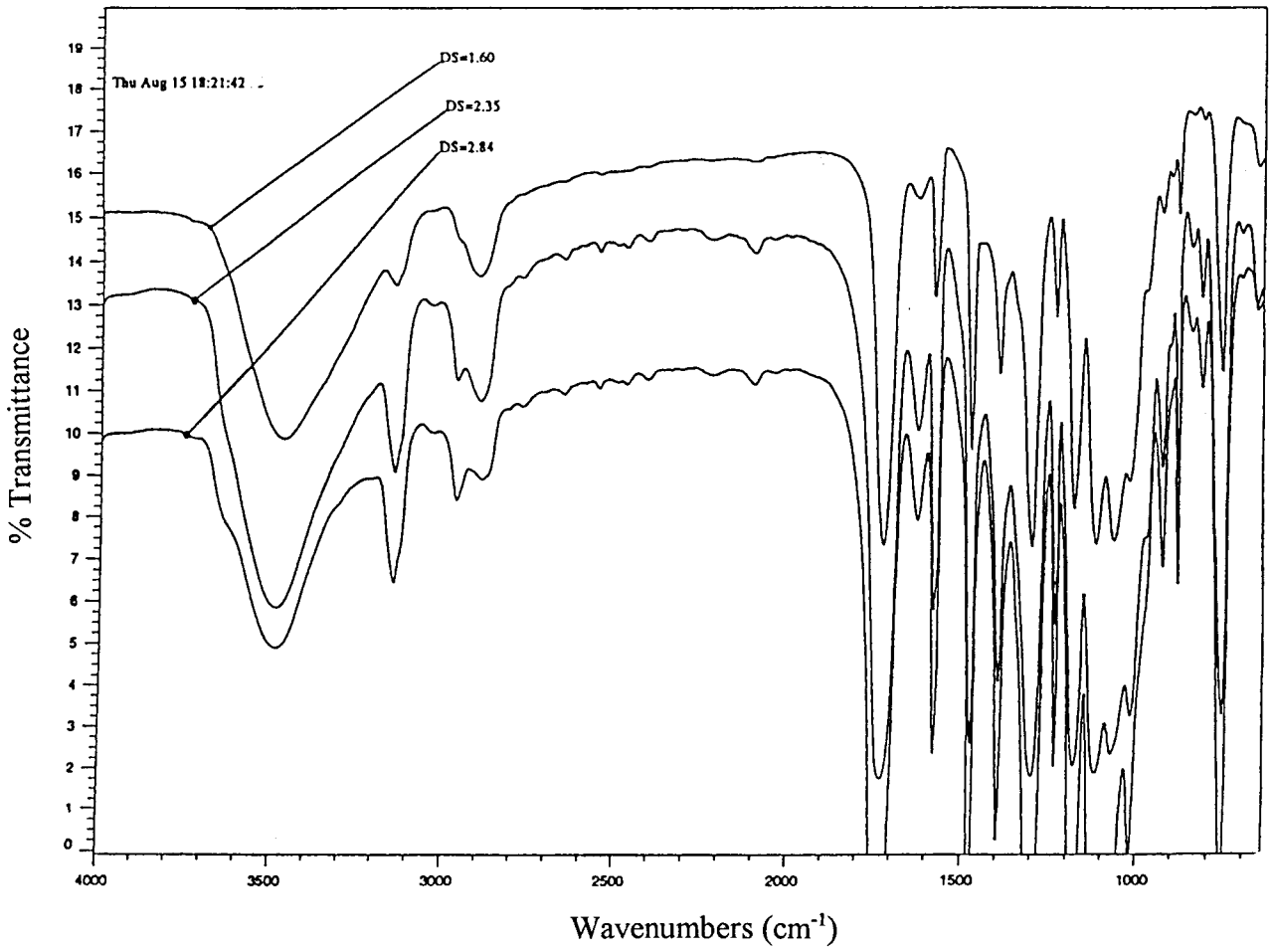


**Figure 2** IR spectra of cellulose furoates (DS = 1.60, 2.35, and 2.84) prepared from a homogeneous reaction.

action, the frequency of $\nu_{OH}$ absorption shifted from 3442.1 to 3488.6, and that of $\nu_{C=O}$ shifted from 1721.4 to 1732.7 $cm^{-1}$ as DS increased from 0.64 to 2.84 (Figs. 4 and 5). Similar frequency shifts of $\nu_{OH}$ and $\nu_{C=O}$ absorption also took place in cellulose furoate specimens obtained from the heterogeneous reaction. The frequency shifts were also shown in Figures 4 and 5.

One of the most important reasons caused the $\nu_{OH}$ and $\nu_{C=O}$ peaks to shift is due to hydrogen bonding.[12] Hydrogen bonding takes place between OH and C=O will lead to the shift of absorption of carbonyl groups ($\nu_{C=O}$) to a lower frequency. Because the increase in the DS reduced the number of hydroxyl groups on cellulose chains, it consequently reduced the sites for hydrogen bonding. The shift was significant for cellulose furoates with various DS prepared from the homogeneous reaction, but not for those from the heterogeneous reaction. For the former reaction, the increase in the DS from 2.35 to 2.84 resulted in shifting the frequency from 1729.7 to 1732.7 $cm^{-1}$. It was a shift of 3.0 $cm^{-1}$. For the latter reaction, the increase in the DS from 2.35 to 2.83 resulted in shifting from 1731.9 to 1732.3 $cm^{-1}$. It was just a shift of 0.4 $cm^{-1}$.

Because hydroxyl and carbonyl groups have the tendency to form intermolecular and intramolecular hydrogen bonding along the cellulose chain, the shift of absorption frequency clearly indicated such a phenomenon taking place in cellulose furoate. The uniformity of substitution reaction taking place in the heterogeneous system is by and large controlled by the accessibility of hydroxyl groups in the cellulose. Hence, most of the unaccessible, residual hydroxyl groups are believed to be trapped in the crystalline structure. Moreover, these hydroxyl groups are not available to form hydrogen bonding with carbonyl group. Hence, the $\nu_{C=O}$ frequencies of cellulose

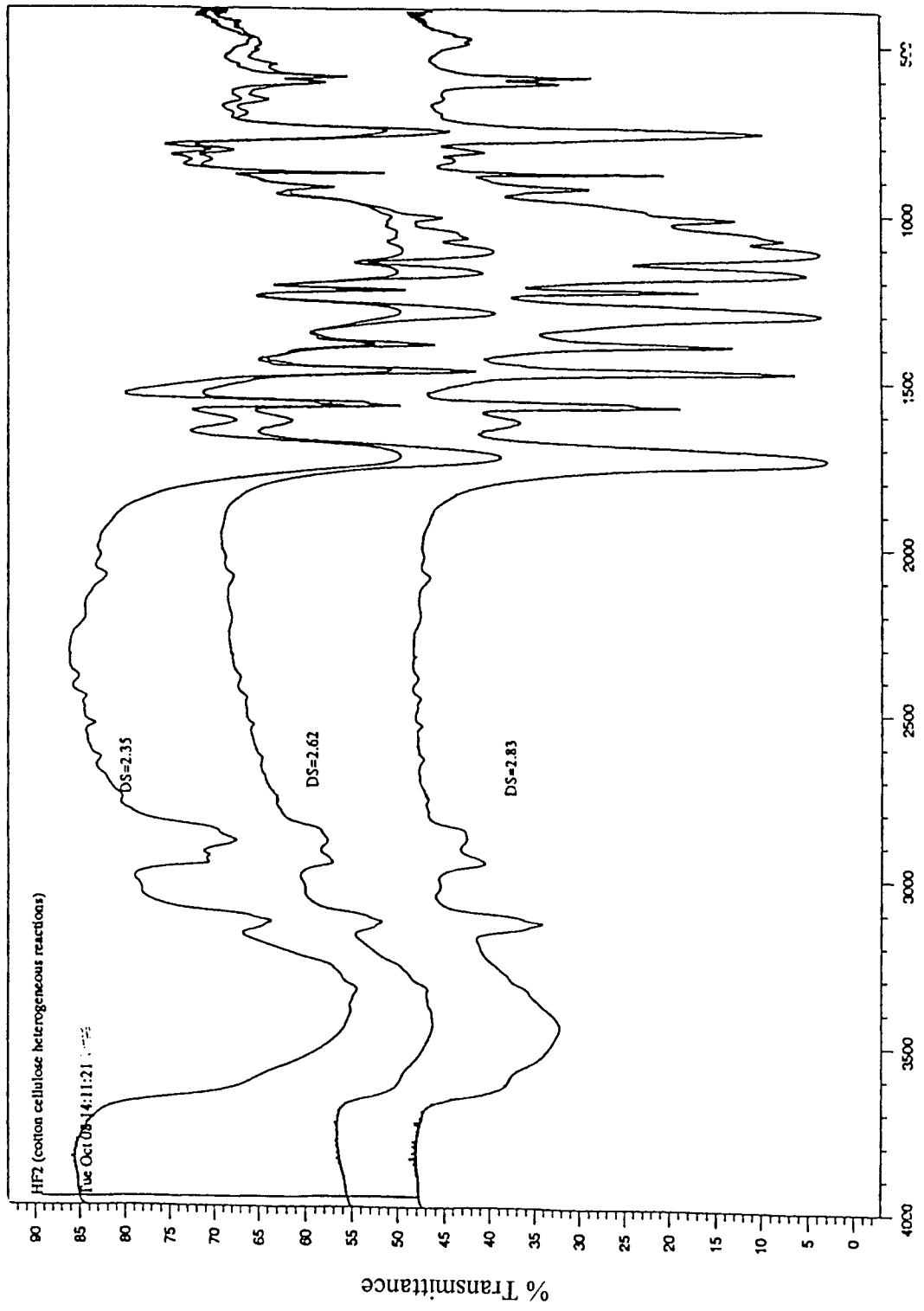


**Figure 3** IR spectra of cellulose furoates (DS = 2.35, 2.62, and 2.83) prepared from a heterogeneous reaction.

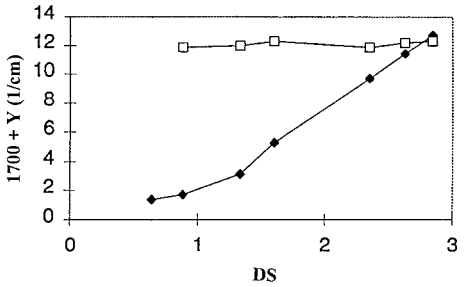


**Figure 4** The frequency shifts of carbonyl group of cellulose furoates with different DS, prepared from heterogeneous (□) and homogeneous (◆) reactions.

furoates derived from the heterogeneous reaction remain at about 1732 $cm^{-1}$ without a significant shift at various DS values. On the other hand, for cellulose furoates derived from the homogeneous reaction, the residual hydroxyl groups at cellulose are available to form hydrogen bonding with carbonyl groups. Because the increase in DS values reduces the number of hydroxyl groups, consequently, the percentage of hydrogen bonds is reduced.

The presence of hydrogen bonding and uniformity of substitution was evident from the shift of $\nu_{OH}$ absorption in cellulose furoate. With a localized distribution of hydroxyl groups, there is a greater probability for formation of hydrogen bonding. As shown in Figure 3, the hydrogen bonding shifted the absorption of $\nu_{OH}$ to a lower frequency.[12]

## Ultraviolet Spectrum (UV)

Cellulose furoate exhibited different UV absorption region from either sodium furoate or 2-furoyl chloride. The UV spectra (Fig. 6) showed that the maximum absorption ($\lambda_{max}$) of cellulose furoate was at about 275 nm in LiCl/DMAc solution. The

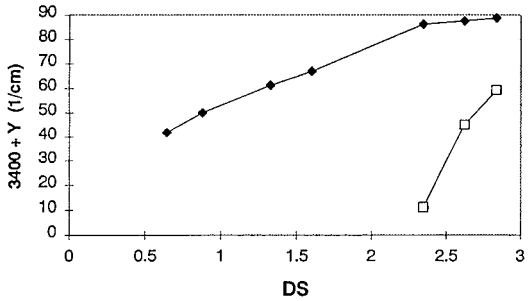


**Figure 5** The frequency shifts of hydroxyl group of cellulose furoates with different DS, prepared from heterogeneous (□) and homogeneous (◆) reactions.

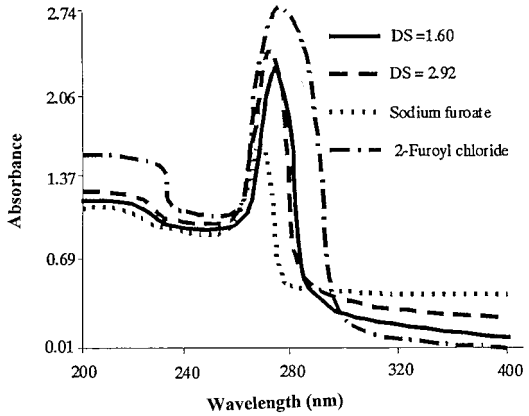


**Figure 6** UV spectra of cellulose furoates in 5% LiCl/DMA, sodium furoate and 2-furoyl chlordie.

absorption was between the maximum absorption of sodium furoate ($\lambda_{max}$ = 270.3 nm) and 2-furoyl chloride ($\lambda_{max}$ = 277 nm) in LiCl/DMAc solution.

## X-Ray Spectroscopy

Analysis of X-ray spectrogram enables the study of major crystal planes for space units in cellulose. These planes for cellulose are represented by peaks with different intensities in the diffractogram, as shown in Figure 7. The diffraction peaks displayed at $2\theta$ = 14.83°, 16.44°, 20.66°, 22.61°, and 34.64° can be identified as corresponding to the planes for 101, $10\bar{1}$, 021, and 002, respectively.[10]

The X-ray diffractograms of cellulose furoates with different DS are also included in Figure 7. Apparently, broader diffraction patterns were observed from cellulose furoate prepared either from a homogeneous or heterogeneous system, indicating that certain crystal structures were either modified or destroyed.[13] Consequently, the crystallinity of cellulose furoate decreased as the DS increased. The diffractogram also revealed that cellulose furoate with similar DS prepared from the homogeneous system contained a more amorphore phase than that prepared from the heterogeneous system. For the latter specimen with a DS of 2.83, the refraction pattern at peaks $2\theta$ = 22.2° (002 plane), 20.0° (021 plane), 18.8°, and 16.6° were still discernible, whereas only a broad absorption pattern was detected from the specimen prepared from the homogeneous system. Because hydrogen bonding is an important factor for the arrangement and coherence of the cellulose chains in the crystal lattice,[14] the loss of crystallinity also suggested the loss of hydrogen bonding in cellulose furoate.

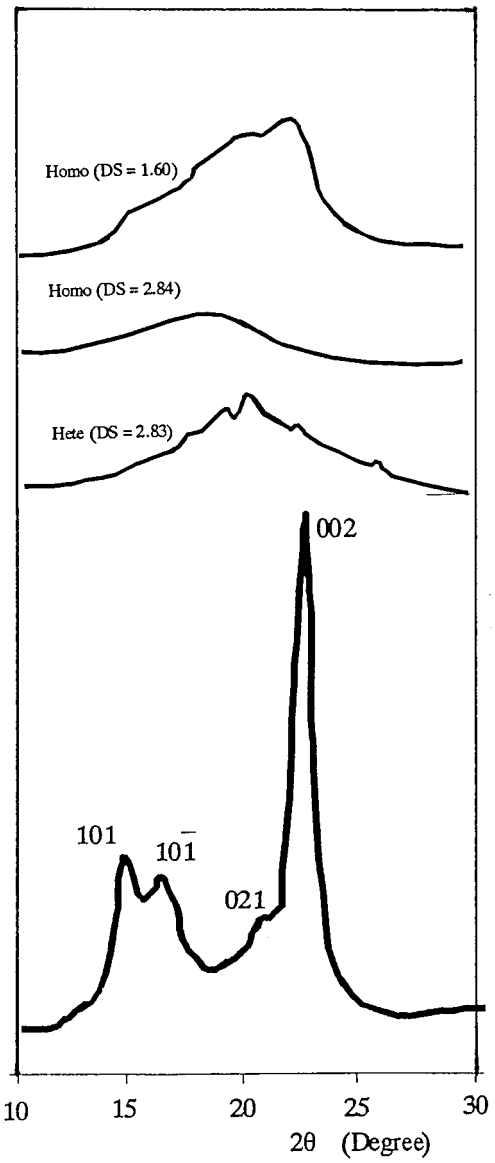


**Figure 7** X-ray diffractograms of cellulsoe fuorates prepared from homogeneous and heterogeneous reactions.

## Nuclear Magnetic Resonance Spectroscopy (NMR)

The success of converting cellulose into cellulose furoate was also substantiated by the NMR study. The $^1$H-NMR spectrum of cellulose furoate with a DS of 1.61 is shown in Figure 8. The NMR spectrum recorded with deuterated DMSO-$d_6$ clearly showed the three signals of three protons on the furan ring. The values of H-5′, H-3′, and H-4′ on furan ring were 7.88, 7.33, and 6.62 ppm, respectively, and the area ratio of the signals was about 1.0 : 1.0 : 1.0.

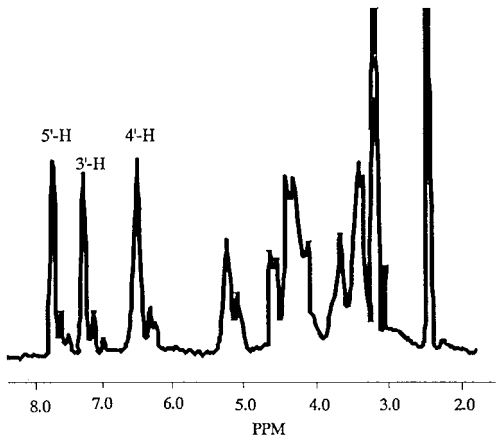


**Figure 8** $^1$H-NMR spectrum of cellulose furoate (DS = 1.61) in DMSO-$d_6$.

## Thermogravimetry Analysis (TGA)

Cellulose and its derivatives are relatively thermally unstable. Upon heating them above 150°C, they appear to undergo internal changes accompanied by decomposition into low-molecular weight, volatile molecules.[15] Cellulose heated above 300°C undergoes a rapid decomposition.[16] Antal[17] summarized the activation energies for the pyrolysis of cellulose materials under 300°C obtained by TGA, which ranged from 138 to 251 kJ/mol.

A typical TGA plot for cellulose furoate is shown in Figure 9. Cellulose furoate was heated at an increment of 20°C/min under nitrogen purge. TGA results showed cellulose furoate has a very similar thermal property to cellulose and cellulose acetate. The thermogram indicated that decomposition started at about 300°C, and had a maximum rate of weight loss at about 360°C. At

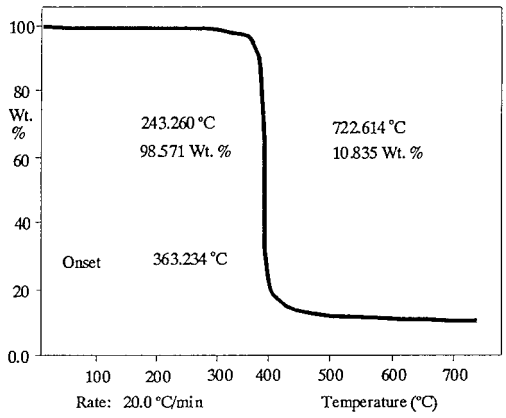


**Figure 9** A TGA thermogram of cellulose trifuroate.

**Table I Decomposition Onset Temperatures (°C) for Cellulose and Cellulose Furoates Determined by TGA**

| | Cellulose Furoate | | |
|---|---|---|---|
| Cellulose | DS = 1.5 | DS = 2.35 | DS = 3.0 |
| 372.4 | 370.0 | 366.0 | 363.2 |

Specimens were run with a heating rate at 20°C/min under nitrogen.

722°C, a char consisting of 10.8% by weight of the original specimen was registered. The decomposition onset temperatures of cellulose furoates with different DS and cellulose are listed in Table I.

### Differential Scanning Calorimetry (DSC) Analysis

The glass transition temperature of cellulose furoate was probed by DSC. The DSC thermograms of cellulose furoate with a DS of 2.57 is shown in Figure 10. The $T_g$ from the second run was 207.4°C. The endothermal peak at the 75 to 135°C range in the first run could be easily assigned to the evaporation of moisture presented in cellulose furoate. The reason to choose the $T_g$ from the second run is to make all the $T_g$ values more comparable.

As it is well known, different techniques yield different $T_g$ values and only those values determined by the same method are comparable. Moreover, differences are caused not only by the nominal composition of the products (molecular mass, degree of substitution, etc.) but also by interbatch variability. No fixed relationship between DS and $T_g$ was obtained, i.e., two cellulose furoate specimens with very close DS (2.88 and 2.89) have very different $T_g$ values (202 and 220°C respectively), as shown in Table II.

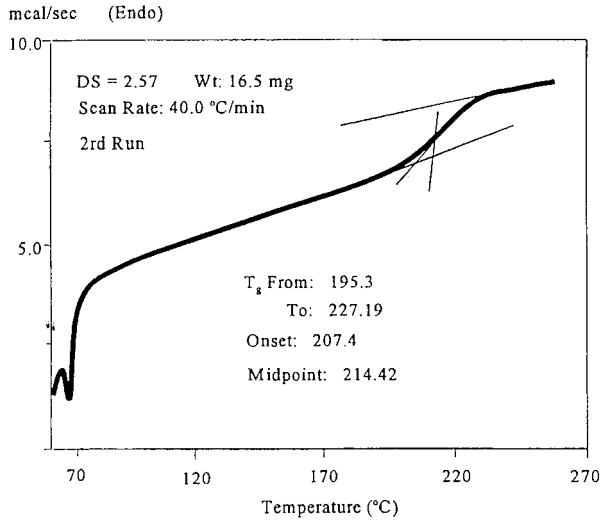


**Figure 10** DSC thermogram of cellulose furoate (DS = 2.57).

**Table II Glass Transition Temperatures ($T_g$) of Cellulose Furoates**

| | |
|---|---|
| Cellulose furoate (DS = 2.43) | 230°C |
| Cellulose furoate (DS = 2.57) | 207 |
| Cellulose furoate (DS = 2.88) | 202 |
| Cellulose furoate (DS = 2.89) | 220 |

### Biodegradation Test

The ability to decompose cellulose is fairly widely distributed among the fungi.[18] One of the major objectives of this research is to prepare an antifungal, rotproofing cellulose fiber. In this study, *Myrothecium verrucaria, Cheatomium globosum,* and *Aspergillus terreus* were used to determine the biodegradability of cellulose furoate. The experimental results for cellulose furoate with various DS treated with these fungi are shown in Table III. For the cellulose control specimen, very thick and fast-growing mycelia was observed. Cellulose furoate with lower DS also exhibited faster fungi grew. As shown in Table III for all fungi tested, it is quite obvious that the borderline for the biolabile cellulose furoates possessed DS between 1.09 and 1.52. This implies that each glucose unit needs at least one substitution to significantly improve the antibiodegradation property.

**Table III Biodegradability of Cellulose Furoates with Different DS**

| | DS of Cellulose Furoate | | | | | |
|---|---|---|---|---|---|---|
| Fungi | 0 | 0.78 | 1.09 | 1.52 | 1.81 | 2.66 |
| Chaetomium globosum | B | B | B | N | N | N |
| Myrothecium verrucaria | B | B | B | N | N | N |
| Aspergillus terreus | B | B | B | N | N | N |

B: Biodegradable.
N: Nonbiodegradable.

**Table IV Solubility of Cellulose Furoates Produced Homogeneously**

| DS | Dioxane | DMSO | DMF | DMAc | 9% LiCl/DMAc | 5% EtOH/$CH_2Cl_2$ |
|---|---|---|---|---|---|---|
| 0.15 | | | | | D | |
| 0.75 | | D | | | D | |
| 1.09 | D | D | D | D | D | D |
| 1.60 | D | D | D | D | D | D |
| 1.98 | D | D | D | D | D | D |
| 2.11 | D | D | D | D | D | D |
| 2.42 | D | D | D | D | D | D |
| 2.66 | D | D | D | D | D | D |
| 2.92 | D | D | | D | D | D |

D: Dissolvable.

The cellulase secreted from fungi only attacks the glucose units without any substitution.

### Solubility Test

The solubility of a cellulose derivative depends upon the nature of the substituent, the degree of substitution, and the distribution of substituted sites. Many solvents were screened to test the solubility for cellulose furoates. Results are shown in Table IV. Regardless of their methods of preparation, cellulose furoates dissolved readily in the cosolvent system such as LiCl/DMAc and ethanol/$CH_2Cl_2$. For the specimens with DS ranged from 1.09 and 2.66, prepared from the homogeneous system, they can be dissolved readily in dioxane, DMSO, DMF, and DMAc. Specimens prepared from the heterogeneous system, only those with DS ranged from 1.09 and 1.98 can be dissolved in DMSO (see Table V). Apparently, cellulose furoates produced heterogeneously are more difficult to dissolve than those produced homogeneously.

A possible explanation of the different solubility between cellulose furoates prepared homogeneously and heterogeneously is the difference in the amount of intermolecular hydrogen bonding being formed in the specimens, and hence, the degree of crystallinity. As discussed earlier, specimens prepared from the heterogeneous system possessed higher amount of crystallinity. For the heterogeneous reaction, the surface of the cellulose may have higher reactivity than the bulk and hence to yield higher DS. Alternately, the internal core of cellulose may have lower reactivity, and hence substitution reaction is low. For the homogeneous reaction, substitution reaction took place throughout the structure to produce cellulose with low crystallinity. Accordingly, cellulose furoates prepared from the homogeneous system can be dissolved more readily than those prepared from the heterogeneous system.

## CONCLUSIONS

1. The furan ring structure of cellulose furoate was confirmed by FTIR, UV, and $^1$H-NMR spectra.
2. TGA thermographs showed cellulose furoate had a very similar decomposing pat-

**Table V Solubility of Cellulose Furoates Produced Heterogeneously**

| DS | Dioxane | DMSO | DMF | DMA | 9% LiCl/DMA | 5% EtOH/$CH_2Cl_2$ |
|---|---|---|---|---|---|---|
| 0.36 | | | | | D | |
| 1.07 | | | | | D | D |
| 2.35 | | D | | | D | D |
| 2.62 | | D | | | D | D |
| 2.83 | | D | | | D | D |
| 2.98 | | | | | D | D |

D: Dissolvable.

tern compared to that of cellulose and cellulose acetate. The thermograph indicated that decomposition started at about 300°C and had a maximum rate of weight loss at about 360°C.

3. The significant different properties between cellulose furoates produced homogeneously and heterogeneously were their solubilities in organic solvents. FTIR spectra showed the absorption of hydroxyl and carbonyl groups was significantly different between the specimens produced homogeneously and heterogeneously. Cellulose furoates produced heterogeneously were not uniformly substituted with a furoate ring, and the localized hydroxyl groups contributed to intermolecular hydrogen bonding, which reduced its solubility in organic solvents.
4. Both DMSO and LiCl/DMAc were good high boiling point solvents, and both EtOH/$CH_2Cl_2$ and dioxane were good low boiling point solvents for the cellulose furoate produced homogeneously.
5. Cellulose furoate produced homogeneously with DS more than 1.09 was able to be protected by selected fungi, namely *Myrothecium verrucaria, Cheatomium globosum,* and *Aspergillus terreus.*

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