Cellulose Furoate. I. Synthesis in Homogeneous and Heterogeneous Systems

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ABSTRACT: Cellulose furoate was synthesized via heterogeneous and homogeneous reactions. Cotton cellulose and wood cellulose were used. Lithium chloride/dimethylacetamide solvent was used to dissolve the cellulose for the homogeneous reaction. The esterification reaction between cellulose and 2-furoyl chloride was systematically studied. It revealed that the activation of cellulose was important for its esterification reaction. Activation by solvent exchange decreased the crystallinity and increased the accessibility of cellulose. X-ray diffraction analysis showed no significant change in the spectrogram after activation of cellulose. The degree of substitution of cellulose furoate was influenced by the molecular weight of the cellulose, the stoichiometry of the reagents, the acid scavenger, and the reaction time. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2649–2655, 2001

Key words: cellulose furoate; heterogeneous and homogeneous systems; cotton cellulose; wood cellulose

INTRODUCTION

Cellulose is the most abundant polymer in the organic world. It is estimated that about 10^{12} tons of cellulose are generated by biosynthesis each year throughout the world.[1] The most common sources of cellulose for industrial use are wood pulp and cotton lint. Highly purified wood pulp is composed of 95–99% cellulose and is known as "chemical cellulose" and "dissolving pulp." Currently, the chemical cellulose worldwide production capacity is more than 6 million tons annually and production of raw cotton is about 20 million tons.[2,3]

As a renewable resource, cellulose is used directly or chemically modified for many applications with specific functions.[4–6] The most commonly used reactions for cellulose chemical modification are esterification, etherification, and crosslinking.

Cellulose furoate is one of the cellulose esters that has potential industrial applications. The approach to identify cellulose furoate uses dates back to the late 1960s.[7,8] A heterogeneous reaction was used to prepare cellulose furoate at that time. The purpose of the research was to evaluate the modified cellulose fiber for its rot-resistance property.

Cellulose can be esterified by reactions with acids, acid chlorides, anhydrides, or unsaturated agents[9,10] such as CS_2, phenyl isocyanate,[11,12] and urea. The esterification of a simple glycoside in a homogeneous system generally indicates the primary hydroxyl group at the C6 position is more reactive than the secondary hydroxyl groups at the C2 and C3 positions. The relative reactivity of the hydroxyl groups at C2 and C3 has an appreciable dependence on the reagents used and the nature of the cellulose.[13]

The objective of this research was to synthesize cellulose furoate and to study its unique properties in order to explore its potential applications.

EXPERIMENTAL

Materials

Cotton pulp cellulose and wood pulp cellulose from Hercules, Inc., and commercial cotton cellulose powder from Aldrich Chemicals Company were used. The cotton and wood pulp celluloses were ground to pass a 60-mesh screen before use. Spectrophotometric grade dimethylacetamide (DMAc) was used for UV analysis. Dimethylsulfoxide was treated with calcium hydride and distilled before use. Reagent grade DMAc, pyridine, and triethylamine were dehydrated over 4-Å molecular sieves before using them for the reactions. The following chemicals and solvents were reagent grade and used without further treatment or purification: 2-furoyl chloride, cupriethylenediamine solution, xylene, carbon tetrachloride, iodine, sodium sulfate, sodium thiosulfate, lithium chloride (LiCl), pyridine, triethylamine, sodium hydroxide, hydrogen chloride acid, ethyl alcohol, methyl alcohol, dioxane, ammonium nitrate, monobasic potassium phosphate, dibasic potassium phosphate, magnesium sulfate with $7H_2O$, dimethylformamide, and dichloromethane.

Determination of Degree of Polymerization (DP) of Cellulose

The DP of cellulose was determined by a viscosity method. The intrinsic viscosity $[\eta]$ was obtained by using a capillary viscometer (Cannon–Fenske routine viscometer). The cellulose was dissolved in $0.5M$ cupriethylenediamine solution to make a 0.1% (w/v) solution. The solution was thermostatted at 25.0°C and converted to DP values using the following equations for cotton cellulose,[14]

$$DP = 190[\eta] \tag{1}$$

and for wood cellulose,

$$DP = 156[\eta] \tag{2}$$

Determination of Crystallinity of Cellulose

The crystallinity of the cellulose was measured by a method using a DC-2 density gradient column made by Techne Inc. Xylene and carbon tetrachlo-

ride were used as the solution. Based on the density data, the crystallinity of the cellulose can be calculated by the following equation:

$$\text{crystallinity} = (V_a - V)/(V_a - V_c) \tag{3}$$

where V_a, V_c, and V are the volumes of an amorphous portion, crystalline portion, and unknown sample, respectively. The values of V_a and V_c were reported as 0.680 and 0.628 cm^3/g, respectively.[15]

Determination of Accessibility of Cellulose

In any chemical reaction involving cellulose, the accessibility of cellulose molecules for the reaction is a major consideration. Although crystallinity is concerned with the solid state, accessibility is concerned with internal volume accessible to the given reactant. In this study the accessibility of cellulose was determined by an iodine absorption method described by Hessler and Power.[16] Three-tenths of a gram of cellulose was treated with 2 mL of iodine solution (5 g iodine and 40 g potassium iodide dissolved in 50 mL distilled water) in a 250-mL beaker. After the cellulose and solution were thoroughly mixed, 100 mL of the saturated solution of sodium sulfate was added into the beaker, which was then stored in the dark for 1 h. The residual iodine remaining in the solution was determined by titrating it with $0.02N$ sodium thiosulfate in which 50 mL of distilled water and 1 mL of 1% starch solution were added. A blank on the original iodine solution before adsorption was determined simultaneously in the same manner. The accessibility was calculated as follows:[16]

$$\text{accessibility} = \text{mg iodine/g sample}$$
$$= [(a - b) \times 2.04 \times 2.54]/0.3 \tag{4}$$

where a is the volume of the $0.02N$ thiosulfate solution for the blank and b is the corresponding volume for the cellulose. The ratio of the milligrams of iodine per gram of cellulose to 412 (the micrograms of iodine absorbed divided by the grams of methocel) gave a value for the amorphous fraction.

Synthesis of Cellulose Furoate Via Homogeneous Reaction

The cellulose was activated before dissolving it in (LiCl/DMAc) solution. The solvent-exchange technique used for cellulose pretreatment was uti-

lized. Water was used as the activating agent. Ten grams of cellulose were activated with 200 mL of distilled water for 48 h. The excessive water was removed by suction. One hundred milliliters of DMAc was then used 3 times to exchange the residual water for the cellulose, each for 24 h; then the DMAc was removed by suction.

Nine percent LiCl/DMAc (w/w) solution was prepared by dissolving LiCl in DMAc at 105°C with mechanical stirring under nitrogen. It was important that after the LiCl/DMAc solution was cooled to room temperature, no LiCl crystal was formed. The activated cellulose was dispersed into the LiCl/DMAc solution at room temperature and stirred with a mechanical stirrer under nitrogen until a clear solution was obtained.

Two grams of activated cellulose were dissolved in 100 mL of 9% LiCl/DMAc in a 250-mL three-necked flask fitted with a nitrogen inlet, an addition funnel, a mechanical stirrer, and a drying tube. Certain amounts of pyridine (or other acid scavengers) in 25 mL of DMAc was added slowly to the cellulose solution. A solution of 2-furoyl chloride in 25 mL of DMAc was then added dropwise, and the stirring was continued for a period of time at a designated temperature. The final product was precipitated as a white powder by pouring the reaction solution into hot distilled water. It was then washed several times with water in a sintered glass filter and then purified by a Soxhlet extractor using methanol as the solvent for 24 h. The product was dried in a vacuum freeze-drier.

Synthesis of Cellulose Furoate Via Heterogeneous Reaction

In order to increase cellulose accessibility, cellulose powder was treated by the solvent-exchange process as described earlier. DMAc was chosen as the solvent for the heterogeneous reaction. The reaction procedure was identical to that used in the homogeneous reaction.

Determination of Degree of Substitution (DS)

The DS for each cellulose furoate sample was analyzed according to a modified Eberstadt method.[17] The procedure consists of a saponification with alcoholic alkali for 16–24 h at a temperature not higher than 30°C. In this method 0.5 g of thoroughly dried cellulose furoate was carefully weighed and transferred to a 250-mL Erlenmeyer flask. Twenty milliliters of a 0.5N solution of so-

Table I   Cellulose Raw Materials

	DP	Crystallinity (%)	Accessibility (%)
Cotton pulp (60 mesh)	1117	51.2	34.3
Activated cotton pulp	1117	42.6	38.6
Wood pulp (60 mesh)	986	43.9	30.2
Activated wood pulp	986	32.5	47.0
Cotton powder (20 μm)	218	55.8	22.6
Activated cotton powder	218	48.1	34.4

dium hydroxide in 955 ethyl alcohol was pipetted into the flask. Another flask with the reagent only was prepared as a blank to standardize the alkali. This avoided errors due to changes in volume of the alcoholic solution with temperature. The flasks were stoppered and set aside for 4 h at no higher than 30°C. At the end, the excess alkali was backtitrated with a standardized 0.5N sodium hydroxide to a phenolphthalein end. The amount of acid added was corrected for the alkali required to establish the end point. The result was calculated by using the following equation:

$$DS = [(\text{mL acid for blank})$$
$$- (\text{mL acid for sample})]$$
$$\times (\text{acid normality})(\text{equiv wt})/\text{sample wt}$$
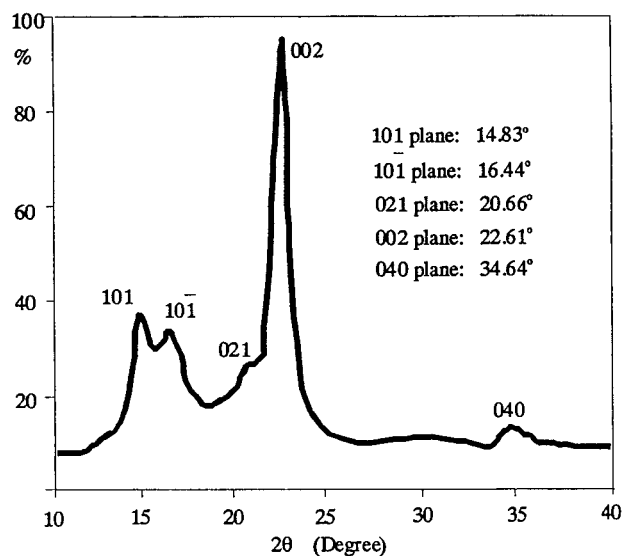
where the equivalent weight (equiv wt) is 444, and the sample weight is in grams.

RESULTS AND DISCUSSION

Analysis of Cellulose Raw Materials

Three kinds of cellulose were used as the raw materials: cotton pulp, wood pulp, and commercial cotton cellulose powder. Their DPs were obtained by viscosity measurements, their crystallinity by density measurements, and their accessibility by iodine absorptions and are shown in Table I.

Of the three types of cellulose materials, cotton pulp cellulose had the highest DP (1117) and accessibility (34.4%), wood pulp had the lowest crys-

Figure 1   An X-ray diffractogram of cotton cellulose.

Figure 2   A simplified reaction scheme for the cellulose reaction with 2-furoyl chloride using pyridine as the acid scavenger.
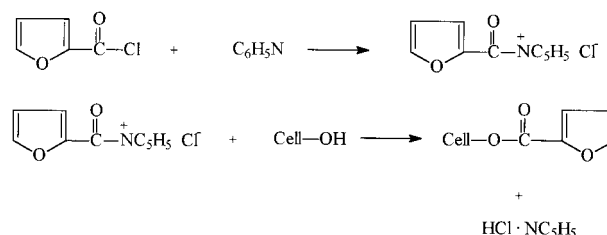
tallinity (43.9%), and commercial cotton cellulose powder had the lowest DP (218) and the lowest accessibility (22.6%). After activation, regardless of their sources, the celluloses decreased their crystallinity and increased their accessibility. Apparently, the activation process increased the cellulose reactivity.

The X-ray analysis showed the main crystal planes for the cellulose space unit. These planes are represented by peaks with different intensities in the diagrams of the X ray as shown in Figure 1. The peak positions of the 101, 10$\bar{1}$, 021, and 002 planes of different celluloses, both activated and unactivated, are summarized in Table II.

From Table II it is clear that those peaks representing the 101, 10$\bar{1}$, 021, and 002 lattice planes
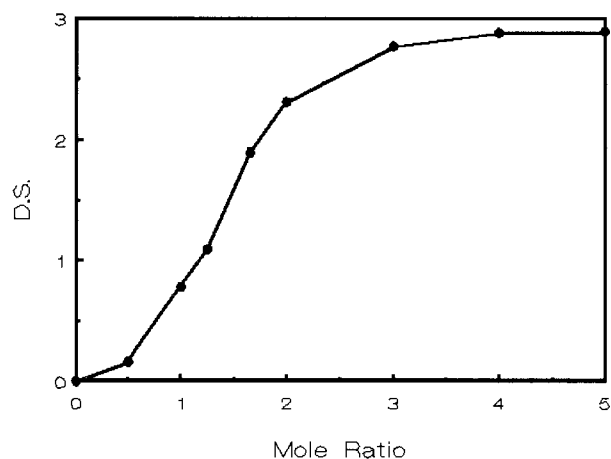
were relatively stable. The activation treatment did not significantly change the values of each plane; neither the shape nor the area of each peak was significantly changed after activation. This implied that no significant lattice deformation or change in the crystallite size was noticed after activation.

Synthesis of Cellulose Furoate in Homogeneous Reaction

The cellulose was dissolved in LiCl/DMAc solvent after activation. The esterification reaction took place between cellulose and 2-furoyl chloride in the homogeneous solution. Pyridine was used as the acid scavenger. A simplified reaction scheme is shown in Figure 2. In this case the hydrogen bonding in the cellulose was destroyed in the LiCl/DMAc solvent. The acid scavenger (pyridine) combined with 2-furoyl chloride to form a better leaving group during the esterification reaction. Pyridine also combined with HCl to form the stable salt and drove the reaction to the anticipated direction.

The relationship between the DS and the stoichiometry of the reagents is shown in Figure 3. The esterification reaction in the homogeneous system with pyridine as the acid scavenger was very fast and reached a DS of 2.0. The reaction rate slowed down thereafter. As shown in Figure 4, it needed only an hour to reach a DS of 2.0 but 30 h to reach a DS of 2.9. Moreover, it is also shown in Figure 3 that the DS reached 1.85 with a 1.65 molar ratio as compared to a DS of 2.88 at a 4 molar ratio. The reaction temperature was not important in the reaction within the range of 25–60°C, as shown in Figure 4. To minimize side reactions, such as acidic degradation, a relatively low temperature was preferred.
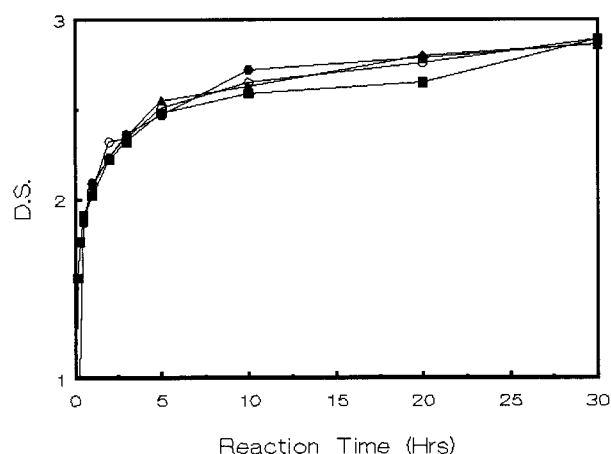
Triethylamine and pyridine were both used as acid scavengers to drive the reaction (Fig. 5). The reaction using pyridine as an acid scavenger was

Table II   X-Ray Diffractogram Positions of Various Celluloses

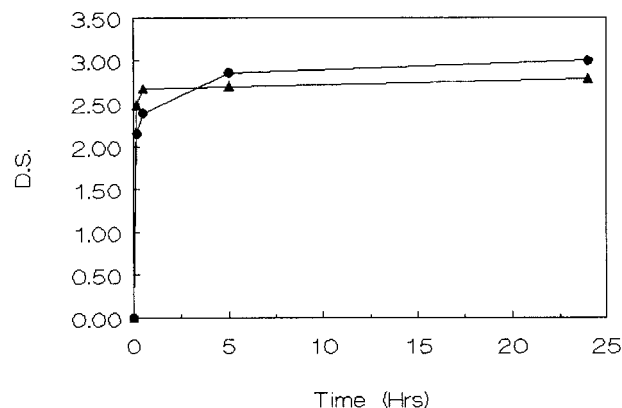| Cellulose Materials	Lattice Plane			
	101	10$\bar{1}$	021	002
Cotton pulp (60 mesh)	14.82	16.39	21.44	22.59
Activated cotton pulp	14.83	16.44	20.66	22.61
Wood pulp (60 mesh)	14.86	16.45	21.31	22.41
Activated wood pulp	14.87	16.61	21.66	22.62
Cotton powder (20 μm)	14.75	16.53	21.96	22.54
Activated cotton powder	14.77	16.57	21.94	22.61

Figure 3 The relationship between the degree of substitution (DS) and molar ratio (2-furoyl chloride/hydroxyl groups in cellulose) with a 1:2 2-furoyl chloride: pyridine ratio for a 20-h reaction time at room temperature.

Figure 5 The relationship between the acid scavengers and the degree of substitution (DS) of cotton cellulose. The molar ratio of cellulose hydroxyl groups to 2-furoyl chloride to acid scavenger was 1:2.5:5 and the reaction temperature was room temperature. (●) Pyridine and (▲) triethylamine.

a homogeneous reaction. On the other hand, when triethylamine was used the solution appeared to be cloudy and a deep yellow color. Although the reaction using triethylamine was a little faster than that of pyridine at the beginning of the reaction, a higher DS was obtained after 5 h from the reaction using pyridine rather than triethylarnine. As the amount of acid scavenger increased, a higher DS was obtained, as shown in Figure 6.

The DP of cellulose raw materials appeared to have some effect on the esterification. Cellulose with a lower DP seemed to yield a higher DS, which is shown in Figure 7. For example, cotton powder had a DP of 218 and yielded a DS that was 19.2 and 7.3% higher than cotton cellulose, which had a DP of 1117, after 1- and 24-h reactions, respectively. Apparently, a cellulose with a lower DP, which has a lower viscosity and thus more mobile molecules, favors esterification. Because the reaction was performed in a homogeneous system, the crystallinity and accessiblility were not determining factors.
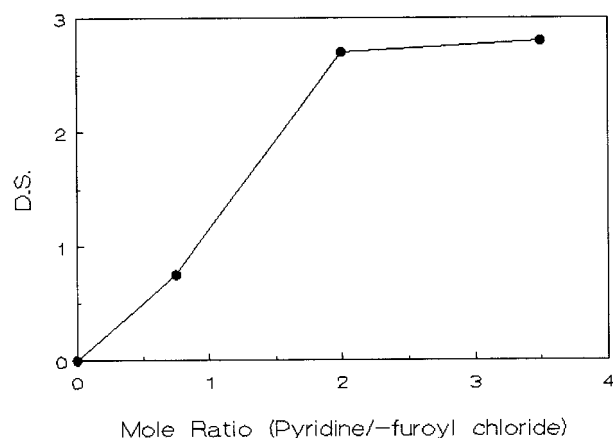

Figure 4 The relationship between the degree of substitution (DS) and reaction time or reaction temperature. The molar ratio of cellulose hydroxyl groups to 2-furoyl chloride to pyridine was 1:2.5:5. The temperatures were (●) 25, (▲) 30, (○) 50, and (■) 60°C.
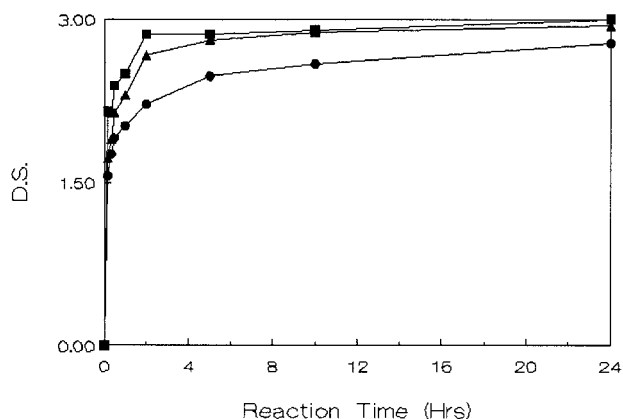

Figure 6 The relationship between the degree of substitution (DS) and the amount of pyridine as the acid scavenger. The molar ratio of cellulose hydroxyl groups to 2-furoyl chloride was 1:2.5, the reaction time was 20 h, and the reaction temperature was room temperature.

Synthesis of Cellulose Furoate in Heterogeneous System

The heterogeneous reaction system is more complicated than the homogeneous one. The accessibility of the hydroxyl group in cellulose toward the esterification reagent is an important factor. Celluloses with and without activation were used for the heterogeneous reaction.

In a previous section we discussed that the activation of cellulose tended to increase the accessibility and decrease the crystallinity of cellulose, regardless of the cellulose sources. In the heterogeneous esterification reaction it was interesting to learn that within 5 h of the reaction the activated wood cellulose achieved the highest DS, followed by activated cotton powder and activated cotton cellulose (see Fig. 8). As the reaction continued to proceed to 10 and 24 h, the cotton powder seemed to respond better toward esterification. For these reaction periods, the activated cotton powder achieved the highest DS, followed by activated wood cellulose and activated cotton cellulose. Unactivated celluloses achieved a lower DS under the same reaction conditions. For example, after a 5-h reaction, the DSs of activated cotton pulp, wood pulp, and cotton powder were 13.8, 12.4, and 4.8 times faster, respectively, than those of unactivated celluloses. Even though accessibility played an important role in promoting esterification, the chain length (i.e., DP) of cellulose tended to also play a role in the heterogeneous reaction system.

Figure 7 The relationship between the degree of substitution (DS) and the degree of polymerization (DP) of cellulose. The molar ratio of cellulose hydroxyl groups to 2-furoyl chloride to acid scavenger was 1:2.5:5, and the reaction temperature was room temperature. The DP was (■) 218, (▲) 986, and (●) 1117.
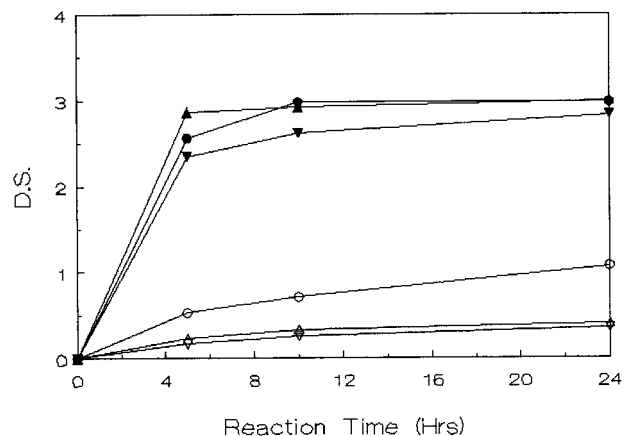
Figure 8 The heterogeneous reaction of different celluloses with furoyl chloride in pyridine. The molar ratio of cellulose hydroxyl groups to 2-furoyl chloride to pyridine was 1:2.5:5, and the reaction temperature was room temperature. (▽) Cotton, (△) wood, (○) cotton powder, (▼) activated cotton, (▲) activated wood, and (●) activated cotton powder.

CONCLUSIONS

Cellulose furoates with various DSs were successfully synthesized either in a homogeneous or heterogeneous system. In the homogeneous system LiCl/DMAc was used as the solvent. The following results were observed.

1. Activating cellulose by solvent exchange decreased the crystallinity and increased the accessibility of cellulose. The X-ray diffraction analysis showed no significant change in the spectrogram, indicating that the cellulose microstructure was not significantly changed after activation.
2. The activated cellulose reacted much faster than the cellulose without activation in the heterogeneous reaction.
3. The DS of cellulose furoate was affected by the cellulose molecular weight, the stoichiometry of the reagents, the acid scavengers, and the reaction time.

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