

Cellulose Furoate. III. Properties and Applications

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Received 22 December 2000; accepted 25 December 2000

ABSTRACT: Cellulose furoates synthesized by a homogeneous reaction was used to make film and fiber. Either colorless or light yellow, transparent cellulose furoate film can be made by solvent cast. Cellulose furoate film with a DS of 2.56 and 20% PEG-400 as the plasticizer displayed 5441 psi maximum tenacity and 21.5% maximum strain. The film without plasticizer has a water vapor permeability of $0.124 \text{ ng} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$. DMTA study identified the T_g of cellulose furoate with a DS of 2.77 was 225°C . As the DS decreased, the T_g shifted toward higher temperature. The success of wet-spun fibers from LiCl/DMAc solution of cellulose and cellulose furoate substantiated cellulose furoate is compatible with cellulose. Unfortunately, the wet-spun fibers lost their mechanical and surface properties, and bioresistant property against *Myrothecium verrucaria*, *Cheatomium globosum*, and *Aspergillus terreus*. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 253–257, 2001

Key words: cellulose furoate; film; wet-spun fiber; viscoelasticity; T_g ; water vapor permeability; biodegradability

INTRODUCTION

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^{1–3} and membrane use.⁴ Only heterogeneous reaction was used to prepare cellulose furoate at that time. In a previous article,⁵ we reported the success of synthesizing cellulose furoate with various degree of substitution (DS) by either a homogeneous or heterogeneous reaction. In a subsequent study,⁶ we characterized the chemical structure of furoate moiety in cellulose furoate by FTIR, UV spectroscopy, and NMR and X-ray spectroscopy. Thermal property was studied by TGA and DSC. Bioresistant property was confirmed by using *Myrothecium verrucaria*, *Cheatomium globosum*, and *Aspergillus terreus*.

In this study, cellulose furoates synthesized by a homogeneous reaction was used to make film and fiber. Mechanical, viscoelasticity, and water vapor permeability properties of the film and mechanical and biodegradability properties of wet-spun cellulose furoate-containing cellulose fiber were investigated.

EXPERIMENTAL

Preparation of Cellulose Furoate Film

Cellulose furoate synthesized by a homogeneous reaction was used to make film. It was dissolved in dioxane at a concentration of 1% (m/v). Then the solution was poured slowly on glass plates to make films. After the solvent was evaporated, the films were peeled off from the plates and left at room temperature for 1 week. If a plasticizer was used, it was added to the solution and stirred for half an hour before casting.

Mechanical Property of Cellulose Furoate Film

Tensile strength of cellulose furoate film was tested by an Instron Universal Testing Machine

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Journal of Applied Polymer Science, Vol. 82, 253–257 (2001)
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(model 4201) in accordance to ASTM standard method D 882-88.⁷ Tensile property was determined at maximum load, and percent elongation was determined at break. Tensile strength was calculated by dividing peak load by film cross-sectional area. Thickness of test films was determined using a handheld micrometer. For each film type and test, separate measurements were taken systematically over the test area to the nearest 0.1 mil (2.54 μm). Five specimens were used for each sample.

Water Vapor Permeability of Cellulose Furoate Film

The water vapor permeability was measured using a variation of the ASTM Standard Method E 96 (ASTM, 1987),⁸ known as the "cup methods." The modified cups were used to determine water vapor permeability of film samples. These cups consisted of a lid and bottom section that were fabricated with poly(methyl methacrylate). Cups were cylindrical in shape, 8.7-cm outside diameter and 4.6-cm inside diameter, with 2.1-cm in depth. Lids were ring shaped with a 8.7-cm outside diameter and an inside diameter of 4.6 cm.

Before testing, the opening in the bottom section of a cup was filled with 18 mL of distilled water which allowed a 9.97×10^{-3} m air gap to exist between a covering film and the free water surface. Silicone grease was uniformly placed on the inside lip of a cup so that a tight seal could be created between the covering film and the bottom section of the cup. After a film sample was mounted on top of the silicone-coated cup's seal ring, the seal was secured by tightening the lid onto the cup bottom with four nylon screws. The exposed film area, through which water vapor transmission could occur was 16.62 cm^2 .

After test samples were mounted, these cups were placed in an environmentally controlled chamber maintained at $25 \pm 2^\circ\text{C}$ and $50 \pm 3\%$ relative humidity. Humidity within the cups was assumed to be nearly 100%. The chamber had a horizontal air flow of 5420 cm/min . Water vapor permeability was determined by measuring weight loss over time for 27.5 h, correct to 0.001 g. Linear regression was used to calculate the slope of a fitted straight line of these weight data, which provided the measured water vapor permeability. According to McHugh et al.,⁹ not accounting for a stagnant air gap between the free water surface and a hydrophilic film leads to an underestimation of film permeability.

Wet Spinning Fiber of Cellulose and Cellulose Furoate Mixture

To investigate the compatibility between cellulose and cellulose furoate, they were dissolved and mixed together and then wet spun to make fibers. Namely, 2% cotton cellulose (60 mesh) in 9% LiCl/DMAc solution was blended with 2% cellulose furoate (DS = 2.14) in 9% LiCl/DMAc solution by mechanically stirring for 2 h and further ultrasonic stirring for 1 h, then set aside over night.

Solution spinning of cellulose/cellulose furoate fibers was accomplished using an in house pilot scale wet spinning unit. The polymer solution was placed in a nitrogen pressurized tank feeding with a gear pump. The solution was pumped through a 0.004 inch diameter spinneret ($L/D = 2.0$) into a coagulation water bath. The formed fiber was continuously taken up and rinsed with water on a 5 inch-diameter roller; take-up speeds of 4–6 m/min were achieved in the process. These fibers were then fed to a draw roll operating at higher speeds providing draw ratios of 3 to 4. The heating temperature between two rollers was controlled at 90–95°C.

Mechanical Properties of The Fiber

An Unstrain Universal Testing Machine (Model 1125) was used in tensile strength tests of the fibers. The linear densities of the fibers were obtained by weighting the fibers to yield the unit as "denier" ($\text{g}/9000 \text{ m}$). Fibers were cut into 2 cm in length and mounted on the center of a paper adapter with 1-cm gap. It was fastened by a tape at both ends. The two ends of the sample adapter were fixed in the test machine, then the side paper was cut off by a pair of scissors.

Dynamic Contact Angle of Fiber

Because the fiber is too small and flexible to test the dynamic contact angle directly, an alternative method was used to collect the data from the film coated on the coverglass instead of testing fiber directly. The same solution used for making fiber was used to coat the cover glass and evaporated in air for 10 min. The coverglass was dipped in ethyl alcohol for 5 min and in water for 1 h, then dried at room temperature for 2 days. The dynamical contact angle of the film was tested in double-deionized water.

Biodegradation Test for the Fiber

Cheatomium globosum, *Myrothecium verrucaria*, and *Aspergillus terreus* were selected for the test.

Table I Tensile Strength of Cellulose Furoate Film with DS of 2.56

PEG-400	Strain at Maximum (%)	Yield at Peak (psi)
0	2.4	1491.9
20	21.5	5445.1
40	34.8	3626.2

Fibers were laid on the top of the agar, which was covered by hyphae and let them set for 48 h. The fibers were picked out and washed by 70% aqueous ethanol solution, and dried in a freeze vacuum dryer for 2 days. It was exposed to the atmosphere at 70°F and 65% relative humidity for 5 h before tensile strength testing.

RESULTS AND DISCUSSION

Mechanical and Physical Properties of Cellulose Furoate Film

Cellulose furoate films were made by solvent casting with dioxane as the solvent. The films were colorless to light yellow and transparent. PEG-400 was used as a plasticizer to make the film more flexible. The mechanical, thermal, and permeation properties of the film were evaluated.

Tensile Strength Property

The tensile strength of cellulose furoate film with a DS of 2.56 was evaluated by an Instron machine. Results are shown in Table I. Apparently, the pure film was very brittle. Its strain at maximum was only 2.4% and the yield at peak was 1491.9 psi. The incorporation of plasticizer PEG seemed to be beneficial. The addition of 30% of PEG-400 improved the strain at maximum to 21.5% and the yield at peak improved to 5445.1. The addition of 40% plasticizer PEG appeared to improve the strain at maximum (to 34.8%) but yield at peak was only improved to 3626.2, which was lower than the addition of 30% plasticizer.

Viscoelasticity Property

DMTA has been widely used to study the viscoelasticity of polymeric films. DMTA characterizes materials based on their state of molecular motion. Molecular motion and physical morphology determine the dynamic moduli (stiffness) and damping (hysteresis).

DMTA senses any changes in molecular mobility in the sample as the temperature is raised or lowered. The time scale required for the molecular motion to manifest itself is determined by the frequency, f , of the impressed sinusoidal stress. A progressive change in storage modulus and damping peak in $\tan \delta$ occurs when the average molecular relaxation time is $1/2\pi f$.

A typical DMTA scan of cellulose furoate with a DS 2.77 is shown in Figure 1. It illustrated the effects of temperature on the storage modulus and $\tan \delta$ of cellulose furoate film. When the DMTA scanned at 3 Hz frequency, a peak of damping factor was detected at about 120°C. This was attributed to the motion of water molecules or/and residual solvent. At this temperature, the storage modulus decreased from 7.9×10^{-8} to 2.0×10^{-8} Pa. Evidently, the presence of water and residual solvent in the film resulted in a remarkable reduction in the storage modulus. As the evaporation of residue solvent and water, which acted as a plasticizer, took place, the film became stiffer even at the increased temperature. Hence, the evaporation of water or residual solvent led to the increase in the storage modulus between 150 and 200°C. The glass transition peak was located at 225°C. At this temperature, the storage modulus decreased from 3.3×10^{-8} to 3.7×10^{-8} Pa.

It is well known that frequency of applied force affects the dynamic mechanical properties of polymeric materials. A typical frequency-multiplexed DMTA scan of cellulose furoate with a DS of 2.77 is shown in Figure 1. As the frequency increased from 0.33 to 30 Hz, the shift in both storage mod-

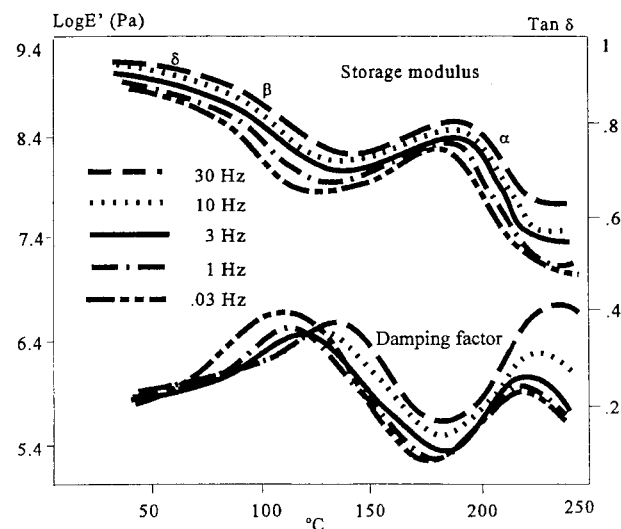


Figure 1 Frequency-multiplexed DMTA scan for cellulose furoate with DS of 2.77.

Table II Glass Transition Temperatures (T_g) of Cellulose Furoate Films with Different Degrees of Substitution (DS)

DS	T_g (°C)
2.43	245
2.57	234
2.77	225

ulus and damping factor to higher temperatures were observed.

Based on the DMTA study, the glass transition temperature, T_g , of cellulose furoates at 3 Hz of frequency are listed in Table II. As the DS increased, it is clear that the transition shifted toward lower temperature.

Water Vapor Permeability (WVP)

In film and packaging applications, gases and vapors pass through a film by permeation, and the amount of gas or vapor that is absorbed by the film is an important factor in determination of film specific applications. Based on the ASTM Standard Method E96, the WVP of cellulose furoate film was measured. The results are summarized in Table III. WVP of pure cellulose furoate film was $0.124 \text{ ng} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$. When PEG-400 was added to the film, the WVP increased significantly. When 20 and 40% of PEG were added to the films, the WVP increased to 0.2 and $0.348 \text{ ng} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$, respectively. Because PEG is hydrophilic, it is believed that the opposite trend would be observed if a hydrophobic plasticizer was added.

Mechanical, Physical, and Biodegradability Properties of Wet-Spun Cellulose Furoate Fibers

Cellulose furoate (DS = 2.14) was dissolved in LiCl/DMAc solution and mixed with cellulose LiCl/DMAc solution for wet spinning. The diam-

Table III Water Vapor Permeability (WVP) of Cellulose Furoate Films (DS = 2.56) with and without PEG-400 Plasticizer at 25°C and 50% Relative Humidity

PEG-400	WVP ($\text{ng} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$)
0	0.124
20	0.200
40	0.348

Table IV Tensile Strength of Wet-Spun Cellulose Fiber Blended with Cellulose Furoate

Cellulose Furoate (%)	Tenacity at Max. (g/den)	Strain at Max. (%)	Modulus (g/den)
0	2.79	13.07	82.94
10	2.51	14.97	70.27
20	2.02	21.84	30.14

eters of the wet-spun fibers were about 0.05 mm. Tensile strength, dynamic contact angle, and biodegradation tests were used to investigate the properties of the fibers.

Tensile Strength

In a previous study,⁶ we recognized that cellulose furoate possesses a unique rot resistant property. It is important to investigate whether the tensile strength of wet-spun cellulose/cellulose furoate fiber is positively or negatively influenced in the presence of cellulose furoate. The results of mechanical testing, including the strain at maximum, tenacity at maximum, and modulus of the fibers are summarized in Table IV. It shows that both tenacity and modulus decreased as the cellulose furoate increased. On the contrary, strain increased as the cellulose furoate increased. The reduce in tenacity and modulus could be due to the loss of cellulose crystallinity during dissolution and mixing with cellulose furoate.

Dynamic Contact Angle

The dynamic contact angles of the fibers were obtained by measuring the corresponding film and using the data as the reference for cellulose/cellulose furoate fibers. The data in Table V shows that the contact angles increased as the content of cellulose furoate increased. This also

Table V Effect of Cellulose Furoate on the Dynamic Contact Angle

Cellulose Furoate (%)	Contact Angle (°)	
	Advancing	Receding
0	26.39	14.78
10	32.30	17.54
20	40.50	22.72

Table VI Changes in the Mechanical Properties after Exposure of Fibers to Selected Fungi

Cellulose Furoate (%)	Tenacity at Max. (%)	Strain at Max (%)	Modulus (%)
0	-7.4 ^a	-4.3 ^a	-20.4 ^a
	-8.0 ^b	-2.8 ^b	-9.1 ^b
	-0.6 ^c	-1.0 ^c	-20.1 ^c
10	-22.0 ^a	-21.8 ^a	-27.4 ^a
	-12.0 ^b	-22.3 ^b	-5.3 ^b
	-3.1 ^c	-10.9 ^c	-13.3 ^c
20	-15.8 ^a	-15.6 ^a	+5.9 ^a
	-48.6 ^b	-53.3 ^b	+18.8 ^b
	-5.9 ^c	-8.2 ^c	+30.9 ^c

^a Tested by *Chaetomium globosum*.

^b Tested by *Myrothecium verrucaria*.

^c Tested by *Aspergillus terreus*.

indicated the surface energy changed after imposing cellulose furoate into cellulose.

Biodegradability

Biodegradability of cellulose furoate fiber is one of the important properties for its utilization. In a previous study,⁶ we established that cellulose furoate with a DS above 1 is resistant to the attack by *Myrothecium verrucaria*, *Cheatomium globosum*, and *Aspergillus terreus*. Hence, in this study, we used the same micro-organisms to test the biodegradability of cellulose/cellulose furoate fiber. The results showed that the cellulose fiber blended with higher cellulose furoate exhibited greater loss of strength (Table VI). The percentage changes here were generated by comparing the data shown in Table IV. In contrast to cellulose, the amorphous portion of the fiber increased after mixing cellulose furoate with cellulose. Although cellulose furoate biodegraded much slower than cellulose, the morphological change, i.e., loss of crystallinity, in cellulose after introduction of cellulose furoate to it certainly contributed to the decline in tensile strength. From the changes in tenacity at maximum, it is obvious that both *Cheatomium globosum* and *Myrothecium verrucaria* were found to degrade the fibers much faster than the *Aspergillus terreus* did.

CONCLUSIONS

Based on the experimental findings, the following conclusions can be drawn:

1. Cellulose furoate film can be made by solvent cast. It is either colorless or light yellow, with good transparency. Cellulose furoate film with a DS of 2.56 and 20% PEG-400 as the plasticizer displayed 5441 psi maximum tenacity and 21.5% maximum strain.
2. Cellulose furoate film without using PEG as the plasticizer has a water vapor permeability of 0.124 ng · m/m² · s · Pa.
3. DMTA study identified the T_g of cellulose furoate with a DS of 2.77 was 225°C. As the DS decreased, the T_g shifted toward higher temperature.
4. The success of wet-spun fibers from LiCl/DMAc solution of cellulose and cellulose furoate substantiated cellulose furoate is compatible with cellulose. Unfortunately, the wet-spun fibers lost their mechanical and surface properties, and bioresistant property against *Myrothecium verrucaria*, *Cheatomium globosum*, and *Aspergillus terreus*.

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