

# Preparation and Surface Activity of Biodegradable Polymeric Surfactants. I. Preparation and Surface Activity of Dextrin Derivatives

Hong-Jung Wang, Keng-Ming Chen

Department of Polymer Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei, Taiwan

Received 5 January 2004; accepted 4 August 2004

DOI 10.1002/app.21914

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Novel dextrin derivative surfactants containing a modified glucoside structure have been prepared in which propylene glycol polyglucosides are reacted with a hydrophobic oxirane-containing material of glycidyl ether with C10–C18 carbon atoms. These surfactants exhibit good surface activities, including surface tension, low foaming, and wetting power. These surfactants also have a good ability to improve the whiteness and wetting power of cot-

ton fabrics in a hydrogen oxide bleaching system. The benefits of these dextrin derivative surfactants are their highly biodegradable properties, which are lacking in traditional surfactants. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 711–717, 2005

**Key words:** biodegradable; surfactants; synthesis; tension

## INTRODUCTION

Surfactants impact all aspects of our daily life, either directly in household detergents and personal care products or indirectly in the production and processing characteristics of molecular structures consisting of a hydrophobic moiety and a polar or anionic moiety.<sup>1,2</sup> However, despite the manifest advantages of traditional surfactants, the demands for biodegradability of effluents have become more rigid, and the need for biodegradable properties is becoming more pressing.<sup>3</sup>

A dextrin is a saccharide that is produced by the dry heating of unmodified starches or from the products resulting from enzyme- or acid-catalyzed hydrolysis of wet starch. Saccharides are considerably more biodegradable because they are the natural foods of bacteria present in sewage or raw river water.<sup>4</sup>

Derivatives based on dextrin (providing the hydrophilic moiety), reacted with a fatty long-chain material (providing the hydrophobic moiety), have an amphipathic structure similar to that of traditional surfactants, except providing more biodegradability.<sup>5–8</sup>

This article describes the preparation and surface-active properties of a series of biodegradable dextrin derivatives in which the hydrophilic–hydrophobic amphipathic structures are modified by the addition of a fatty long chain to the dextrin. The surface-active properties studied in this article include the surface tension, foaming, and wetting power. The application of the bleaching processes of cotton fabrics is also studied, and the biodegradation of these surfactants is measured by various methods.<sup>9</sup>

## EXPERIMENTAL

### Materials

Propylene glycol, dextrin, epichlorohydrin boron trifluoride etherate, and fatty alcohol ( $n = 8, 12, \text{ or } 16$ ), purchased from Hayash Pure Chemical Co. (Japan), were reagent-grade. Sodium dodecylbenzene sulfonate (ABS) was supplied by Sigma-Aldrich Co. (UK) and used to compare the biodegradability of dextrin derivative surfactants. The dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) test reagents (Merck, Whitehouse Station, NJ) were used without further purification.

### Preparation of the dextrin derivatives

The preparation of the dextrin derivatives is presented as in Scheme 1. The dextrin, which provided

Correspondence to: H.-J. Wang (leaphoo@yahoo.com.tw).

Contract grant sponsor: National Science Council (Taiwan, Republic of China); contract grant number: NSC-90-2216-E-011-013.



### Step 2

A fatty alcohol (e.g., decyl alcohol; 0.1 mol) and some boron trifluoride (BF<sub>3</sub>) catalyst were mixed with stirring at 50–59°C and then slowly dropped into epichlorohydrin (0.1 mol) in 1 h. The mixture was heated for 2 h at the same temperature; it was then cooled and left overnight. The next day, 40% NaOH was added for neutralization in half an hour, and the temperature was raised to 80°C for 30 min of reaction. Then, water was added to the mixture with stirring, and separate oil and water layers remained. The water layer was removed.

### Step 3

To the synthesis product of step 1, 50% NaOH was added for neutralization, and the temperature was raised to 147°C for 40 min of reaction. Then, the water was removed. A temperature of 140–147°C was maintained, and then there was a slow drop in the synthesis product of step 2 in 1 h. Heating was continued for 1 h. Finally, the reaction solution was purified by the addition of ethanol; the undissolved impurities were separated by filtration, and the ethanol and water were removed from the filtrate with a rotary evaporator. The final product was dried in a vacuum oven.

### Analysis

The structures of the final products were verified by <sup>1</sup>H-NMR, Fourier transform infrared (FTIR), and elemental analysis (EA). <sup>1</sup>H-NMR spectra were recorded with a Bruker AM-300WB spectrometer, IR spectra were measured with a Japan Spectroscopic Co. FT/IR-3, and EA results were from a PerkinElmer 240 C meter (Norwalk, CT).

### Measurements

#### Surface tension

Surface tension measurements were performed by the Wilhelmy plate method with a Kyowa Kaimenagaku Co. CBVP-A3 tension meter (Japan) on surfactant solutions of various concentrations in triple-distilled water at 25°C.

#### Contact angle

Contact-angle measurements were taken with a Face Co. CA-5 150 meter (Japan).

#### Foaming ability

The foaming ability was determined according to the Ross–Miles test. The concentration was 1 g/L. Foam

production was measured by the height of the foam initially produced, and foam stability was measured by the height after 3 min.

### Scouring and wetting tests

A rapid laboratory dyeing machine was used to study bleaching of a gray cotton fabric by hydrogen peroxide. The bleaching recipe included: H<sub>2</sub>O<sub>2</sub> (20%) 10 g/l, NaOH 5 g/l, NaSiO<sub>3</sub> 5 g/l, auxiliaries 2 g/l, liquor ratio (30:1), temperature (80°), time (40 min). After the bleaching, the reflectance of the cotton fabrics were measured using an Apply Color Spectrophotometer (ACS) and the results were used to calculate whiteness values.<sup>10</sup> The bleached fabrics were also used to evaluate the wetting ability by the measure of height of water penetration to fabrics.<sup>11</sup>

### Biodegradability

The biodegradation percentage is the ratio of BOD to COD times 100. This value is typically reported after 5, 10, 20, 25, and 30 days. Some studies suggest that if 50% or more biodegradation occurs within 20 days, the product may be considered biodegradable and would be largely removed from the wastewater system. However, there is not unanimous agreement on this definition. Some say that compounds that consume oxygen in any amount, at any rate, will eventually biodegrade, and therefore biodegradability becomes a subjective measure. Different methods of determining the biodegradation percentage may give different results. To make meaningful comparisons, the same test methods and calculations must be used.

In this study, we also compare traditional surfactants, such as alkyl benzene sulfonate (ABS) and Triton X100.

For the COD test, Merck COD reagents were used, and measurements were made with a Hach model DR4000U spectrophotometer. DO values were measured with a YSI, Inc., model 5100 dissolved oxygen meter. The BOD level was determined by the subtraction of this DO level from the DO level found in the original sample taken 5–30 days previously: BOD = mg/L DO (original sample) – mg/L DO (after incubation). The BOD measure is the amount of oxygen consumed by organic matter and associated microorganisms in a solution over a 5-day period.

## RESULT AND DISCUSSION

### Preparation

In this study, to obtain dextrin derivative surfactants containing a modified glucoside structure, dextrin was

TABLE I  
EA of Dextrin Derivative Surfactants

No.	Compound group	EA (%)			
		C		H	
		Found	Calcd	Found	Calcd
A	Decyl alcohol	54.31	56.28	10.31	9.60
B	Myristyl alcohol	61.45	59.40	10.53	10.1
C	Stearyl alcohol	62.38	61.96	11.08	10.5

reacted with propylene glycol to obtain a propylene glycol polyglucoside somewhat more lipophilic than dextrin in the first step. Then, the resulting propylene glycol polyglucosides were reacted with a hydrophobic oxirane-containing material of glycidyl ether with C10–C18 carbon atoms.

However, the obtained dextrin derivatives were mixtures of modified oligoglucosides and polyglucosides, and the mixtures had nonionic properties.<sup>4</sup>

The EA analysis of the final products is shown in Table I.

A typical IR spectrum of the dextrin derivatives prepared in this study (Fig. 1) displayed bands at 2851–2940 ( $-\text{CH}_2$ ), 3449–3647 ( $-\text{OH}$ ), 1455 ( $\text{C}-\text{H}$ ), and 800–1200  $\text{cm}^{-1}$  ( $\text{C}-\text{C}$ ). These bands were characteristic of the desired compound.

The compound structure was further supported by the  $^1\text{H-NMR}$  spectrum, as illustrated for compound A in Figure 2. Figure 2 shows signals at  $\delta = 0.8\text{--}1.0$  ppm ( $-\text{RCH}_3-$ ),  $\delta = 1.2\text{--}1.4$  ppm [ $-(\text{CH}_2)_n-$ ], and  $\delta = 3.3\text{--}4.0$  ppm ( $\text{R}-\text{CH}_2-\text{OH}$ )

### Surface tension

The dextrin derivatives prepared in this study had an amphipathic structure similar to those of traditional surfactants and other polymeric surfactants. The dextrose and hydroxyl groups in the structure provided the hydrophilic moiety, and the long-chain alkyl groups provided the hydrophobic moiety. In aqueous solutions, the amphipathic structures of surface-active-material molecules are concentrated at the surface and reduce the surface tension. The reduction of surface tension in the presence of dextrin derivative surfactant solutions is shown in Figure 3. This illustrates the very effective lowering of the surface tension of these materials.

Increases in the length of the long-chain alkyl group result in increased surface activity. This, as expected, is due to the increase in the hydrophobicity of the surfactants increasing the concentration of surfactants at the surface.<sup>1</sup>

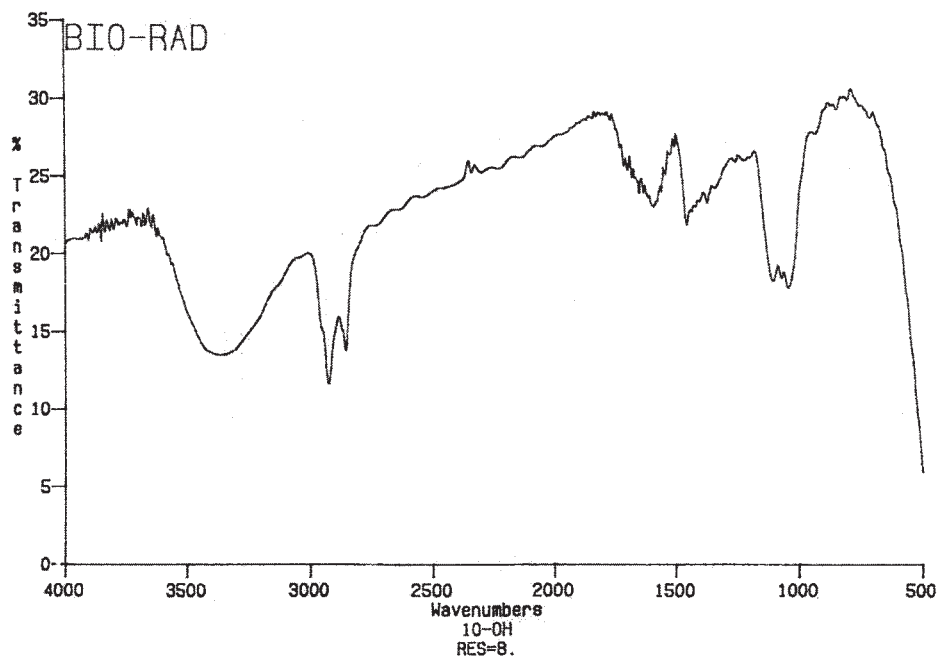


Figure 1 FTIR spectrum of compound A.

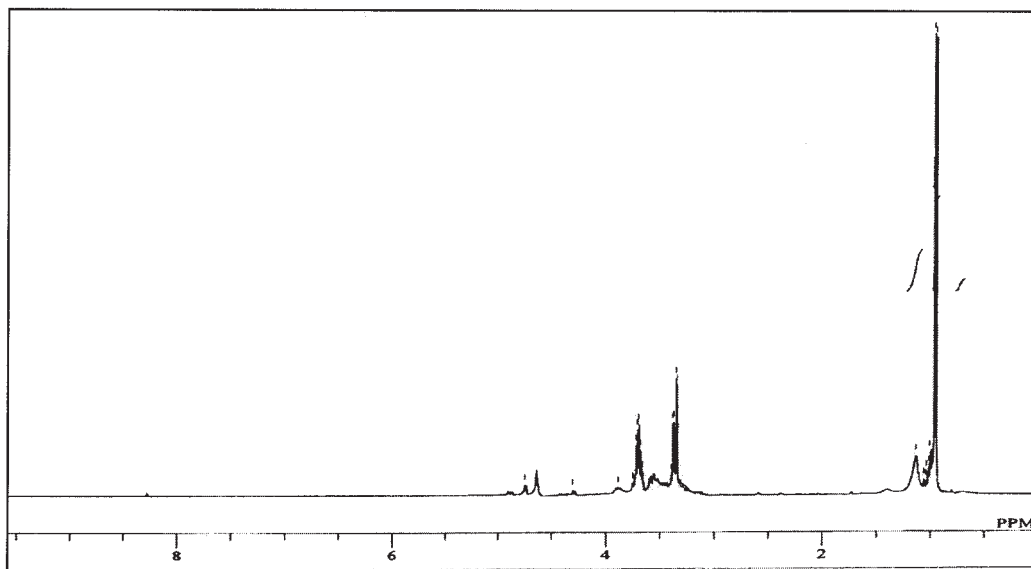


Figure 2  $^1\text{H-NMR}$  spectrum of compound A.

### Wetting power

The wetting power of a surfactant is one of its most important surface properties. For example, in laundry cleaning or textile processing, the wetting power of surfactants may accelerate the diffusion or penetration of alkali chemicals and dyes into fibers and improve the detergency or dyeing effects.

The contact angles formed between solutions of dextrin derivatives and an acrylic plastic plane and cotton fabric are shown in Table II. The angles were smaller than those found with water, and this indicates that all the solutions of all the products possessed the power to wet the acrylic plastic and the fabric.

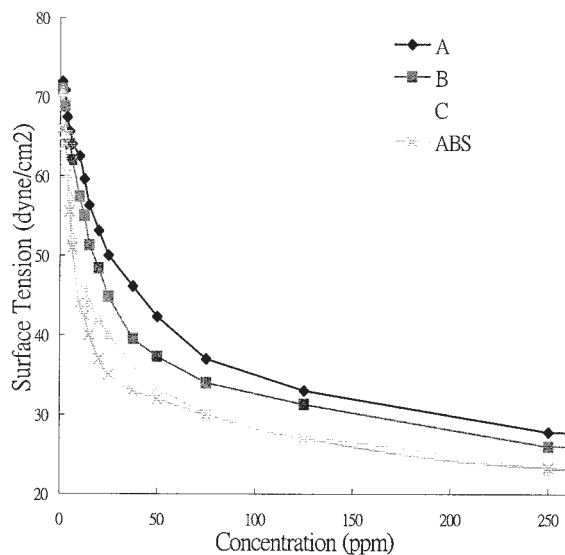


Figure 3 Surface tension of dextrin derivative surfactants.

### Foaming properties

Foaming is a complex matter and by no means well understood, although foam is of great practical importance, for instance, in cosmetics, and sometimes must be suppressed because of its unfavorable effects. Foams are coarse dispersions of gas in relatively small volumes of liquid and thus are mostly nonequilibrium systems that need surfactants for limited stabilization. However, the low foaming tendency of surfactants is an important property in some recent applications, such as mechanical dishwashing agents and dyeing auxiliaries in modern textile-dyeing processes.

Table III shows the foaming properties, including the initial height of the foam and the foam height after 3 min, of dextrin derivatives. In comparison with other alkyl polyglucosides, in which a higher alcohol reacts directly with polyglucoses, the modified dextrin derivatives prepared in this article show lower foaming ability. These lower foaming properties are probably due to the presence of multihydrophilic groups causing a considerable increase in the area per molecule and producing less cohesive force in the surface.<sup>5,8</sup>

TABLE II  
Contact Angles of Solutions of Dextrin  
Derivative Surfactants

Compound	Acrylic film ( $^{\circ}$ )	Cotton fabric ( $^{\circ}$ )
H <sub>2</sub> O	75	122
A	47	59
B	40	53
C	33	50
ABS	44	51

**TABLE III**  
Foaming Properties of Dextrin Derivative Surfactants

Compound	Foam height (mm)	
	Initial	After 3 min
A	30	17
B	25	12
C	20	10
ABS	150	60

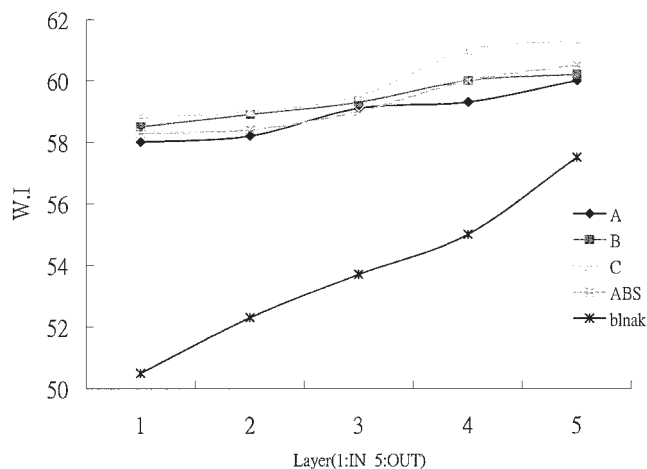
### Scouring and wetting test properties for use in bleaching auxiliaries

In the processes of the textile industry, scouring and bleaching are carried out to prepare cloth for dyeing. The scouring and bleaching treatments do not rely primarily on the use of traditional surfactants. Nevertheless, rapid and even wetting of cloth is of major importance, and to assist with this, some auxiliaries may be added.

The ability of a dextrin derivative surfactant to improve the whiteness and wetting power of cotton fabrics in a hydrogen peroxide bleaching system is shown in Table IV and Figure 4. The presence of dextrin derivative surfactants increases the effects of oxidation on bleaching baths in the process and prepares more purified fabrics for the next process of dyeing or printing.

### Biodegradation

After use, all surfactants used in laundry detergents, cleaning agents, and dyeing auxiliaries are passed quantitatively into wastewater. Because of this fact, the constant input of surfactants into the environment requires a particular ecological characterization of this class of compounds. There are many test methods for determining the biodegradation of surfactants.<sup>6,12,13</sup> The results of the total biodegradation of the dextrin derivatives prepared in this study are shown in Figure 5. Apparently, these are considerably more biodegradable because they are the natural foods of bacteria present in sewage or raw river water.



**Figure 4** Ability of dextrin derivative surfactants to improve the whiteness (W.I. = whiteness index).

### CONCLUSIONS

Novel dextrin derivative surfactants containing a modified glucoside structure have been prepared in which dextrin is reacted with propylene glycol to obtain a propylene glycol polyglucoside somewhat more lipophilic than dextrin in the first step. Then, the resulting propylene glycol polyglucosides are reacted with a hydrophobic oxirane-containing material of glycidyl ether with C10–C18 carbon atoms.

These surfactants exhibit good surface activities, including surface tension, low foaming, and wetting power. These surfactants also have a good ability to improve the whiteness and wetting power of cotton fabrics in a hydrogen oxide bleaching system. These dextrin derivative surfactants have excellent properties, in that they are much more biodegradable than traditional surfactants.

The authors are grateful to S. U. Fan and P. L. Chen for their assistance.

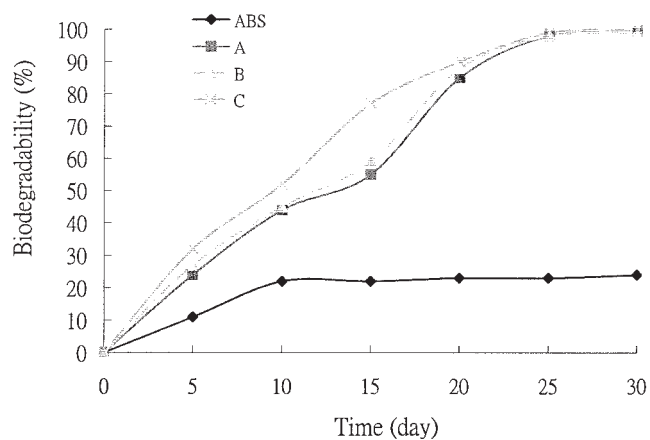
### References

1. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978; p 174

**TABLE IV**  
Ability of Dextrin Derivative Surfactant to Improve the Wetting Power [JIS-L-1096 Water Absorption Speed Test Method B<sub>2</sub> (Byreck Method)]

	Absorption height (mm)				
	Blank	A	B	C	ABS
After treatment 1 (inner)	21	31	33	56	46
After treatment 2	24	36	37	57	50
After treatment 3	26	37	40	61	56
After treatment 4	28	41	47	64	60
After treatment 5 (outer)	32	45	51	71	67





**Figure 5** Biodegradability of dextrin derivative surfactants.

2. Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 19; p 87.
3. Lin, L. H.; Chiang, C. Y.; Chen, K. M. *J Appl Polym Sci* 2002, 86, 2727.
4. Balzer, D.; Lauder, H. *Nonionic Surfactants*; Marcel Dekker: New York, 2000; p 365.
5. Chen, K. M.; Tsai, C. C. *Am Oil Chem Soc J* 1988, 65, 1346.
6. Liu, H. J.; Lin, L. H.; Chen, K. M. *J Appl Polym Sci* 2002, 86, 3005.
7. Liu, H. J.; Lin, L. H.; Chen, K. M. *J Appl Polym Sci* 2003, 88, 1236.
8. Wang, H. R.; Chen, K. M. *Am Oil Chem Soc J* 1992, 69, 60.
9. Weijers, S. R. *Biodegradability*; Ministry of Defence Interim Defence Standard 42-42.
10. AATCC Test Method 110-2000, *Whiteness of Textiles*, 2000.
11. JIS-L-1096, *Water Absorption Speed Test Method*, 1999.
12. Langdon, W. K. U.S. Pat. 4,011,389 (1977).
13. Schick, M. T.; Fowkes, F. M. *Surfactant Biodegradation*; Marcel Dekker: New York, 1987; p 513.