NOTES

Effect of Toluene on Cellulose Ethylation

Ethyl cellulose has several important applications as thermoplastic material, including its use as inhibitor in rocket propellant, a high-quality dielectric material in radio industry and a special film of protective coating, etc. Some investigators[1-3] have reported the manufacturing process of this material including the mass transfer effects, the kinetics of alkali cellulose reaction, and the applications of phase transfer catalysts. The objective of this article is to present some effects of toluene on ethylation of cellulose such as the ethylation rate and the product qualities etc. In addition to serve as a diluent, the toluene also greatly improved the product properties, especially helped to form the thermotropic liquid crystal of ethyl cellulose which has received great attention in recent years.

ETHYLATION RATE

The ethylation rate of alkali cellulose was enhanced by using toluene as showed in Figure 1. The toluene might have two functions during the ethylation. First, the toluene dissolved ethyl chloride and thus promoted its diffusion into the alkali cellulose. Second, the toluene dissolved the ethyl cellulose with high degree of substitution (DS). Thus the unreacted part of cellulose can further contact with ethyl chloride to continue forming ethyl cellulose.

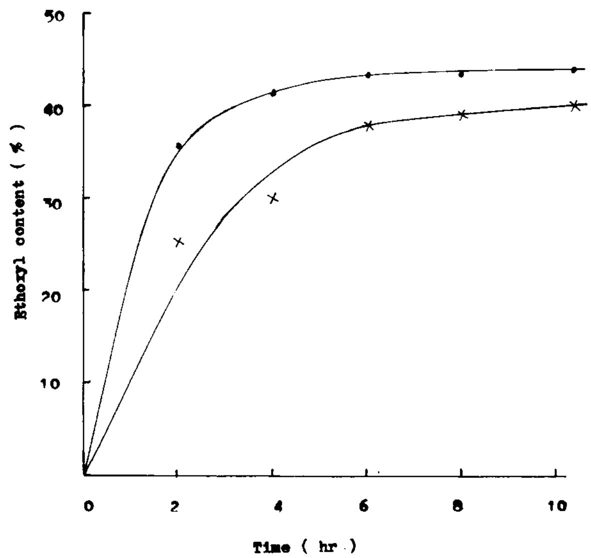

Figure 1 Relation between ethoxyl content and reaction time. Ethyl chloride 20 mL; (●) ratio of toluene to cellulose 7.75 mL/g; (×) toluene 0.

THE RATIO OF TOLUENE TO CELLULOSE

Although the addition of toluene in ethylation of alkali cellulose has considerable effects to accelerate the reaction rate, it was not correct that the more the toluene used, the better the results were. It was found that if the ratio of toluene to cellulose was about 5 mL/g, the products obtained possessed better properties as seen in Figure 2. When the reaction time was 2 h (see below curve), the ethoxyl content increased at first with increasing the ratio, passed the maximum at 5 mL/g, and decreased. The reaction rate decreased at the ratio higher than 5 mL/g was considered as the result of the excess dilution of ethyl chloride. If the reaction time was longer (6 h), the curve could not go down.

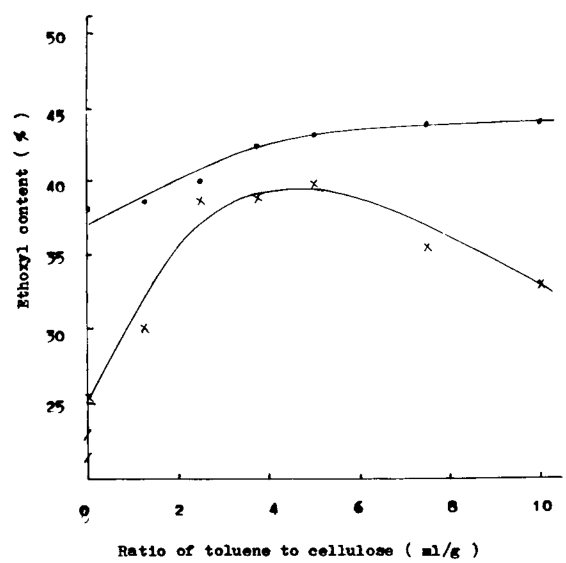

Figure 2 Effect of ratio of toluene to cellulose on ethylation. Ethyl chloride 20 mL; reaction time: (●) 6 h; (×) 2 h.

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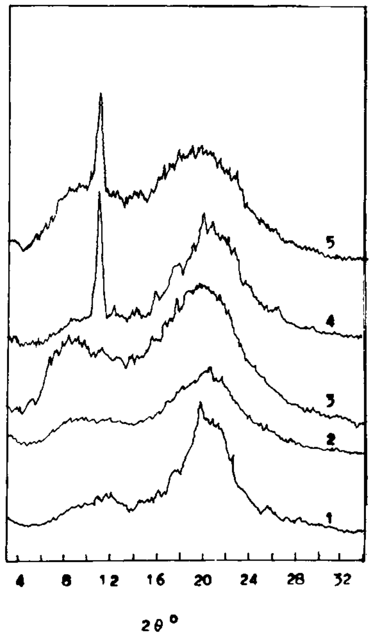


Figure 3 The X-ray diffractograms of ethyl cellulose: (1) toluene to cellulose ratio 7.75 mL/g, ethoxyl content 23%; (2) toluene to cellulose ratio 7.75 mL/g, ethoxyl content 33%; (3) toluene to cellulose ratio 7.75 mL/g, ethoxyl content 43%; (4) without use of toluene, ethoxyl content 25%; (5) without use of toluene, ethoxyl content 45%.

X-RAY DIFFRACTION

The X-ray diffraction patterns of ethyl cellulose prepared under different conditions were shown in Figure 3. It indicated that the peaks became smooth even at a low ethoxyl content (25%) in the presence of toluene in ethylation. On the other hand, the products still showed a sharp peak at $2\theta = 12°$ due to the crystal plane (101) of cellulose II even in a high ethoxyl content (45%) in the absence of toluene in the process of ethylation. It demonstrated that the toluene led to an efficient diffusion and to a homogeneous reaction of ethyl chloride throughout the cellulose fibers.

THERMOTROPIC LIQUID CRYSTALLINITY

The ethyl cellulose would exhibit liquid crystal behavior in a certain condition.[4,5] The thermotropic liquid crystal of ethyl cellulose prepared under different conditions was observed by a polarized light microscope with a heat stage. The results were illustrated in Table I and Figure 4. We can conclude that when the ratio of toluene to cellulose was about 5 mL/g, the ethyl cellulose has a lower solid phase–mesophase transition temperature (150°C) and a broader range of mesophase–isotropic phase transition temperature (ΔT).

Table I Thermotropic Liquid Crystallinity of Ethyl Cellulose Produced under Different Conditions

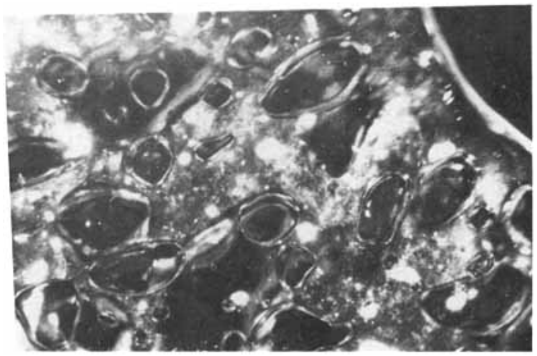
No.	Ratio of Toluene to Cellulose (mL/g)	Ethoxyl Content (%)	T_{kn}[a] (°C)	T_{ni}[b] (°C)	ΔT[c] (°C)	Phenomena in Liquid Crystals
1	0	45	181	205	24	A lot of microfibers
2	1.25	39	176	205	29	A lot of microfibers
3	2.50	40	180	205	25	Some microfibers
4	3.75	43	152	221	69	No visible microfibers
5	5.00	43	150	222	72	No visible microfibers
6	10.00	43	158	206	48	Some microfibers

[a] T_{kn} = crystal to liquid crystal transition temperature.
[b] T_{ni} = liquid crystal to isotropic transition temperature.
[c] $\Delta T = T_{ni} - T_{kn}$.

Table II Solubility of Ethyl Cellulose in Acetone[a]

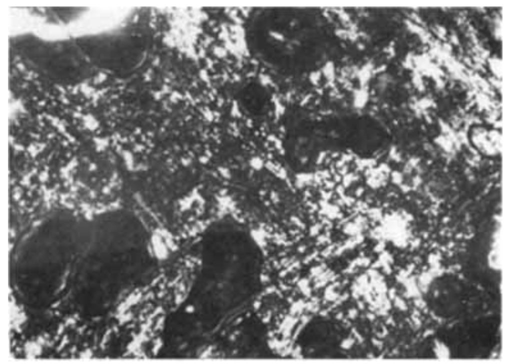
No.	Ratio of Toluene to Cellulose (mL/g)	Ethoxyl Content (%)	Solubility
1	0	45	Insoluble
2	1.25	39	Insoluble
3	2.50	40	Borderline solution
4	3.75	43	Complete solution
5	5.00	43	Complete solution
6	10.00	43	Complete solution

[a] Reaction time 6 h; ethyl chloride 10 mL/g.



(a) at 195 °C

(b) at 150 °C



(c) at 171 °C

Figure 4 Polarized light microscopy photomicrographs: (a) toluene to cellulose ratio 0, ethoxyl content 45%; (b) toluene to cellulose ratio 5.00 mL/g, ethoxyl content 43%; (c) toluene to cellulose ratio 10.0 mL/g, ethoxyl content 43%.

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