Cyanoethylation of Cellophane

There have been many reports on cyanoethylation of macromolecular organic substances with reactive hydrogen atoms. These substances consist of a wide variety of polymer such as cotton,[1–3] starch,[4] protein,[5] pulp, and poly(vinyl alcohol).[7,8] For the cyanoethylated cotton, it is said that the resistance to heat, acid damage, and microbiologic attack increases with extent of reaction and it was found that the dyeing properties can be improved.[1] Cyanoethylated cellulose has also been noted as a material with a high dielectric constant.[9,10]

Cyanoethylation of cellulose has been largely carried out in a heterogeneous reaction system as a fabric form, while only to a smaller extent in homogeneous systems. In this study, cyanoethylation of cellophane was conducted in a heterogeneous system by a one-step process in sodium hydroxide aqueous solution containing acrylonitrile, as a series of studies of chemical modification of polymeric films. The effects of the concentration of NaOH, acrylonitrile, wetting agent (sodium lauryl sulfate), and temperature on the conversion and the uniformity of reaction were investigated to determine the optimum condition for obtaining a partially cyanoethylated cellophane with retention of film form.

The water-vapor transmission rate was measured as one of the changing properties of cellophane by cyanoethylation. The results will be discussed in correlation with solubility and crystallinity.

EXPERIMENTAL

The cellophane films used here, which were supplied by Tokyo Cellophane Co. Ltd., were extracted by hot water for 24 hr and dried under vacuum. A small amount of cellophane (ca. 1 g) was placed in a 200-ml Erlenmeyer flask, and the appropriate volume of acrylonitrile was added. After further addition of the desired quantity of aqueous NaOH solution containing wetting agent, the atmosphere in the flask was replaced with N_2, and the flask was stoppered and shaken in a thermostated shaking apparatus at 40°C. After the prescribed time, the reaction was stopped by neutralizing with dilute acetic acid, and the films were washed adequately with fresh water followed by drying under vacuum.

The films are tinted a pale white at the conclusion of the reaction, but are transparent enough for the measurement of IR spectra, where the absorbance at 2240 cm^{-1} increases with increasing reaction time. The uniformity of the reaction was determined by observing the appearance of the film surface and checking the absorbance at 2240 cm^{-1} on various parts of the film. The films were analyzed for nitrogen content, which was also calculated from the weight gain of the products.

The water vapor transmission rates were measured by the cup method.

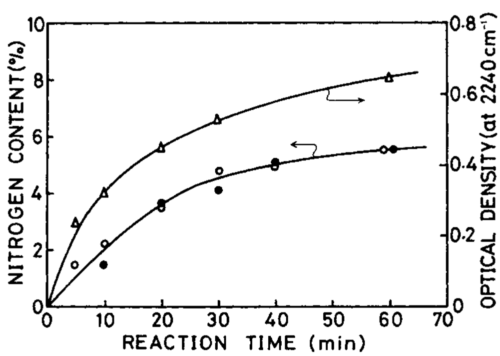

Fig. 1. Cyanoethylation of cellophane: (O) analyzed; (●) calculated.

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TABLE I
Effect of Sodium Lauryl Sulfate Concentration on Uniformity of Treatment[a]

Experiment no.	Volume of substances added in reaction system[b] Water, ml	2.5% Sodium lauryl sulfate, ml	Nitrogen content of product, %	Uniformity of treatment[c]
1	3.46	0	5.2	O
2	2.43	0.86	5.3	O
3	1.65	1.77	5.3	O
4	0.70	2.55	5.2	O
5	0	3.44	5.1	O

[a] Reaction temperature, 40°C; reaction time, 30 min; water/cellophane = 5.
[b] Cellophane weighed about 1 g; 50 ml acrylonitrile and 1 ml 10% sodium hydroxide, controlled constant at about 2.3%, were added.
[c] O, uniform; Δ, partly uniform; ×, nonuniform.

RESULTS AND DISCUSSION

It is well known that some subsequent reactions, e.g., hydrolysis, occur in cyanoethylation. That is to say, the cyanoethyl group introduced to the cellophane changes to carboxyethyl via the carbamoylethyl group in the presence of an alkaline catalyst. Since the hydrolysis becomes pronounced in an excess of hydroxyl ion or at high temperature, it is important to determine a suitable temperature for cyanoethylation. From some preliminary experiments and by taking into account many reports so far presented, the reaction temperature was fixed at 40°C. Under these experimental conditions, it was confirmed that the cyanoethylated cellophane shows no absorption by carbonyl in the IR spectrum.

It is also a well-known fact that acrylonitrile undergoes addition reaction of water in the presence of the alkali catalyst. Therefore, water had to be used as little as possible in cyanoethylation. Considering this fact, the weight ratio of water/cellophane was held at 5 or less in the following experiments.

A typical example of cyanoethylation is shown in Figure 1. As can be seen, excellent agreement between the nitrogen content analyzed and that calculated from the weight gain was obtained.

TABLE II
Effect of Sodium Hydroxide Concentration on Uniformity of Treatment[a]

Experiment no.	Volume of substances added in reaction system[b] Water, ml	10% Sodium hydroxide, ml	Concentration of sodium hydroxide, %	Nitrogen content of product, %	Uniformity of treatment[c]
6	5.00	0	0	0	O
7	4.75	0.25	0.5	2.2	O
8	4.50	0.50	1.0	4.0	O
9	4.00	1.00	2.0	5.5	O
10	3.00	2.00	4.0	7.3	Δ
11	2.00	3.00	6.0	8.4	×

[a] Conditions same as in Table I.
[b] Cellophane weighed about 1 g, and 50 ml acrylonitrile was added.
[c] See key in Table I.

TABLE III
Effect of Acrylonitrile Concentration on Uniformity of Treatment[a]

Experiment no.	Acrylonitrile added,[b] ml	Nitrogen content of product, %	Uniformity of treatment[c]
12	2	1.5	O
13	5	3.8	O
14	10	5.5	O
15	20	5.9	O
16	40	5.7	O

[a] Reaction temperature, 40°C; reaction time, 30 min.; NaOH/water = 2/50 amount of water:50 ml.
[b] Acrylonitrile was added in sodium hydroxide aqueous solution maintained constant at 2% with 1 g cellophane.
[c] See key in Table I.

TABLE IV
Effect of Temperature on Uniformity of Treatment[a]

Experiment no.	Reaction tempera-ture, °C	Nitrogen content of product, %	Uniformity of treatment[b]
17	20	0.5	O
18	30	2.2	O
19	40	4.2	O
20	50	6.0	Δ
21	60	7.2	×

[a] Reaction time, 30 min.; NaOH/water = 1/50; cellophane, 1 g; acrylonitrile, 50 ml.
[b] See key in Table I.

Effect of Concentration of Reagents on Conversion and Uniformity of Cyanoethylation Reaction

Effect of Sodium Lauryl Sulfate. In an attempt to investigate the influence of the addition of wetting agent, cellophanes were reacted with acrylonitrile at 40°C for 30 min under conditions of various concentrations of sodium lauryl sulfate. Results are shown in Table I. It can be seen that the addition of sodium lauryl sulfate has no influence on the yield of the product and the uniformity of the reaction.

Effect of Sodium Hydroxide. Cyanoethylation was carried out by varing the concentration of sodium hydroxide. As can be seen in Table II, the extent of cyanoethylation increased with increasing alkali concentration, but the uniformity of the film became worse. A uniform film was obtained at an alkali concentration of less than 2%.

Effect of Amount of Acrylonitrile. Acrylonitrile was added to 2% aqueous sodium hydroxide solution containing cellophane, and the solution was then maintained at 40°C for 30 min. From Table III, it is seen that the uniformity is independent of the amount of acrylonitrile, while the degree of cyanoethylation increases with increasing acrylonitrile concentration, with subsequent constant value at more than approximately 13%.

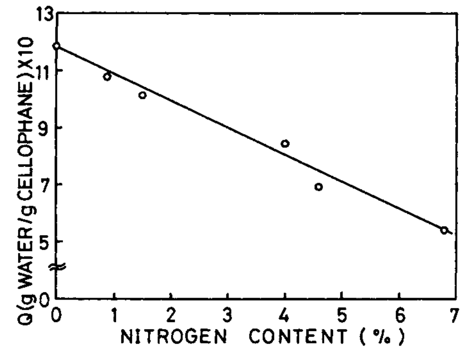

Fig. 2. Amount of equilibrium sorption of water vapor for cyanoethylated cellophane (at 40 C, 90% R.H.).

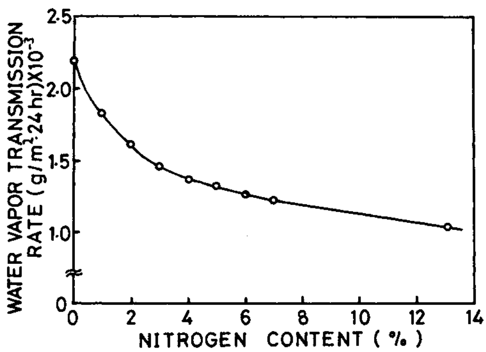

Fig. 3. Water vapor transmission rate of cyanoethylated cellophane.

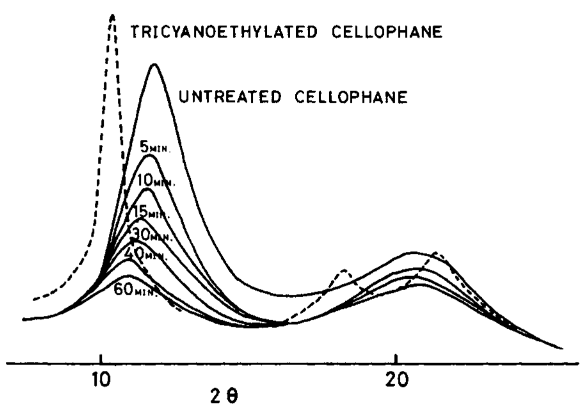

Fig. 4. X-ray diffraction patterns of cyanoethylated cellophane. (Figure denotes the reaction time.)

Effect of Temperature on Uniformity of Reaction

The results are shown in Table IV. The degree of cyanoethylation increased with increasing temperature but beyond 60°C, each of ununiformity was obtained.

Water Solubility and Water Vapor Transmission Rate of Cyanoethylated Cellophane

The water solubility in the cyanoethylated cellophane was measured from equilibrium sorption at 40°C, 90% R.H. (Fig. 2). The solubility decreased linearly with nitrogen content. This is believed to be due to the fact that the hydroxyl groups of cellulose are replaced with more hydrophobic cyanoethyl groups.

Water vapor transmission rate also decreased with increasing the number of cyanoethyl groups, which can be expressed in terms of the nitrogen content. The results are shown in Figure 3. In the figure, a rapid decline in the water vapor transmission rate is observed in the initial stage of the reaction, which may be attributed to the reduction in crystallinity (see Fig. 4). Therefore, it is concluded that the water vapor transmission rate decreases on account of the dual decrease in water solubility and crystallinity of the modified cellophane.

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