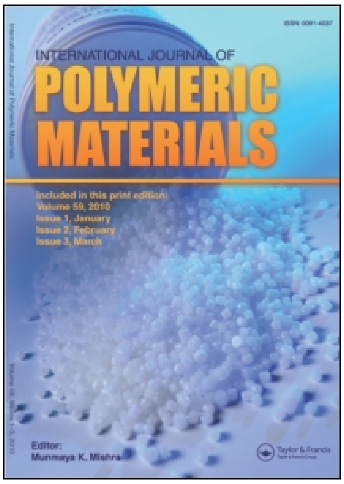

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Molecular Structure and Electrical Insulating Properties of Grafted and Cyanoethylated Cellulose

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Cyanoethylation of cellulose and Grafting of cellulose {bleached viscose wood pulp (VWP)} & cyanoethyl cellulose are carried out. The nitrogen content of these cellulose derivatives is determined. Grafted cyanoethyl cellulose has the highest nitrogen content (12.5%). FT/IR spectra of these derivatives showed a new band at $2225\,\mathrm{cm}^{-1}$ in the spectra of cyanoethyl and grafted cellulose which is the characteristic band for $—C{\equiv}N$ stretching vibration. Also, a new band appeared at $1720\,\mathrm{cm}^{-1}$ in case of grafted cyanoethyl cellulose, which is the characteristic band for $C{=}O$ stretching vibration. The crystallinity index (A 1435/A $900\,\mathrm{cm}^{-1}$) of cyanoethyl cellulose is lower than that in case of cellulose and grafted cellulose. The thermal study shows three endothermic peaks for grafted cyanoethyl cellulose while as cellulose, grafted and cyanoethyl cellulose has one endothermic peaks. The dielectric properties depend on the nitrogen content. These observations are closely correlated with the structure of the products such as types of side groups and the interaction between them.

Keywords: Grafted cellulose; cyanoethylated cellulose electrical insulating properties; molecular structure

1. INTRODUCTION

The versatility of acrylonitrile is shown by its ability to react with any compound possessing a label hydrogen atom thereby placing a great interest in the modification of macromolecular substance [1,2].

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*Corresponding author.

Among the macromolecular substances that have been cyanoethylated and grafted, the largest amount of work has been conducted with polymer containing OH groups [3]. Cellulose is the most already studied reaction, due to its physical and chemical properties, for us as fiber, paper, film and plastic. The availability of the reactive sites in cellulose represented by OH groups, make it ideal raw material for cyanoethylation, carboxymethylation [4, 5], grafting [6–8], and acetylation [9]. Cyanoethyl cellulose properties ranging from organic soluble thermoplastic products [10] to water soluble chemicals [11]. Cyanoethylation was also used to convert wood into thermoplastic material a means to utilize low quality wood species as well as wood waste materials. Partial cyanoethylation of cellulose has been studied to increase the thermal, chemical and microbial resistance [12]. Cellulose has been also cyanoethylated to obtain a highly substituted products which was used as an electrical materials [13, 14].

In this study the cyanoethylation and grafting of cellulose and cyanoethyl cellulose with acrylonitrile are carried out. The molecular structure of the derivative is followed by infrared spectroscopy. Also the dielectric properties and thermal analysis of these derivatives are also investigated.

2. EXPERIMENTAL

The material used in this study is bleached viscose wood pulp delivered from El-Nasr company for viscose Rayon, Koffer El-Dawar, Egypt and has the following analysis, α cellulose 94.2, hemi-cellulose 3.6 and ash content 0.5%.

2.1. 1-Cyanoethylation of Cellulose

20 gm of viscose pulp was socked in 100 ml NaOH solution (10%) with 2 gm urea at 25°C for 30 mint. Add 50 ml of acrylonitrile, then heat the mixture at 40°C for 2 hrs. Add 30 ml of glacial acetic acid and left the mixture for 5 minutes. Add 250 ml of ethyl alcohol with stirring. Filter and wash with ethanol tell neutrality. Drying in vacuum at 50°C.

2.2. Grafting of Cellulose and Cyanoethyl Cellulose

2.5 gm of cellulose or cyanoethyl cellulose was add to 7.5 ml acrylonitrile. After 5 mints add 60 ml of 0.1% ceric ammonium nitrate in nitric acid of 1% concentration. After two hours, the grafted cellulose and grafted cyanoethyl cellulose were filtered and washed tell neutrality and dry in vacuum at 50°C.

2.3. Nitrogen Content Estimation

Nitrogen content of the produced derivatives was estimated by using kehldal method and listed in Table I.

2.4. Spectral Measurements

The infrared spectra were carried out using Jacco FT/IR 300 E spectrophotometer. The samples were measured as KBr discs.

Crystallinity index of these materials was calculated from the infrared red spectra [15].

2.5. Dielectric Measurements

Specimen discs of dry samples about 1.2 mm thickness and 1.2 cm diameter were prepared by compressing powder at 5 ton/m^2. The disc surface was coated with silver past to achieve better contact. The dielectric measurements were carried out in the frequency range 0.1–100 KHz using AG–4311 B R C L meter. The measuring cell consists of two parallel plates of copper, of 12 mm diameter attached to movable micrometer. It was calibrated using stander samples.

TABLE I Nitrogen content of cellulose and its derivatives

Compound	*Nitrogen content %*
Cellulose	–
Cyanoethyl cellulose	1.5
Grafted cellulose	5.5
Grafted cyanoethyl cellulose	12.5

2.6. Thermal Analysis

Thermal analysis of these materials were carried out using a computerized PERKIN-ELMER. (DTA 7) Thermal Analysis System. Heating rate was 10°C/min.

3. RESULTS AND DISCUSSION

3.1. Infrared Spectra

In this work the molecular structure of cellulose and its derivatives was studied using infrared spectroscopy. The infrared absorption spectra of cellulose (A), cyanoethyl cellulose (B), grafted cellulose (C) and finally the grafted cyanoethyl cellulose (D) were recorded in the region 200-4000 cm^{-1} as shown in Figure 1. From this figure it is interesting to notice that, cyanoethyl cellulose (B) show a very weak band at

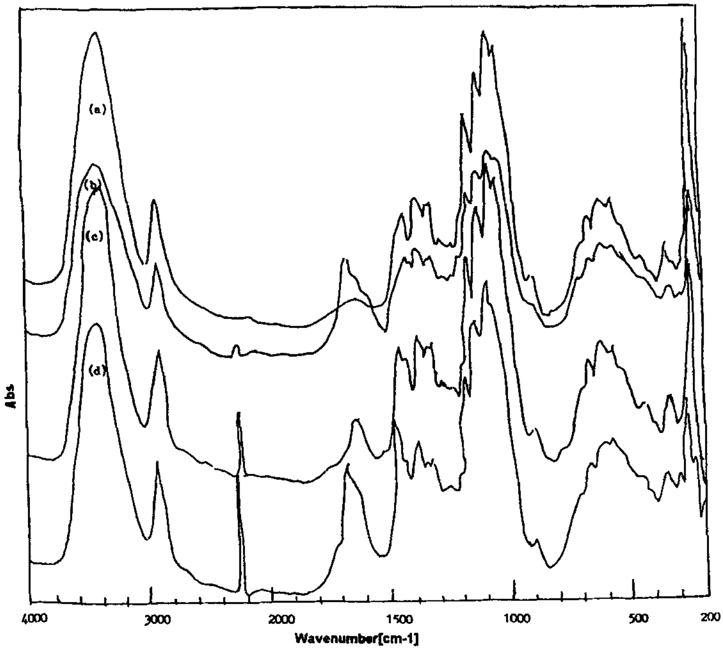


FIGURE 1 Infrared spectra of cellulose (a), cyanoethyl cellulose (b), grafted cellulose (c) and grafted cyanoethyl cellulose (d).

2223 cm^{-1} which is the characteristic band of C$\equiv$N stretching vibration. Also two weak bands appeared at 1640 and 1680 cm^{-1} which are characteristic for CO st of amide group vibration overlapped with carbonyl of COOH vibration. This indicates the formation of amide and carboxyl group during cyanoethylation of cellulose as a side reaction. This was confirmed by the low nitrogen content (1.5%). On the other hand, the infrared spectra of the grafted cellulose show the characteristic band of CN vibration with high intensity than that in case of cyanoethyl cellulose. Also the bending CN vibration appeared at 1440 cm^{-1}. This indicated that the grafted cellulose has a higher quantity of the CN group than cyanoethyl cellulose. This can be confirmed by the higher nitrogen content of grafted cellulose (5.5%) than cyanoethyl cellulose (1.5%). In case of grafted cyanoethyl cellulose the infrared spectrum show a strong absorption band for CN stretching vibration at 2220 cm^{-1}. Also two new bands appeared at 1660 cm^{-1} and 1720 cm^{-1} which related to the amide and carboxyl group respectively, this may be due to the higher nitrogen content of grafted cyanoethyl cellulose (12.5%). Due to the grafting of cyanoethyl cellulose CO vibration of amide group appeared at 1690 and a carboxyl band at 1720 cm^{-1}. These bands are not found in cyanoethyl cellulose. The appearance of these bands in the grafted cyanoethyl cellulose can be attributed to the grafting with acrylonitrile, which was occurred not only on the hydroxyl group of cellulose, but also on the carbon atom of the cellulose by free radical technique. So this help for the appearance of the amide and carboxylic bands at 1650 – 1690 and 1720 cm^{-1} respectively. Crystallinity index of cellulose and its derivatives were shown in Table II.

From this table, it is clear that the crystallinity index of cellulose and its derivatives have the following sequence

Cellulose > grafted cellulose > cyanoethyl cellulose > grafted cyanoethyl cellulose.

TABLE II Crystallinity index of cellulose and its derivatives

Compounds	*CrI* (*A* 1435/*A* 900 *cm*$^{-1}$)
Cellulose	3.6
Cyanoethyl cellulose	3.0
Grafted cellulose	3.2
Grafted cyanoethyl cellulose	2.4

Cyanoethylation causes a decrease in the crystallinity index of the cellulose due to the swelling of cellulose, which was resulted from the presence of sodium hydroxide, which was used, in the cyanoethylation process. Also the introducing of the cyanoethyl group in cellulose causes a decrease in the crystallinity index. So, the grafted cyanoethyl cellulose has the lowest CrI.

3.2. Dielectric Properties

The dielectric constant ε', dielectric loss ε'' and dissipation factor $\tan\delta$ for the cellulose and its derivatives were measured over the frequency range (0.1 – 100 KHz). Generally, it can be noticed that the dielectric properties ε', ε', and $\tan\delta$ decreases with increasing frequency. Figure 2, shows the dielectric constant ε' of the cellulose and its derivatives at different frequency. It is clear from the figure that, the dielectric constant of cellulose has the highest values than other derivatives taking the sequence cellulose > cyanoethyl cellulose > grafted cellulose > grafted cyanoethyl cellulose over all the frequency used. Cellulose is partially amorphous polymer and contains dipolar side groups.

The permanent dipoles are thus unable to reorient independently of the main chain. Dielectric relaxation in cellulose must therefore

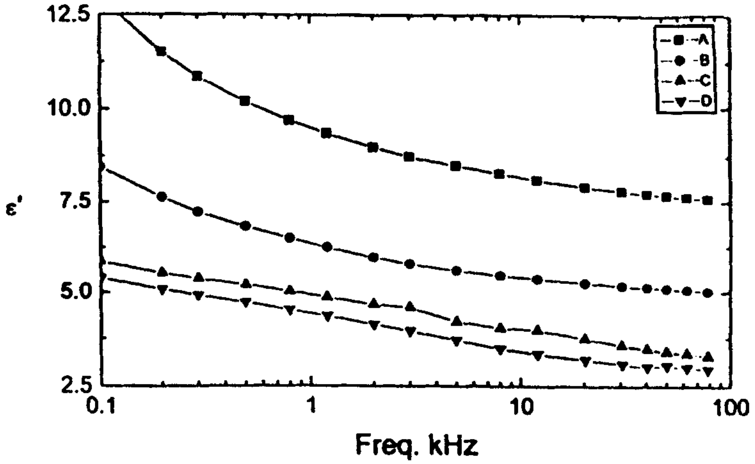
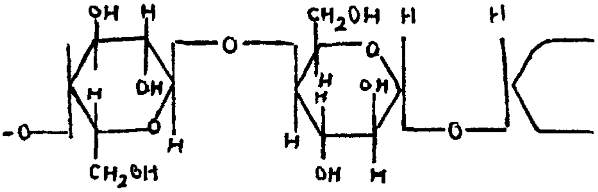


FIGURE 2 Dielectric constant *vs.* frequency: (A) V.W.P.; (B) cyanoethyl cellulose; (C) graft cellulose; (D) graft cyanocellulose.

involve simultaneous main-chain and side-chain motions. As the alcoholic methyl content in cellulose increases the relaxation process due to the orientation of methyl group's B process appears. In the case of side substituents of different size and polarity by cyanoethylation and grafting of cellulose will affect the intra and intermolecular interaction and the mobility of the units. The Expected structures of the produced products are as follows:

(A) R—OH (cellulose)



$\mathrm{R{-}OH + CH_2{=}CH{-}CN \rightarrow}$ (B) $\mathrm{R{-}O{-}CH_2{-}CH_2{-}CN}$

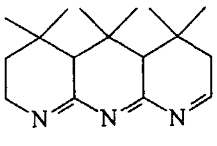
$\mathrm{R{-}O{-}CH_2{-}CH_2{-}CONH_2}$

$\mathrm{R{-}O{-}CH_2{-}CH_2{-}COONa}$

(C) $\mathrm{R{-}O{-}CH_2{-}CH_2{-}CN}$

$\mathrm{R{-}CH_2CH_2{-}CN}$

(D) B + C



From (Fig. 2), it is clear that the dielectric constant ε' values decreases from cellulose to finally grafted cyanoethyl cellulose which has higher value of nitrogen content than the cyanomethyl and grafted cellulose. This can be attributed to that the length of the side chain polymerized acrylonitrile attached to the cellulose structure is enough to form ring structure [1]. This structure was formed in case of the high nitrogen content samples *i.e.*, in case of grafted and grafted cyanoethyl cellulose.

This ring structure causes a restriction for the functional groups which enhances intermolecular interaction and decreases the mobility of these functional groups, and consequently decreases the dielectric constant values. This can be confirmed by the infrared spectra which show a band of CN st vibration at 1640 cm^{-1}. This band is more pronounced in case of grafted cyanoethyl cellulose which contains a higher nitrogen content than cyanoethyl cellulose. Figures (3, 4) shows the dielectric loss ε dissipation factor ($\tan\delta$) *versus* frequency. It is clear from these figures that ε and $\tan\delta$ decreases by increasing the reaction between acrylonitrile and alcoholic groups in cellulose. Also the dielectric intensities are reduced with increasing frequency as shown in Figures (3, 4). The values of the power factor $\tan\delta$ of the grafted cellulose and grafted cyanoethyl cellulose are lower than that of cellulose and cyanoethyl cellulose taking the values (0.15–0.012) which are in the range of the insulating materials. Also we can notice that C and D samples showed have nearly equal values of $\varepsilon^{=}$ and $\tan\delta$ and are more or less stable overall the frequency range.

Figure 5 show that the dielectric constant ε' and dielectric less ε'' values decrease smoothly with increasing nitrogen content in the cellulose derivatives.

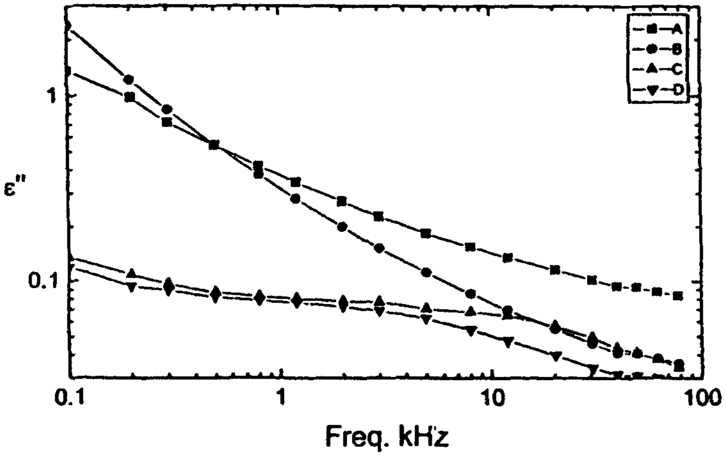


FIGURE 3 Dielectric loss *vs*. frequency: (A) V.W.P.; (B) cyanoethyl cellulose; (C) graft cellulose; (D) graft cyanocellulose.

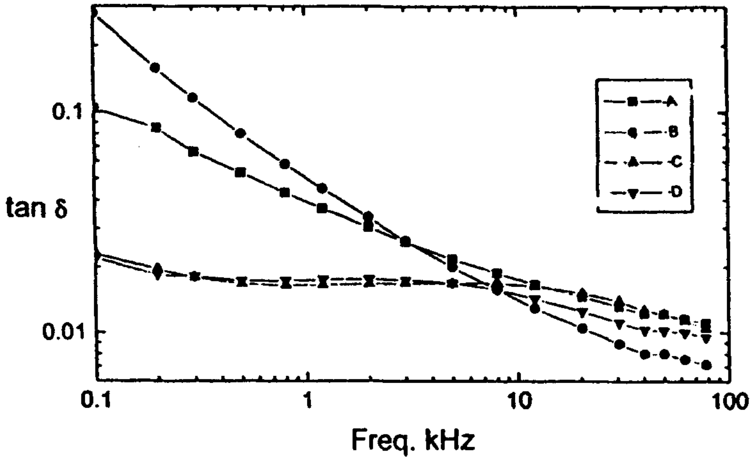


FIGURE 4 tan δ *vs.* frequency: (A) V.W.P.; (B) cyanoethyl cellulose; (C) graft cellulose; (D) graft cyanocellulose.

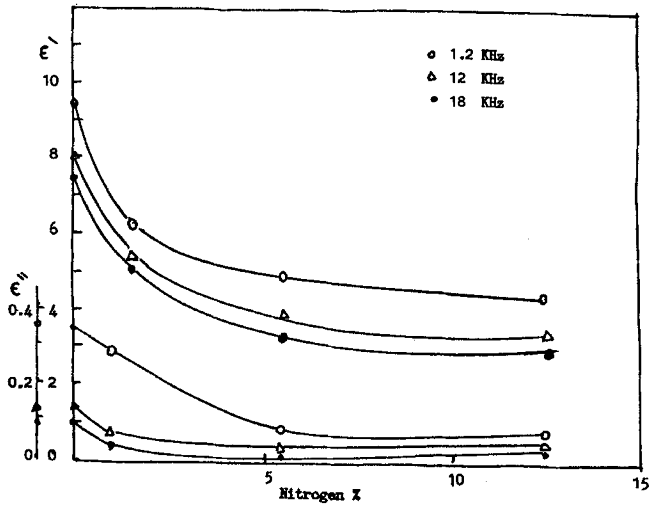


FIGURE 5 Relation between the dielectric constant (ε') and dielectric loss (ε'') and nitrogen content at different frequencies for cellulose and its derivatives.

The results can be summarized that, the changes in the dielectric properties are associated with the nitrogen content introduced by different treatment. This observation is closely correlated with the structure of the products such as types of side groups and the cross links between them.

3.3. Thermal Analysis

Another tools to show the effect of introducing cyanoethyl groups on the thermal stability of treated cellulose was discussed as follow.

Cyanoethylation reaction always involves a loss in reagent to the side reaction because of the high reactivity of acrylonitrile. In this side reaction, water with cellulose giving various side products [3].

$$\begin{aligned} R{-}OH + CH_2{=}CH{-}CN \xrightarrow{NaOH} & R{-}O{-}CH_2{-}CH_2{-}CN \\ & R{-}O{-}CH_2{-}CH_2{-}CONH_2 \\ & R{-}O{-}CH_2{-}CH_2{-}COONa \end{aligned}$$

Depending upon nitrogen content, the cyanoethyl cellulose a softening temperature and melting temperature. So, from Figure 6, it is seen from the differential thermal analysis curves that an endothermic peaks at 339°, 321° and 296°C for cellulose, grafted cellulose and cyanoethyl cellulose respectively. In case of cyanoethyl cellulose, its endothermic peak is lower than grafted cellulose with acrylonitrile although it contains a lower nitrogen content (1.5%) than grafted cellulose (5.5%). This can be attributed to the increase of swelling of cellulose during the cyanoethylation process. This swelling causes an increase in the amorphous part which decomposed readily than the crystalline part in cellulose. Also cyanoethylation of cellulose decreases the endothermic peak of the produced cyanoethyl cellulose.

In general, the presence of cyano groups in the cellulose produced from cyanoethylation or grafting of cellulose causes a decrease of the endothermic peak of cellulose. In case of grafted cyanoethyl cellulose, which has a higher nitrogen content (12.5%) than the cyanoethyl cellulose or grafted cellulose, *i.e.*, high cyanoethyl groups, a more endothermic peaks are formed. Endothermic peaks were observed at 254, 324 and 413°C in case of grafted cyanoethyl cellulose. The first peak was formed due to the presence of cyanoethyl group, with larger scale than grafted and cyanoethyl cellulose, corresponding to the melting of the grafted cyanoethyl cellulose. The second peak is assigned to the

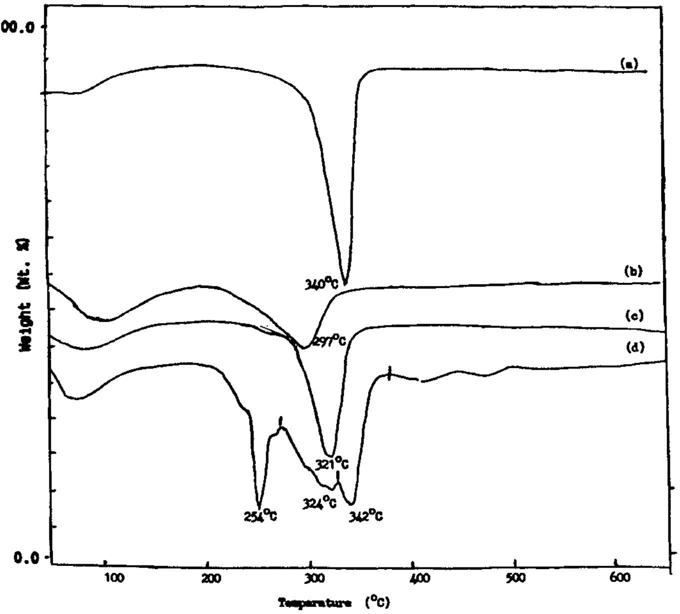


FIGURE 6 Differential thermal analysis (DTA) of cellulose (a), cyanoethyl cellulose (b), grafted cellulose (c) and grafted cyanoethylated cellulose (d).

depolymerization of cellulose [16]. The third peak can be believed to the decomposition of cellulose [17].

So, from the above thermal analysis discussion, it is clear that the increase of cyanoethyl groups causes an increase of fiber elasticity as well as disordered regions.

References

[1] Hon, D. N. S. and Ou, N. H. (1989). *J. Polym. Sci. Chem.*, Ed. 27, 2457.
[2] El-Shinawy, N., Nada, A. M. A. and El-Kalyoubi, S. F. (1986). *Cellul. Chem. Technol.*, **20**, 233.
[3] Hon, D. N. S. and Sanduis, J. M. (1989). *J. Polym. Sci. P(A) Polym. Chem.*, **27**, 4143.
[4] Yousef, M. A., Nada, A. M. A. and Ibrahem, A. A. (1989). *Cellul. Chem. Technol.*, **23**, 505.
[5] Mobarak, F. M. and Nada, A. M. A. (1983). *Svensk Paper Stud.*, **86**, 120.
[6] Nada, A. M. A., El-Kalyoubi, S. F. and El-Rowainy, I. (1989). *Polym. Plast. Technol. and Eng.*, **28**(4), 439.
[7] Nada, A. M. A. and Yousef, M. A. (1989). *Acta Polymerica*, **40**(7), 439.

[8] Nada, A. M. A. and Yousef, M. A. (1996). *Encycleopedia of Polymer Sci. and Technol.*, Ch. 34.

[9] Ibrahem, A. A. and Nada, A. M. A. (1986). *Acta Polymerica*, **37**(5), 320.

[10] Fridrich, K. G. (1945). Pat. 2, 375, p. 847.

[11] Mc.Greger, J. H. and Pugh, C. (1951). *J. Soc. Dyers Colour*, **67**, 74.

[12] Bikales, N. M. and Segal, I. (1991). Cellulose and Cellulose Derivatives, P. 3. John, Wiley and Sons. New York, USA.

[13] Hall, J. A. (1954). *Text. Res. J.*, **130**, 103.

[14] Morook, Toshiro (1987). *Wood Research*, **40**, 45.

[15] Conner, R. T. O., Dupre, E. F. and Mitcham, D. (1958). *Text Res. J.*, **28**, 382.

[16] Chatterjee, P. R. and Schwenker, P. F. (1972). *Tappi*, **55**, 111.

[17] Schwenker, R. F., Beat, L. R. and Zuccarello, R. K. (1964). American Dyestuff Reporter, **P817**, 30.