Thermoplasticization of Bagasse by Cyanoethylation

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ABSTRACT: To develop a new technique for the effective utilization of bagasse, cyanoethylation was attempted to see if bagasse could be converted into a thermoplastic material. The effects of various reaction parameters (temperature, time, alkali concentration, and acrylonitrile-to-bagasse ratio) on the extent of the cyanoethylation reaction were studied. Fourier transform infrared spectroscopy was done to demonstrate the occurrence of cyanoethylation; thermogravimetric analysis, to study the thermal stability of the produced cyanoethylated bagasse; X-ray diffraction, to follow the change in the supramolecular structure; and scanning electron microscopy of hot-pressed cyanoethylated bagasse to show the occurrence of thermoplasticization. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1965–1978, 2001

Key words: bagasse; cyanoethylation; thermoplasticization

INTRODUCTION

Previous investigators have demonstrated that thermomoldable products can be produced by extensively modifying wood meal or fiber by chemical modification.[1] Cyanoethylation was one of the chemical reactions used for this purpose.[2–8] Morita et al.[2] prepared cyanoethylated wood (CE-wood) using Buna wood meal. The CE-wood, which had a nitrogen content of 9–10%, demonstrated thermal flow at 246°C. Kiguchi[3] investigated the conditions for achieving hot-melted surfaces of wood, keeping the wood structure intact by the mean of liquid- or vapor-phase cyanoethylation. The hot-melted surface of the CE-wood obtained had a high level of glossiness, but its water resistance was poor. Cyanoethylation was also carried out to convert wood meal into thermoplastic material.[4] The CE-wood obtained exhibited melting temperatures ranging from 240°C to 270°C depending on the nitrogen content. China fir wood was modified by cyanoethylation using a low concentration of aqueous NaOH solution saturated with NaSCN as the preswelling agent and catalyst.[5] CE-wood with a nitrogen content of 8.8–9.7% could be molded into semitransparent and homogeneous films or sheets by hot pressing at 160°C. The cyanoethylation process was found somewhat to affect the integrity of the wood's histologic structure.[6] The structural changes of modified wood conferred some desired properties, that is, solubility and thermoplastic behavior, but some undesirable alteration effects also could appear.

Little work has been conducted so far on cyanoethylation of agro-based fibers. Jute fibers were cyanoethylated using benzene and dioxane as diluents for acrylonitrile.[7] Jute fibers were delignified progressively, and their effect on the cyanoethylation reaction was studied. The reactivity of holocellulose toward cyanoethylation was higher than that of lignin. In previous studies[1,8] bagasse was shown to be converted into thermoplastic material by means of esterification using succinic

anhydride. In this study cyanoethylation of bagasse was investigated with the aim of obtaining a thermoformable product. The cyanoethylation chemistry, the change in crystallinity as a result of cyanoethylation, and the thermal stability of the produced cyanoethylated bagasse (CE-B) are discussed.

EXPERIMENTAL

Materials

Edfu Pulp Company, Edfu, Egypt, supplied bagasse in the form of 2- to 3-cm-long fibers. The chemical composition of bagasse is 21.4% lignin, 25.9% hemicellulose, 78.3% holocellulose, 55.3% alpha cellulose, and 1.4% ash. The fibers were milled using 20-mesh screen, extracted with ethanol–benzene (2:1 v/v) for 6 h, washed with distilled water, and then left to air dry. All chemicals and solvents used were reagent grade and used without further treatment or purification.

Cyanoethylation

Two grams air-dried bagasse were soaked in an aqueous NaOH solution [with a concentration of 5, 10, and 15% (w/w)] for 30 min with continuous stirring at room temperature. Then the mixture was filtered and the alkali squeezed to pick up a gain of 150%, and it was then transferred to a 100-mL Erlenmeyer flask, to which acrylonitrile was added. The ratios used were 1:10, 1:15, and 1:20 acrylonitrile:bagasse (w/v). The flasks were closed and heated in a shaking water bath at 40°C or 60°C for 1–4 h. The resulting reaction mixture was poured into a container containing 50% ethanol, stirred, and then filtered. To remove byproducts, the isolated solid product was then washed, first in the 50% ethanol, then in 50 mL of 10% acetic acid solution, then thoroughly with distilled water, and finally with 100% ethanol. The purified CE-B was then vacuum-dried at 60°C until at a constant weight.

The nitrogen content was used as a measure of the extent of cyanoethylation. The micro-Kjeldahl method was used for nitrogen determination.[9]

Characterization of Cyanoethylated Bagasse

FTIR Analysis

A JASCO 300-E Fourier transform infrared (FTIR) spectrometer was used to analyze changes in the chemical structure of cyanoethylated bagasse (CE-B). All measurements were carried out using the KBr pellet technique.

Thermogravimetric Analysis

A Perkin–Elmer thermogravimetric analyzer was used to study the thermal properties of CE-B. The heating rate was set at 10°C/min over a temperature range of 50–750°C. Measurements were carried out in a nitrogen atmosphere, with a rate of flow of 50 cm^3/min. For each measurement 7 mg of the oven-dry sample was used.

X-ray Diffraction Measurements

A Philips X-ray diffractometer was used to record X-ray diffraction patterns of untreated and CE-B samples. For each measurement a disk was prepared by compressing a 0.3-gram sample under a pressure of 50 MPa. The equatorial diffraction patterns were recorded from $2\theta = 5$–35 using Cu-Kα radiation at 40 KV and 25 mA.

Pressing a Cyanoethylated Bagasse Sample into Pellets

Cyanoethylated bagasse (CE-B) was pressed into a mold 1 cm in diameter in a press at 70, 140, and 170°C under a pressure of 50 MPa for 8 min.
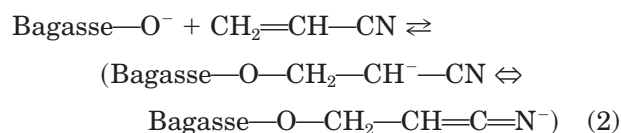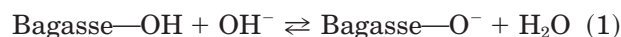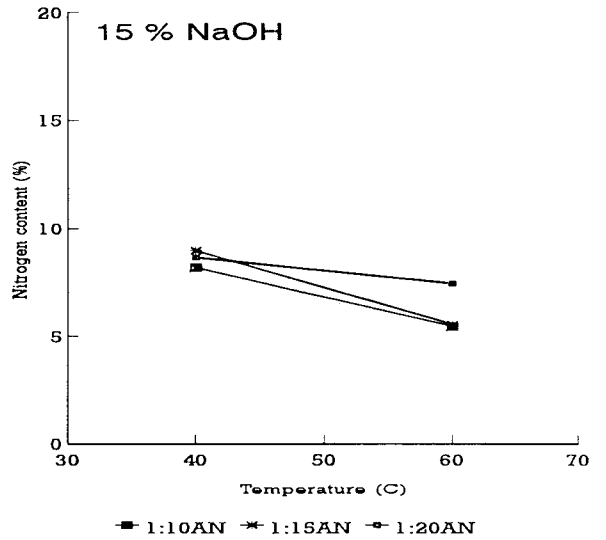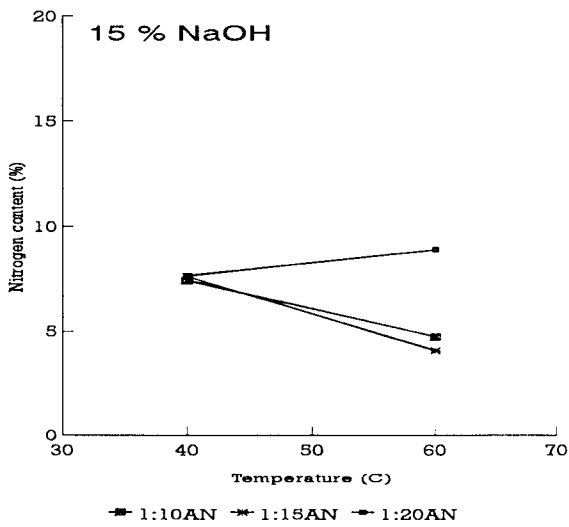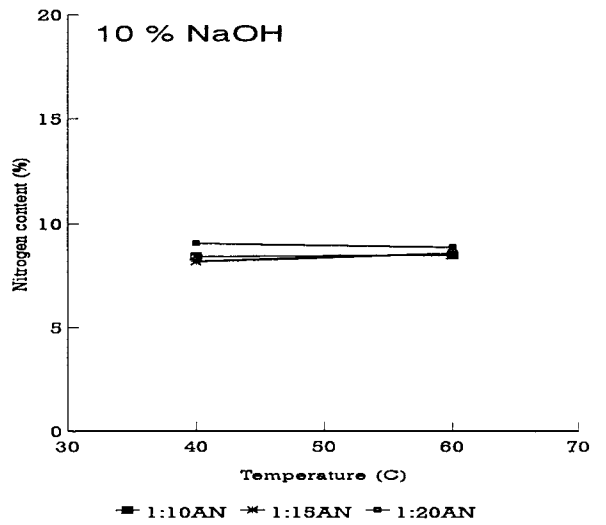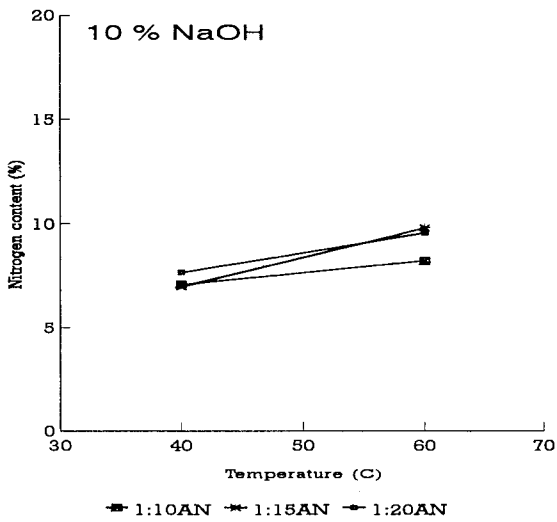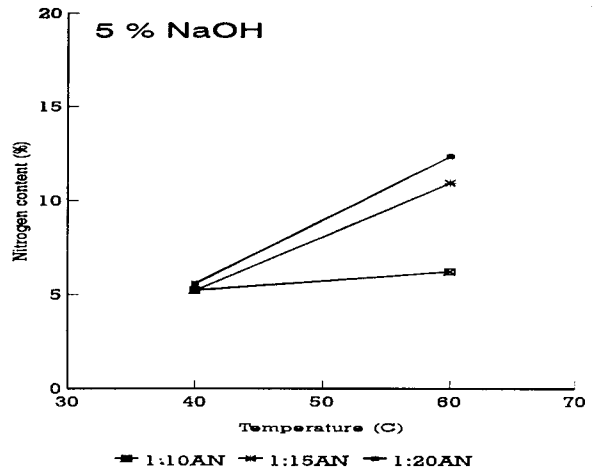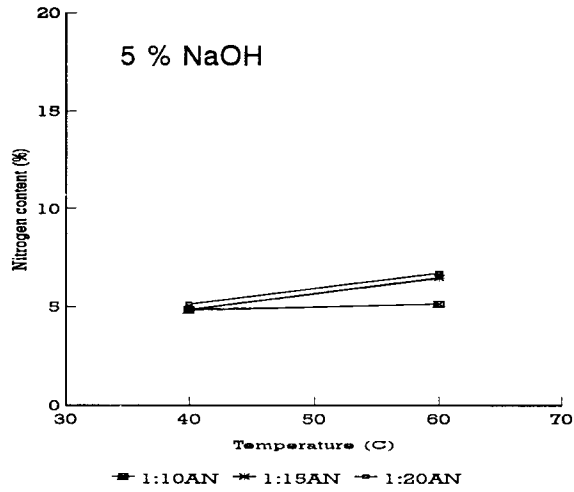
Scanning Electron Microscopy

The cross sections of the hot-pressed pellets made from CE-B samples were examined with a JOEL scanning electron microscope. All specimens were coated with gold before scanning.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on the Extent of Cyanoethylation of Bagasse

The extent of the cyanoethylation reaction was expressed in terms of nitrogen content. The mechanism for calculating the cyanoethylation reaction of bagasse constituents is shown in the following equations:

$$Bagasse\text{—}OH + OH^- \rightleftarrows Bagasse\text{—}O^- + H_2O \quad (1)$$

$$Bagasse\text{—}O^- + CH_2\text{=}CH\text{—}CN \rightleftarrows$$

$$(Bagasse\text{—}O\text{—}CH_2\text{—}CH^-\text{—}CN \Leftrightarrow$$

$$Bagasse\text{—}O\text{—}CH_2\text{—}CH\text{=}C\text{=}N^-) \quad (2)$$

(a)

(b)

Figure 1   Effect of reaction temperature on nitrogen content of CE-B: (a) after 1 h, (b) after 4 h.
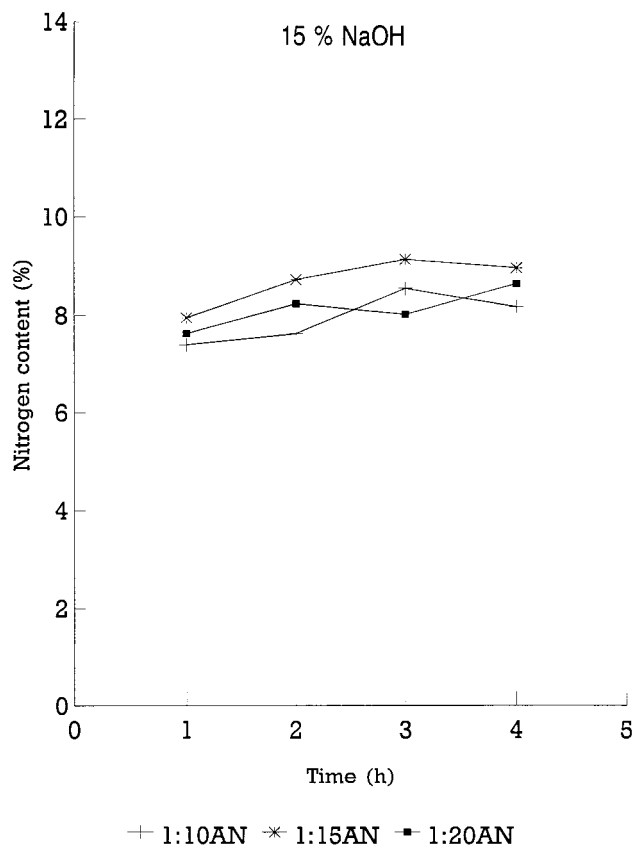
Figure 2 Effect of reaction time on nitrogen content of CE-B at 40°C.

(Bagasse—O—CH_2—CH^-—CN ⇔

    Bagasse—O—CH_2—CH=C=N^-) + H_2O ⇌

        Bagasse—O—CH_2—CH_2—CN + OH^- (3)

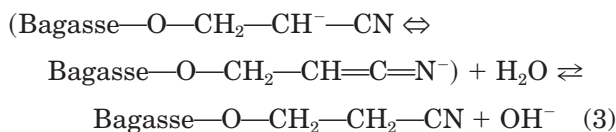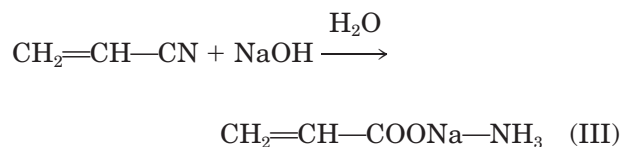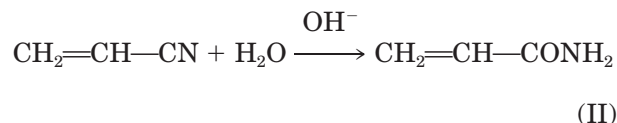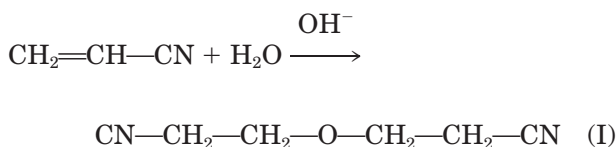These reactions are reversible, so reaction conditions must be selected that favor the forward reaction. In addition, the cyanoethylation reaction involves a loss in the reagent to the side reactions because of the high reactivity of acrylonitrile (AN). Therefore, an excess of AN should be added in order to produce the given derivative.[10–12] Water competes with bagasse constituents in the cyanoethylation reaction giving various side products as follows:

$$CH_2=CH—CN + H_2O \xrightarrow{OH^-}$$

    CN—CH_2—CH_2—O—CH_2—CH_2—CN   (I)

$$CH_2=CH—CN + H_2O \xrightarrow{OH^-} CH_2=CH—CONH_2$$

(II)

$$CH_2=CH—CN + NaOH \xrightarrow{H_2O}$$

    CH_2=CH—COONa—NH_3 (III)

The side products II and III may further react with the hydroxyl groups of bagasse constituents to form:

$$Bagasse—OH + CH_2=CH—CONH_2 \xrightarrow{OH^-}$$

    Bagasse—CH_2—CH_2—$CONH_2$ (IV)

$$Bagasse—OH + CH_2=CH—COONa \xrightarrow{OH^-}$$

    Bagasse—CH_2—CH_2—COONa   (V)
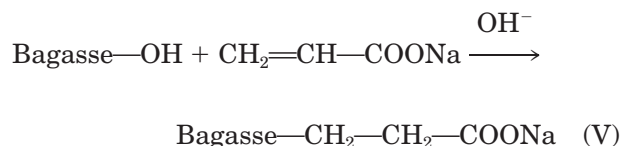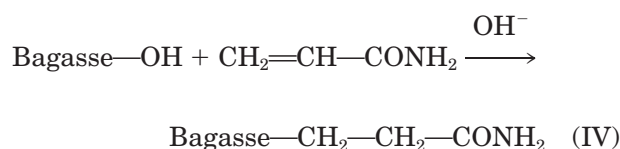
The formation of product (V) results in etherification of bagasse without affecting the nitrogen content of the product.

The effects of the different reaction parameters, such as temperature (40–60°C), time (1–4 h), alkali concentration (5–15%), and the acrylonitrile:bagasse (AN:B) ratio (1:10–1:20), were studied to determine the optimum conditions that will enhance the cyanoethylation reaction. The results are discussed in detail in the following sections. Cyanoethylated bagasse (CE-B) with a wide range of nitrogen contents (from about 5% up to 13%) can be obtained.

Effect of Reaction Temperature

Figure 1 shows the effect of reaction temperature on the nitrogen content of the produced CE-B at different AN:B ratios and alkali concentrations after 1 and 4 h. From Figure 1 it is obvious that the effect of reaction temperature was dependent on alkali concentration and reaction time. An increasing reaction temperature, from 40°C to 60°C, resulted in an increase in the nitrogen content at a 5—10% alkali concentration after 1 h [Fig. 1(a)]. At a higher alkali concentration (15%), an increasing reaction temperature resulted in a
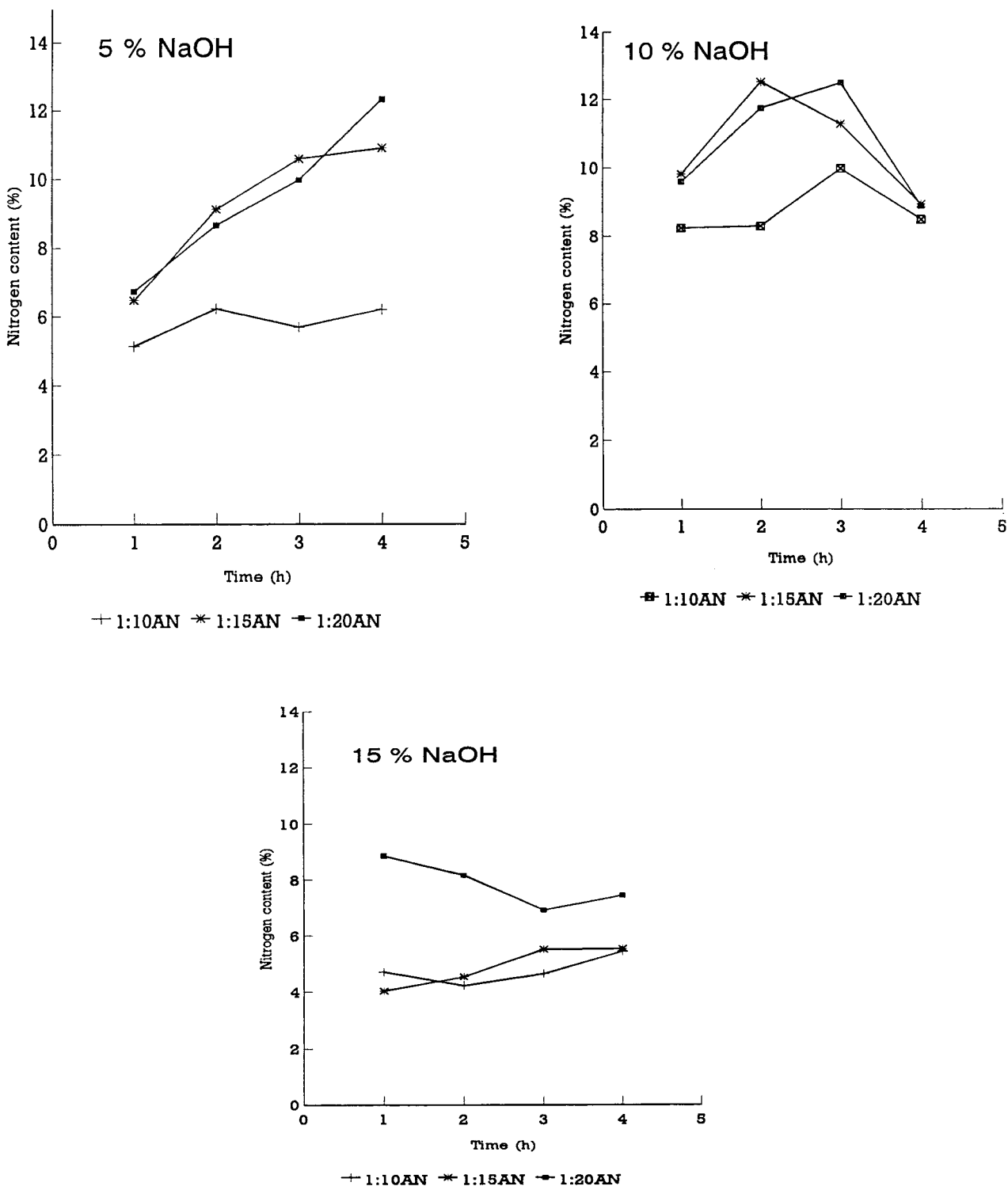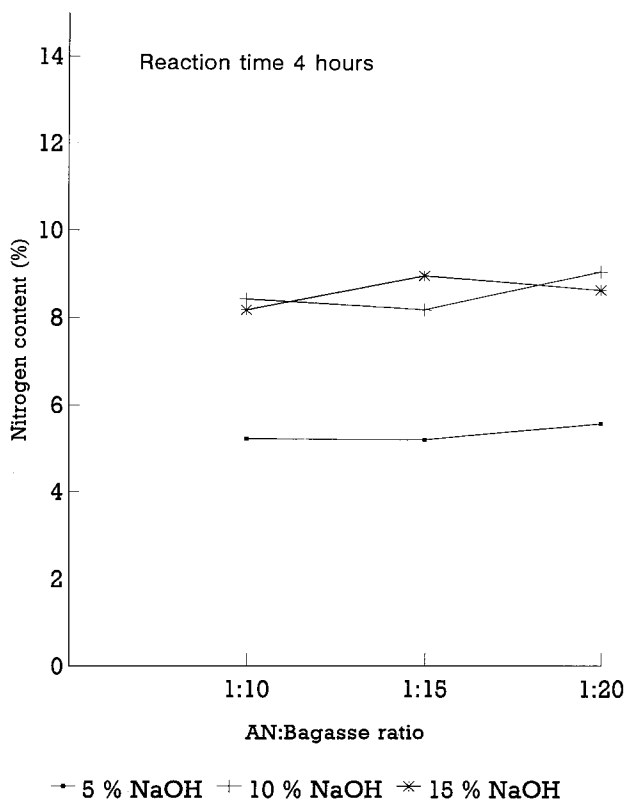
Figure 3 Effect of reaction time on nitrogen content of CE-B at 60°C.

decrease in nitrogen content except at the 1:20 AN:B ratio. Figure 1 represents the general pattern of the effect of temperature on the nitrogen

content after 2 and 3 h using different AN:B ratios. After 4 h [Fig. 1(b)], increasing the reaction temperature from 40°C to 60°C resulted in an

$\cdot$ 5 % NaOH + 10 % NaOH ✳ 15 % NaOH

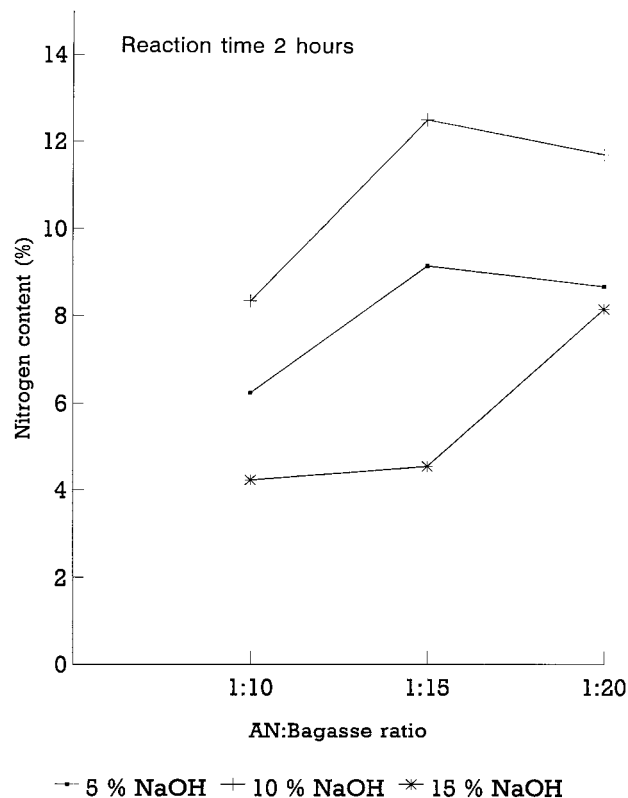**Figure 4** Effect of AN:bagasse ratio on nitrogen content of CE-B at 40°C.

increase in the nitrogen content of CE-B only at a low alkali concentration (5%); at higher alkali concentrations (10% and 15%) an increasing reaction temperature resulted in a decrease in the nitrogen content. The decrease in nitrogen content at high alkalinity and temperature may be due to cleavage of the ether linkage.[10] In addition, McGregor[11] found that a high temperature combined with high alkalinity promotes reactions that tend to result in lower yields and instability of the product. In another study of cyanoethylation of wood,[4] it was found that increasing the reaction temperature from 50°C to 70°C resulted in a decrease in the nitrogen content of CE-wood with alkali concentrations of 5–15%, reaction times of 1–3 h, and an AN:wood ratio between 1:20 and 1:5.
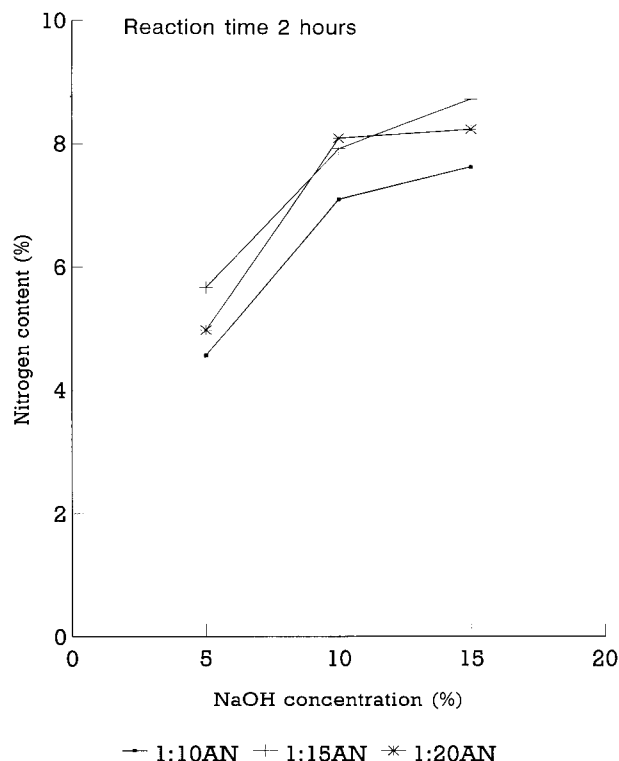
Effect of Reaction Time

Figure 2 shows the general pattern of the effect of time on nitrogen content at 40°C with different alkali concentrations and AN:B ratios In particular, Figure 2 shows the effect of increasing reaction time on the nitrogen content of CE-B at 40°C using 15% NaOH and different AN:B ratios. An increasing reaction time was observed (Fig. 2) to have an insignificant consequence on the nitrogen content of CE-B because a slight increase in the nitrogen content occurred as a result of increasing the reaction time from 1 h to 4 h.

At 60°C the effect of increasing the reaction time on the nitrogen content of CE-B was dependent on alkali concentration and AN:B ratio (Fig. 3). At a 5% alkali concentration and with 1:15 and 1:20 AN:B ratios, the nitrogen content increased with increasing reaction time, while at a 1:10 AN:B ratio, no change occurred in the nitrogen content after 2 h of reaction. At a 10% alkali concentration and with 1:10–1:20 AN:B ratios, nitrogen content increased as the reaction time increased up to 3 h. At longer reaction times, a drop in the nitrogen content of CE-B took place. The increase in nitrogen content of CE-B at longer reaction times can be associated with the extended period of contact between AN molecules and bagasse constituents, which may have induced adequate diffusion of the AN molecules

$\cdot$ 5 % NaOH + 10 % NaOH ✳ 15 % NaOH

Figure 5 Effect of AN:bagasse ratio on nitrogen content of CE-B at 60°C.

Figure 6 Effect of NaOH concentration on nitrogen content of CE-B at 40°C.

through the bagasse cell walls, but long reaction times in combination with excessive reaction conditions are detrimental to the formation of the cyanoethylated product.[4] At 15% alkali concentration, an increasing reaction time did not significantly affect the nitrogen content except that a decrease in the nitrogen content occurred with the of a 1:20 AN:B with an increasing reaction time.

Effect of Acrylonitrile:Bagasse Ratio

Figure 4 represents the general pattern of the effect of the acrylonitrile:bagasse (AN:B) ratio on nitrogen content at 40°C using various alkali concentrations and reaction times. With a reaction time of 4 h, increasing the AN:B ratio did not significantly affect the nitrogen content of the produced CE-B (Fig. 4). Figure 5 represents the general pattern of the effect of the AN:B ratio on the nitrogen content at 60°C using various alkali concentrations and reaction times. With a reaction time of 2 h, increasing the AN:B ratio significantly affected the nitrogen content of the produced CE-B (Fig. 5). This effect, however, was

dependent on alkali concentration. At alkali concentrations of 5% and 10%, no increase in the nitrogen content was observed when the AN:B ratio was increased above 1:15. At a 15% alkali concentration, increasing the AN:B ratio from 1:10 to 1:20 resulted in an increase in the nitrogen content. Since the cyanoethylation reaction always involves a loss in reagent from the side reactions because of the high reactivity of AN, a high AN:B ratio is desirable to produce the cyanoethylated derivative.[12]

Effect of Alkali Concentration

The alkali was used primarily as a catalyst in the reaction but also at the same time as a swelling agent. The extensive hydrogen bonding of cellulose effectively crosslinks the chain segments to form a crystalline structure. A swelling agent such as an alkali supplies the necessary energy to break the hydrogen bonds of the cellulose.[12] Pretreatment with an alkali creates anions, which, because of their enhanced reactivity,[13] are capable of attacking the relatively positive carbon atom of each AN molecule. In addition, pretreatment provides the amount of water necessary for the reaction because water molecules act as the proton donors in the production of the cyanoethylated derivative.

Figure 6 represents the general pattern of the effect of alkali concentration on the nitrogen content at 40°C at different AN:B ratios and with different reaction times. With a reaction time of 2 h, increasing the alkali concentration from 5% to 10% resulted in a significant increase in the nitrogen content of the produced CE-B, while a slight to insignificant increase in the nitrogen content was observed when the alkali concentration was increased more than 10% (Fig. 6). An increasing alkali concentration produces an increase in nitrogen content because it degrades lignin in the middle lamella and inside the cell wall, thereby exposing the cellulose for reaction.[14] Also, increasing the alkali concentration makes a greater proportion of the crystalline area of the cellulose accessible for the reaction. On the other hand, at 60°C (Fig. 7) with reaction times up to 3 h, increasing the alkali concentration more than 10% had a detrimental effect on the extent of cyanoethylation; with a longer reaction time (4 h) and AN:B ratios of 1:15 and 1:20, increasing the alkali concentration more than 5% resulted in a drop in the nitrogen content of the produced CE-
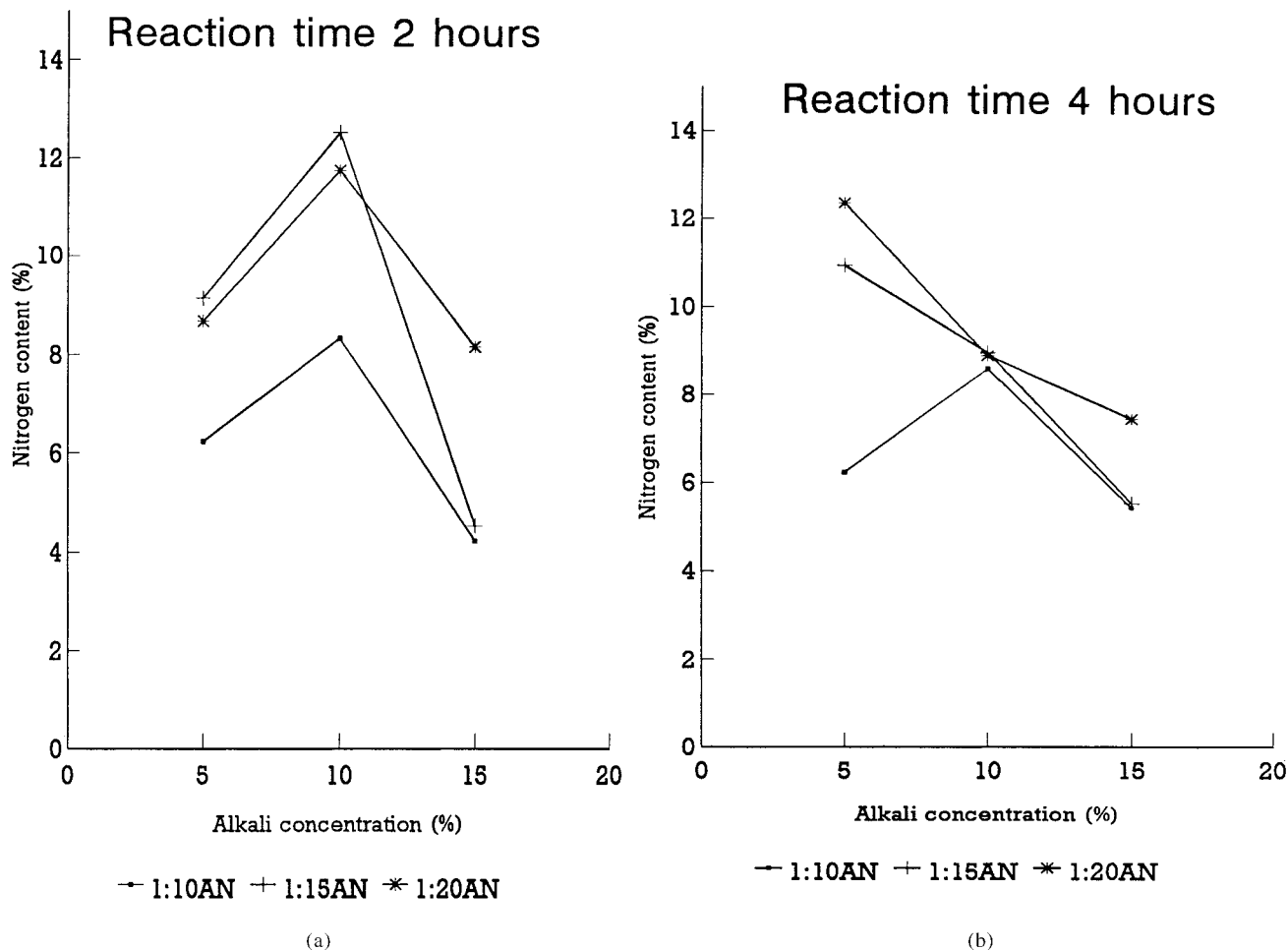
(a)

(b)

Figure 7 Effect of NaOH concentration on nitrogen content of CE-B at 60°C.

B. As mentioned before, a combination of long reaction time, high alkali concentration, and high temperature results in reversibility of the cyanoethylation reaction and hydrolysis of the products.[11,12]

CE-B with a high nitrogen content (12.4%) was obtained using a 5% alkali concentration after 2 h of reaction at 60°C. The low alkali concentration used in the reaction is favorable for avoiding loss of hemicellulose, low-molecular-weight cellulose, and lignin, and it thereby increases the reaction yield.

FTIR Spectra of Cyanoethylated Bagasse

The change in chemical structure of bagasse as a result of cyanoethylation was followed using FTIR spectroscopy. Figure 8 shows the FTIR spectra of both the untreated bagasse and the cyanoethylated bagasse (CE-B) samples. An absorption band around 2240 cm^{-1} resulting from the nitrile group's stretching vibration can be seen. Table I shows the ratio of the absorbance of the CH_2 stretching-vibration band at 2900 cm^{-1} to that of the hydroxyl group at 3450 cm^{-1} (A_{CH}/A_{OH}) and its correlation to the nitrogen content of CE-B. The results show that all CE-B samples have a $A_{CH}:A_{OH}$ ratio significantly higher than untreated bagasse. This is because of the cyanoethylation reaction at the hydroxyl groups and the introduction of the cyanoethyl group, as shown in the reaction equations. However, increasing the nitrogen content did not result in an increase in the $A_{CH}:A_{OH}$ ratio. In part, this may be because of the heterogeneity of bagasse and the possibility of homopolymerization of the acrylonitrile and the formation of polyacrylonitrile chains along the cellulose. This would result in
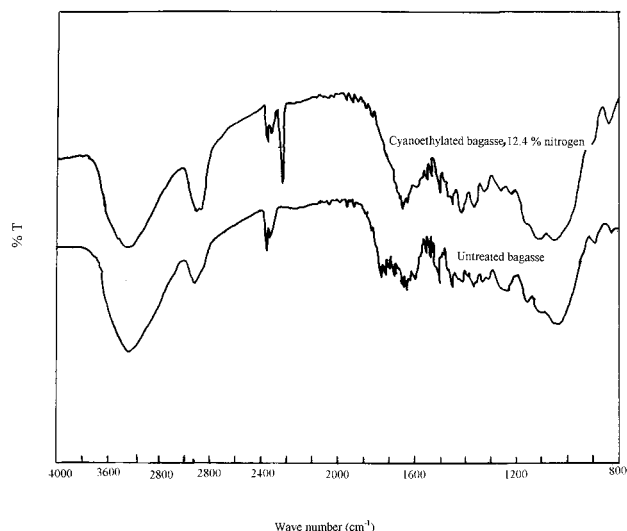
Figure 8 IR spectra of untreated and cyanoethylated bagasse samples.

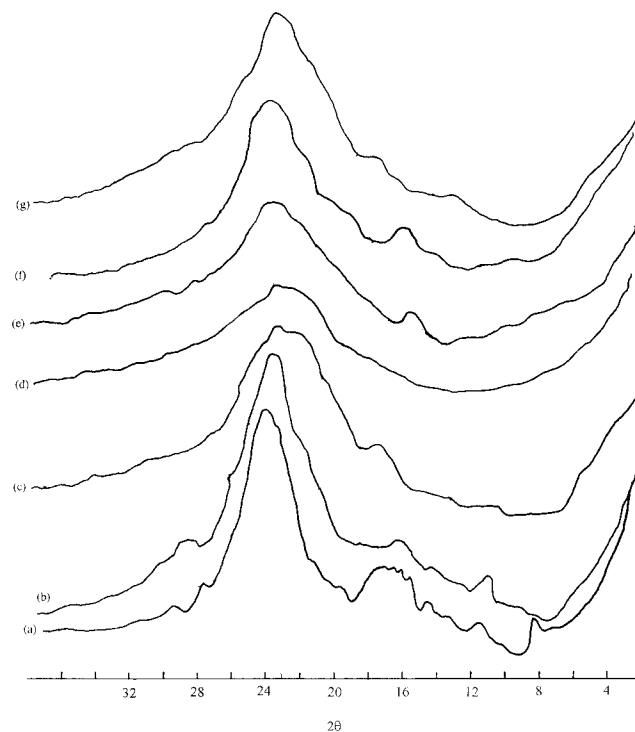increasing the nitrogen content of CE-B without affecting the ratio of the hydroxyl groups.

X-ray Diffraction Analysis

The effect of cyanoethylation on the crystallinity of cellulose in bagasse was studied using X-ray diffraction analysis. Cellulose is not a thermoplastic because of its high crystallinity.[15] However, its crystalline structure may be disrupted by substitution of its hydroxyl groups with a suitable chemical reagent.[16] This decrystallization process may improve cellulose thermoplasticity since the introduced groups play a role as a plasticizer.

The X-ray diffraction patterns of both the untreated bagasse and the cyanoethylated samples are shown in Figure 9. Untreated bagasse exhibited a typical cellulose I pattern, with reflections


Figure 9 X-ray diffraction patterns of cyanoethylated bagasse. Percentage of nitrogen: (a) untreated bagasse, (b) 5.1%, (c) 8.7%, (d) 12.4%, (e) 8.9%, (f) 9.1%, (g) 9.1%.

at $2\theta = 22$ and $2\theta = 17$. The reflection peak at $2\theta = 22$, which was derived from the 002 plane of the cellulose I lattice, was slightly shifted to lower 2θ values after cyanoethylation to a nitrogen content

Table I   Ratio of Intensity of CH$_2$ Absorption Band to that of OH Absorption Band and its Correlation to Nitrogen Content of Cyanoethylated Bagasse

Nitrogen Content (%)	Reaction Condition	A_{CH}/A_{OH}
Untreated	None	0.32
5.1	5%, 60°C	0.71
8.7	5%, 60°C	0.53
12.4	10%, 60°C	0.64

Table II   Crystallinity Index (Cr I) of Cyanoethylated Bagasse and Its Correlation to Nitrogen Content

Sample No.	Reaction Conditions	Nitrogen Content	Cr I
Untreated	—	—	0.61
1	5% NaOH, 60°C, 1 h, 1 : 10 AN : B	5.1	0.59
2	5% NaOH, 60°C, 2 h, 1 : 10 AN : B	8.7	0.29
3	5% NaOH, 60°C, 4 h, 1 : 20 AN : B	12.4	0.075
4	10% NaOH, 60°C, 1 h, 1 : 20 AN : B	8.9	0.31
5	10% NaOH, 60°C, 4 h, 1 : 20 AN : B	9.1	0.47
8	10% NaOH, 40°C, 2 h, 1 : 15 AN : B	8.1	0.25
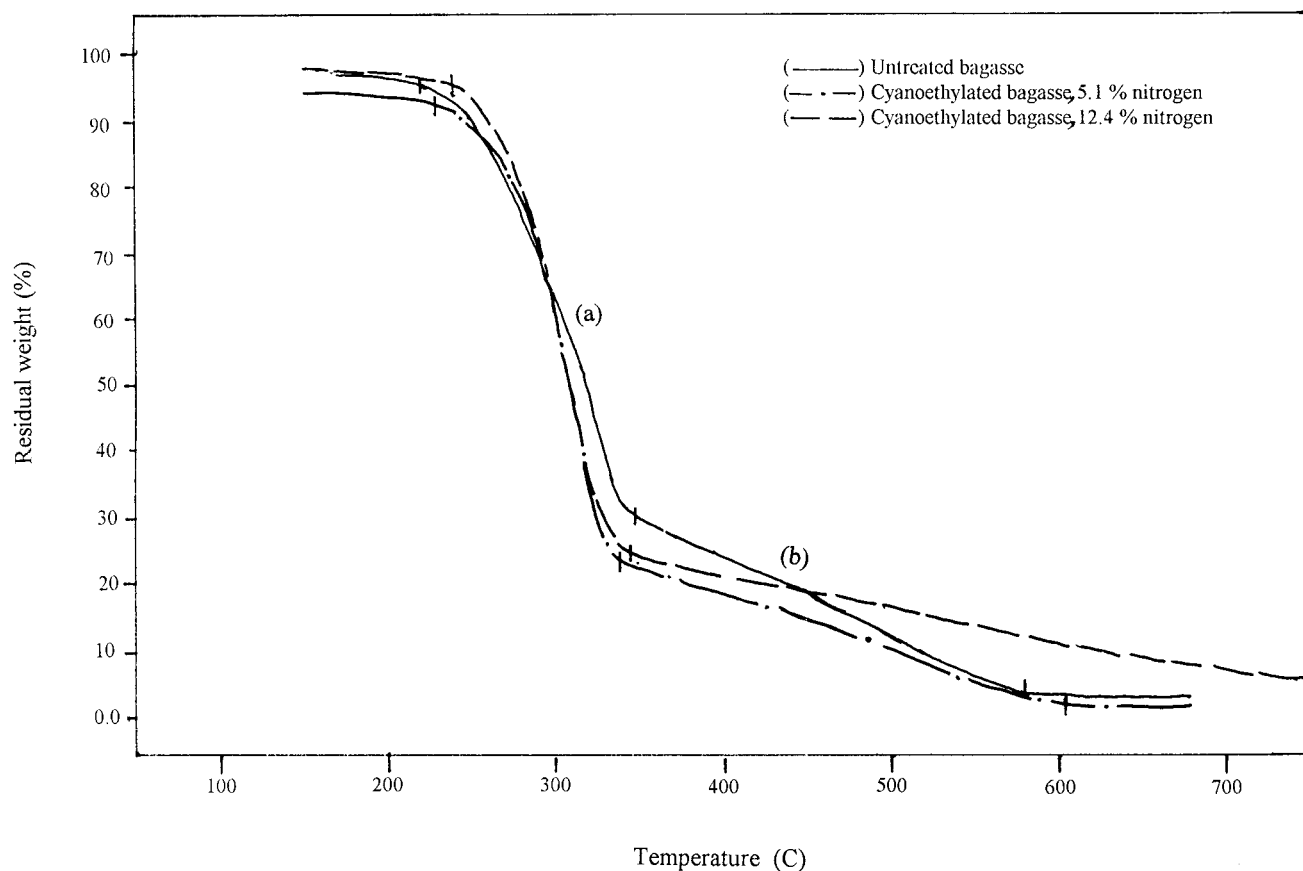
Figure 10 TGA curves of untreated and cyanoethylated bagasse samples.

of 8.7% or higher. The new scattering curves of CE-B samples were lower in intensity and broader in shape as compared to the untreated bagasse. The peak around $2\theta = 17$ for the untreated bagasse is assigned to the reflection of the 101 and 101' lattice planes of cellulose I. After cyanoethylation the intensity of this peak gradually decreased with increasing nitrogen content of samples. Cyanoethylation resulted in reduction in the crystallinity of bagasse, as shown by a decrease of the crystalline diffraction peaks.

Table II gives the calculated crystallinity index (Cr I) of CE-B samples from their diffractograms correlated to their nitrogen content. Cr I was calculated as follows[17]:

$$Cr\ I = 1 - \text{Amorphousness ratio (AmR)}$$

where AmR = amorphous width (AmW) divided by crystalline height (CrH)

The height of the 101' peak over the minimum point between the 101 and 101' peaks is the CrH,

Table III   TGA Results of Untreated and Cyanoethylated Bagasse Samples

Nitrogen Content (%)	Onset Weight Loss Temperature (C) of Stage A	Onset Weight Loss Temperature (C) of Stage B	Ash Formation Temperature (C)
Untreated	205	342	592
5.1	217	340	610
12.4	227	345	747

and the distance from the last-mentioned minimum point to the more or less vertical right-hand-side line of the 101′ the peak is the AmW (as a 2θ angle expressed in radians).

Untreated bagasse has a Cr I of 0.61. On the other hand, the Cr I of CE-B samples with a nitrogen content of 5.1%, 8.7%, and 12.4% were, respectively, 0.59, 0.29, and 0.075. These samples were prepared using 5% NaOH at 60°C. The significant drop in crystallinity with a 12.4% nitrogen content is interesting because a low alkali concentration was used to prepare this sample. Cyanoethylation of bagasse is expected to take place in both crystalline and amorphous regions of the cellulose in addition to the expected reaction at the hydroxyl groups of hemicellulose and lignin.
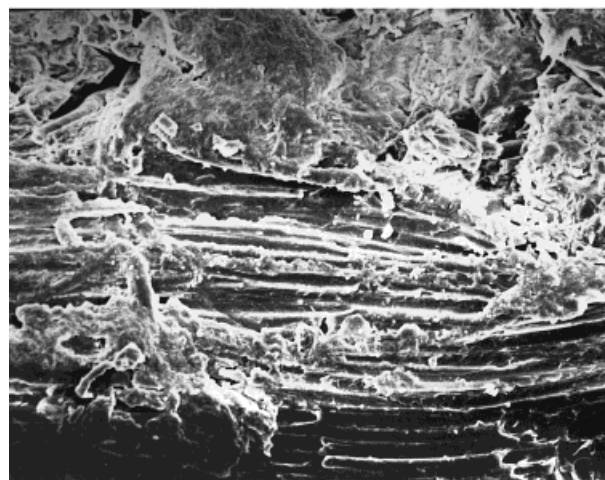
From Table II, comparing the Cr I of the sample 2 to that of sample 4 and the Cr I of sample 2 to that of sample 8 shows that increasing the concentration of alkali used in the reaction with a reaction temperature from 40°C to 60°C slightly increased the Cr I of the sample although the nitrogen content of these samples is close. This may be because of increased dissolution of the amorphous components as a result of increasing the alkali concentration and the reaction temperature. In addition, a comparison of the Cr I of sample 4 (Cr I = 0.31) to that of sample 5 (Cr I = 0.47) shows that increasing the reaction time at the same alkali concentration resulted in a significant increase in the Cr I although the nitrogen content of these samples is close. This may be
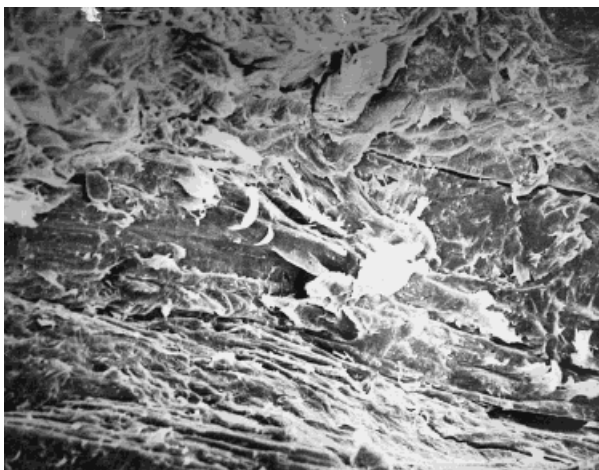

Figure 12   SEM of CE-B composite having 5.1% nitrogen: (a) pressed at 70°C, (b) pressed at 170°C.

because of more dissolution of the amorphous components as time increased.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of both untreated bagasse and the CE-B samples was done in order to study the thermal stability of the produced CE-B so as to determine the most suitable temperature range for molding the products. The TGA diagram of untreated bagasse and the CE-B samples is shown in Figure 10, where the TGA curves of the untreated bagasse and CE-B samples exhibit two main weight-loss stages, denoted as stages a and b. The onset temperatures of the

Figure 11   SEM of untreated bagasse composite pressed at 170°C for 8 min.

(a)

(b)
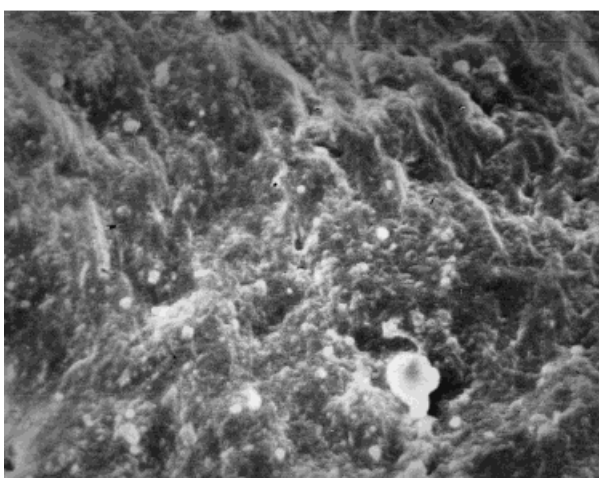
(c)

Figure 13 SEM of CE-B composite having 8.7% nitrogen: (a) pressed at 70°C, (b) pressed at 140°C, and (c) pressed at 170°C.

weight loss of stage a, which is the onset temperature of the generation of noncombustible gases such as CO_2, CO, and acetic acid[18] were 205°C, 217.5°C, and 227.5°C for untreated bagasse, CE-B with a nitrogen content of 5.14%, and CE-B with a nitrogen content of 12.4%, respectively. This increase in the onset degradation temperature may be due to the inclusion of polar cyanoethyl groups, which leads to an increase in the bonding strength between the fiber chains; consequently, more energy—that is, a higher temperature—is needed for decomposition. Although a decrease in the onset degradation temperature with increasing nitrogen content is expected because the CE-B starts to lose its fiber structure, the onset degradation temperature of the sample having a 12.4% nitrogen content was higher than that of the sample having a 5.14% nitrogen content. It may be that the increase in the number of the polar cyano groups compensates for the possible increased destruction of the structure.[19] On the other hand, the onset degradation temperatures of stage b, which are the result of pyrolysis and loss of fiber structure, were 342°C, 340°C, and 345°C for the untreated bagasse, the CE-B with a nitrogen content of 5.1%, and the CE-B with a nitrogen content of 12.4%, respectively.

The residual masses remaining at the end of the degradation process were 3.6%, 1.8%, and 5.9% for untreated bagasse, CE-B having 5.1% nitrogen, and CE-B having 12.4% nitrogen, respectively. The temperatures at which the degradation process ended (called ash formation temperature in Table III) were 592°C, 610°C, and 747°C for untreated bagasse, CE-B having 5.1% nitrogen, and CE-B having 12.4% nitrogen, respectively. This means the energy needed for decomposition of CE-B is more than that required for decomposition of untreated bagasse, and this energy increased with increasing the level of the cyanoethylation of the sample.

SEM of CE-Bagasse Composites

As reported above, CE-B samples were thermally stable up to a temperature of about 217°C. This work also investigated the occurrence of plasticization, for which SEM was conducted on cross sections of CE-B samples with different nitrogen contents that had been pressed into pellets at 70°C, 140°C, and 170°C.

The SEM picture of untreated bagasse pressed at 170°C is shown in Figure 11. The texture of cell walls is clearly seen, and the fibers are separate.
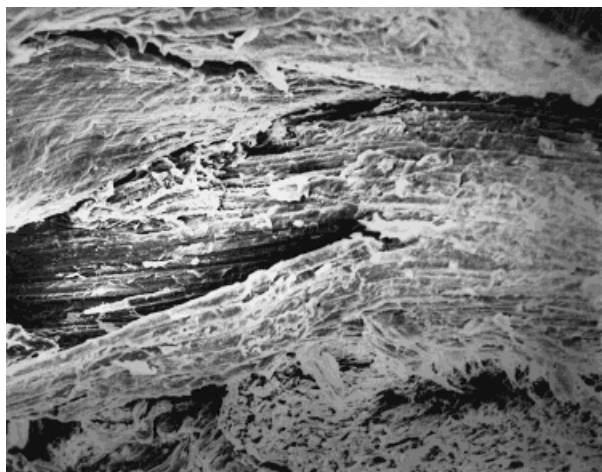
(a)
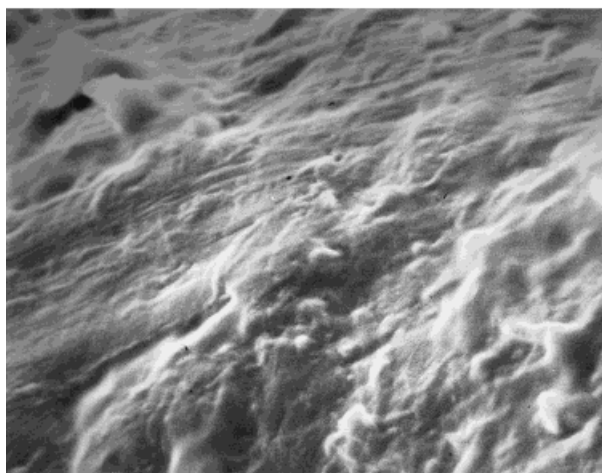
(b)

Figure 14 SEM of CE-B composite having 12.4% nitrogen: (a) pressed at 70°C, (b) pressed at 140°C.

Figure 12(a) shows the SEM picture of a CE-B sample with low nitrogen content (5.1%) pressed at 70°C, in which the fibers were still distinguishable. Figure 12(b) shows the SEM picture of the same sample pressed at 170°C. A slightly melted area is seen at the top of the picture, but the fibers were still separate and distinguishable. X-ray diffraction results showed that the crystallinity of this sample was close to that of untreated bagasse.

Figure 13(a–c) shows the SEM pictures of a CE-B sample with a moderate nitrogen content (8.7%) pressed at 70°C, 140°C, and 170°C,. In the sample pressed at 70°C [Fig. 13(a)], voids are still remarkable although a melted area is seen be-

tween the fibers. At 140°C and 170°C [Fig. 13(b,c)], melting of the sample during pressing is clear. The resulting pellets had a brown color with a smooth and hard surface. X-ray diffraction results showed low crystallinity of this sample.

Figure 14(a,b) show the SEM pictures of a CE-B sample with a high nitrogen content (12.4%) pressed at 70°C and 140°C. The pictures re similar to those obtained for the above sample at the same pressing temperatures. X-ray results showed that the crystallinity of this sample was very low.

CONCLUSIONS

Bagasse can be converted into thermoplastic material by mean of cyanoethylation at a moderate cyanoethylation level (a nitrogen content of about 9% or higher). The CE-B thus produced can be easily molded into sheets or bulks in any shape by simply heating and pressing.

The interplay of the reaction variables, such as temperature, time, alkali concentration, and AN:B ratio, is complex, and it is important to arrange the reaction conditions in favor of the cyanoethylation reaction. Reaction temperature and alkali concentration were the most effective factors in controlling the extent of the cyanoethylation reaction.

Cyanoethylation results in significant change in the suprastructure of bagasse. Also, the cyanoethylation of bagasse fiber results in an increase in its thermal stability.

REFERENCES

1. Hassan, M. L.; Rowell, R. M.; Fadl, N. A.; Yacoub, S. F.; Christainsen, A. W. J. Appl Polym Sci 2000, 76, 561.
2. Morita, M.; Sakata I. J Appl Polym Sci 1986, 31, 831.
3. Kiguchi M.; Gakkaishi, M. 1990, 36(8), 651.
4. Hon, D. N.-S.; San Luis, J. M. J Polym Sci, Part A: Polym Chem 1989, 27, 4143.
5. Quanying, Y.; Xianghua, T. Linchan Huaxue Yu Gongye 1995, 15(4), 31.
6. Adelaida, L.; Constatin, T.; Aurelia, C.; Mihaela, N.; Gheorghe R. Rev Roum Chim 1995, 40(7–8), 743.
7. Saha, A. K.; Mitra, B. C. J Appl Polym Sci 1996, 62, 733.

8. Hassan, M. L.; Rowell, R. M.; Fadl, N. A.; Yacoub, S. F.; Christainsen, A. W. J Appl Polym Sci 2000, 76, 575.

9. Browning, B. L. Methods of Wood Chemistry; Interscience: New York, 1967; Vol. 2.

10. Daul, G. C; Reinhardt, R. M.; Reid, J. D. Text Res J 1955, 25, 246.

11. McGregor, J. H. J Soc Dyers Color 1951, 67, 66.

12. Callihan C. O. In Cellulose Tech Res; Turbak, F., Ed.; American Chemical Society: Washington, DC, 1975.

13. Bikales N. M. U.S. Pat. 2,857,239 (1958).

14. Cellulose Derivatives in Wood Chemistry, Fundamentals and Applications; Sjostrom E., Ed.; Academic: New York, 1981; Chapter 9.

15. The Structure of Cellulose; Atalla R. H., Ed.; American Chemical Society: Washington, DC, 1987.

16. Hon, D. N.-S. Polymernews 1988, 13, 134.

17. Ant-Wourinen, O. Evaluation of the Crystallinity of Cellulose from the X-ray Diffraction Pictures; Reprinted from Paperi Ja Puu; Papper och Trä No. 8, Frenkellin Kirjapaino Osakeyhtiö: Helsinki, 1955.

18. Sefain, M. Z.; Naoum, M. M.; Fadl, M. H.; El-Wakil, N. A. Thermochimica Acta 1994, 231, 257.

19. LeVan S. L. In Concise Encyclopedia of Wood and Wood-Based Materials; Scniewind, A. P., Ed.; Pergamon Press, p. 271–273 (1989).