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MODIFICATION OF JUTE FIBRE BY BIFUNCTIONAL DIAZONIUM SALTS IN THE PRESENCE OF VARIOUS MORDANTS

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ABSTRACT

Jute Fibre was treated with bifunctional diazonium salts under the influence of some mordants (copper sulphate, nickel sulphate, potassium dichromate and potassium permanganate) in acidic and basic media. The formation of complex in the polymer system (complexed fibre) has been observed by the infrared spectra and nitrogen content estimation. The physico-mechanical properties, viz. tensile strength, tenacity, elongation at break, moisture regain, shrinkage and loss in weight of jute fibre has been studied. The tensile strength, tenacity, elongation at break and moisture regain properties of the treated (dyed) fibre are found lower in comparison with those of raw (control) fibre. However, higher tensile strength and tenacity of the complexation fibre in comparison to diazonium salts treated fibre are observed. The dyed fibre in basic media shows higher fibre strength as compared to the fibre which dyed in acidic media. The nature of the shades developed on jute fibre is also reported.

Keywords: Jute fibre, bifunctional benzenediazonium salts, mordants.

INTRODUCTION

Efforts have been made to modify the jute fibre by various reactions viz. etherification[1], esterification[2], alkylation[3], acylation[4], polymerization[5-8] etc. on jute fibre. Besides these various workers applied dyes on jute fibre to make it attractive and improve its quality. In some previous studies the effects of monoazo dyes[9-10] on some physical properties of jute fibre has been studied. Mahapatra and Puspa[11] synthesized a multidonor azo dyes and their polymeric complex.

In continuation to the previous studies[9,10] jute fibre complexes have been prepared by treating it with the bifunctional diazonium salts in the presence of mordants. The physico-mechanical properties of these complexed fibre have been studied.

EXPERIMENTAL

Material and Methods

Jute fibre (Tossa) was collected from Jute Research Institute, Dhaka, Bangladesh. The middle part of the jute fibre taken for the present investigation. It was cleaned manually and washed with water. The fibre was then dried with a hot air blower and cut into pieces of 25 cm in length. Bundles were made taking 0.5 g fibre in each case and were used. These bundles were used for the subsequent experiments.

Preparation of various diazonium salts

The standardized diazotization methods[12] were used to prepare the following diazonium salts:

1. benzene-1,2-diazodium chloride
2. benzene-1,3-diazodium chloride
3. benzene-1,4-diazodium chloride

These diazonium salts were characterized by spectral analysis

Treatment of Jute fibre with various bifunctional benzene diazonium salts

Ten bundles (0.5 g each) of jute fibre were treated with alkali (5% NaOH solution) in a beaker and were cooled for ten minutes at about 5°C in an ice bath. A freshly prepared cooled solution of benzene-1,4-diazonium chloride was then added slowly to the above mixture with constant stirring for about 10 minutes. The bundles were then washed with soap solution followed by water and finally dried with a hot air blower. Similar treatment of jute bundles were carried out by using other bifunctional benzene diazonium chloride (viz. benzene-1,3-diazonium chloride and benzene-1,2-diazonium chloride) salts.

Similar treatments were carried out on jute fibre in acidic media.

The physico-mechanical properties of these treated fibres were determined. The results are summarized in Table -1.

Treatment of Jute fibre with various bifunctional benzene diazonium salts in the presence of mordants

Ten bundles (0.5 g each) of jute fibre were taken with alkaline $CuSO_4$ solution in a beaker and stirred at 30°C for half an hour. The fibres were then separated out in another beaker and cooled for ten minutes at about 5°C in an ice bath. Similar operations were carried out using alkaline $NiSO_4$, $KMnO_4$ and $K_2Cr_2O_7$ solutions as treating agents. A freshly prepared cooled solution of benzene-1,4-diazonium chloride was then added slowly to the above treated bundles of fibre mixing with constant stirring for about 10 minutes. The bundles were washed with soap solution followed by water and finally dried with a hot air blower. Similar operations were carried out also by using other bifunctional benzene diazonium chlorides (benzene-1,3-diazonium chloride and benzene-1,2-diazonium chloride).

Similar treatments were carried out on jute fibre in acidic media.

The physico-mechanical properties of these treated fibres were determined. The results are summarized in Table 2, Table 3 and Table 4.

Determination of tensile strength

Tensile strength of jute fibre was measured following the ASTM standard[12].

Determination of tenacity

Tenacity of raw and treated fibre was calculated from the experimental results of tensile strength by using the standard formula[13].

Determination of elongation at break

The elongation at break of treated and untreated fibres was calculated as follows[14]

$$\%\ \text{elongation at break} = \frac{\text{extension of fibre at break}}{\text{gauge length}} \times 100$$

where gauge length is the initial length of material under test between upper and lower jaws fixing the material.

Determination of moisture regain property

For the determination of moisture regain property the sample of jute fibre was dried at 105°C to a constant weight at the standard atmosphere (relative humidity 65°C ± 2°C) for 48 hrs. The dried fibre was then kept in conditioned atmosphere for 48 hrs. The weight of the fibre was taken in an analytical balance. The percentage of moisture regain was calculated by using the following relation[15].

$$R = \frac{b - a}{a} \times 100$$

where,

R = percentage of moisture regain

a = dried weight of a sample

b = weight of the sample after absorption of moisture

Determination of loss in weight

The jute fibre was dried by blowing hot air to a constant weight. The dried fibre was then treated with suitable reagent. The treated fibre was again dried to a constant weight. The percent loss in weight was calculated from the following relation.

$$W_L = \frac{W_f - W_i}{W_i} \times 100$$

where,

W_i = initial weight of dried jute fibre

W_f = final weight of treated and dried jute fibre

W_L = loss in weight in percentage

Determination of percentage shrinkage

For the determination of percent shrinkage jute fibre sample was cut to a size of 25 cm in length. It was then cleaned and converted into a bundle weighing 0.5 g. Each bundle was then treated separately with different chemical reagents. The treated bundle of fibre was then washed thoroughly with soap solution and water for several times, dried and finally length was measured again. The percent shrinkage was calculated from the following relation.

$$L_{sh} = \frac{L_f - L_i}{L_i} \times 100$$

where, L_i = initial length of dried jute fibre (25 cm)

L_f = final length of treated and dried fibre

L_{sh} = length shrinkage in percentage

Estimation of nitrogen

The nitrogen on fibre after treating chemicals was estimated following Kjheldhal method[16].

Table - 1 : Effect of various bifunctional benzenediazonium salts in acidic and basic media

Control & various diazonium salts	Colour produced on jute fibre	Tensile strength lb/tex	Tenacity gm/D	Elongation %	Moisture regain %	Shrinkage %	Loss in weight %	Quantity of nitrogen %
Control	Yellowish	8.58	2.28	5	11.30	-	-	-
1,4-benzene diazonium salts	Light yellow (Coral brown)	7.87 (8.00)	2.08 (2.12)	5.80 (6.10)	8.30 (8.00)	Nil (1.00)	2.90 (2.50)	4.17 (4.30)
1,3-benzene diazonium salts	Yellow (Cofee)	7.52 (7.60)	1.99 (2.01)	6.20 (6.50)	8.70 (8.50)	Nil (1.00)	3.10 (2.84)	4.00 (4.20)
1,2-benzene diazonium salts	Yellow (Golden brown)	7.26 (7.34)	1.92 (1.94)	6.80 (7.50)	9.50 (9.00)	Nil (1.00)	3.40 (3.00)	3.70 (3.91)

Table - 2 : Effect of 1,4-bifunctional benzenediazonium salts in presence of various metallic salts in acidic and basic media

Control & various metallic salts	Colour produced on jute fibre	Tensile strength lb/tex	Tenacity gm/D	Elongation %	Moisture regain %	Shrinkage %	Loss in weight %	Quantity of nitrogen %
Control	Yellowish	8.58	2.28	5	11.30	-	-	-
Copper sulphate	Golden (Brown)	7.15 (7.22)	1.90 (1.92)	6.12 (6.20)	9.70 (9.20)	Nil (0.80)	4.14 (4.00)	3.68 (3.75)
Nickel sulphate	Red oxide (Reddish)	7.35 (7.50)	1.95 (1.99)	6.00 (6.27)	9.62 (9.15)	Nil (0.70)	4.30 (4.20)	3.81 (4.00)
Potassium dichromate	Deep brown (Yellow)	7.77 (7.67)	2.04 (2.06)	6.21 (6.45)	8.78 (8.62)	Nil (0.71)	4.50 (4.20)	4.10 (4.32)
Potassium permanganate	Yellow (Pink)	7.98 (8.05)	2.12 (2.14)	6.19 (6.39)	8.38 (8.15)	Nil (0.75)	4.70 (4.50)	4.31 (4.35)

RESULTS AND DISCUSSION

Investigations were carried out by treating jute fibres with bifunctional benzene diazonium salts in alkaline media in the presence of metallic salts. It was observed that the tensile strength of bundles of fibres when dyed with various bifunctional benzene diazonium salts (such as benzene-1,2-diazonium salt, benzene-1,3-diazonium salt, benzene-1,4-diazonium salt) decreased as compared to the raw fibre. The decrease in tensile strength is probably caused by the fact that lignin, the binding material of fibre, is easily dissolved out in alkali solution[17]. In addition to this, cellulose is also partially soluble in alkali solution and leads to the formation of alkali

Table - 3 : Effect of 1,3-bifunctional benzenediazonium salts in the presence of various metallic salts in acidic and basic media

Control & various metallic salts	Colour produced on jute fibre	Tensile strength lb/tex	Tenacity gm/D	Elongation %	Moisture regain %	Shrinkage %	Loss in weight %	Quantity of nitrogen %
Control	Yellowish	8.58	2.28	5	11.30	-	-	-
Copper sulphate	Light golden (Brown)	7.30 (7.40)	1.94 (1.96)	6.00 (6.15)	9.80 (9.28)	Nil (0.90)	4.00 (3.90)	3.70 (3.81)
Nickel sulphate	Golden (Reddish)	7.50 (7.62)	1.99 (2.02)	5.95 (6.22)	9.70 (9.26)	Nil (0.73)	4.21 (4.15)	3.92 (4.06)
Potassium dichromate	Deep brown (black)	7.80 (7.95)	2.07 (2.11)	6.17 (6.38)	8.82 (8.71)	Nil (0.80)	4.50 (4.10)	4.16 (4.40)
Potassium permanganate	Yellow (Red)	8.10 (8.20)	2.15 (2.18)	6.15 (6.31)	8.43 (8.30)	Nil (0.81)	4.60 (4.40)	4.32 (4.44)

Table - 4 : Effect of 1,2-bifunctional benzenediazonium salts in presence of various metallic salts in acidic and basic media

Control & various metallic salts	Colour produced on jute fibre	Tensile strength lb/tex	Tenacity gm/D	Elongation %	Moisture regain %	Shrinkage %	Loss in weight %	Quantity of nitrogen %
Control	Yellowish	8.58	2.28	5	11.30	-	-	-
Copper sulphate	Light golden (Red oxide)	7.40 (7.55)	1.98 (2.02)	5.90 (6.10)	9.86 (9.35)	Nil (0.98)	3.00 (2.94)	3.75 (3.92)
Nickel sulphate	Golden (Post office red)	7.67 (7.82)	2.05 (2.07)	5.80 (6.06)	9.81 (9.37)	NIl (0.80)	3.30 (2.91)	3.99 (4.11)
Potassium dichromate	Deep brown (Sunrise)	7.96 (8.05)	2.11 (2.13)	6.13 (6.25)	8.91 (8.80)	Nil (0.85)	2.78 (2.39)	4.20 (4.46)
Potassium permanganate	Yellow (Light pink)	8.34 (8.44)	2.11 (2.13)	6.00 (6.20)	8.47 (8.36)	Nil (0.90)	2.07 (2.30)	4.38 (4.50)

The results in the parantheses are in basic media cellulose[18]. Similarly, the hemicellulose of jute fibre is also dissolved out in sodium hydroxide[18]. Fats and waxes of jute fibre are also hydrolysed in alkaline media[17]. Thus, through such dissolution of the components of jute fibre, its compactness and crystallinity are partially lost, resulting in the decrease of tensile strength[16].

The tensile strength of dried jute fibre in acidic media was also found to decrease. This may be due to degradation of cellulose, hemicellulose of jute fibre.

However, it was observed that the tensile strength of dyed fibre in basic media is higher than that in acidic media. This may be due to the shrinkage of the length of jute fibre thereby increases the thickness of the fibre in acidic media. This also increases the orientation of polymer and formation of additional hydrogen bonds[19].

The tensile strength of dyed fibre with benzene diazonium salt was found in the following order:
benzene-1,4-diazonium salt > benzene-1,3-diazonium salt > benzene-1,2-diazonium salt

But when the fibre was dyed in the presence of metallic salts the dyed fibre with benzene-1,2-diazonium salt shows higher tensile strength in comparison to the dyed fibre with benzene-1,3-diazonium salt and benzene-1,4-diazonium salt. This may be due to the fact that the five membered ring complex formed by benzene-1,2-diazonium salt with metal ion is more stable according to Bayer theory[16] than others. The order of tensile strength of the dyed fibre on treatment with metallic salts is as follows-

$KMnO_4 > K_2Cr_2O_7 > NiSO_4 > CuSO_4$

This order shows that higher is the oxidation state of metal higher is the stability of the complex. The fibre treated with $KMnO_4$ shows higher tensile strength than that of the fibre treated with $K_2Cr_2O_7$ because of higher oxidation of Mn than that of Cr. Though the oxidation state of both of Cu and Ni in $CuSO_4$ and $NiSO_4$ is same (+2), the stability of Ni-complex is greater than that of the stability of Cu complex. This is due to the fact that the Jahn-Teller distortion effect is absent in Ni-complex and that effect is present in Cu complex. Hence, the fibre treated with $NiSO_4$ shows higher tensile strength as compared to the tensile strength of the fibre treated with $CuSO_4$.

The elongation at break of the treated fibre is greater as compared to the elongation at break of the raw fibre. It is observed that the elongation at break of treated fibre in alkaline media is higher than the treated fibre in acidic media. This may due to the shrinkage in length of the fibre and the cell wall thickness is increased.

The moisture regain property of the treated fibre is found to decrease in every case. This may be due to the introduction of phenyl ring which behaves as a hydrophobic species. The moisture regain character of the treated fibre in alkaline media is decreased that that in acidic media. This is perhaps due to the fact that in alkaline media the rate of coupling reaction of diazonium salts with phenolic compound (lignin) on jute fibre is higher than in acidic media.

The treated fibre in alkaline media shows somewhat shrinkage in length. This is because in alkaline media contraction of length of the fibre takes place causing increase of thickness of fibre[19]. In acidic media shrinkage in length of the fibre is nil.

The fibres after dyeing with bifunctional azo compounds in the presence of various metallic salts show the following IR bands at

1) 410-425 cm^{-1} which is due to the $\nu_{M-N.}$ These bands indicate the formation of complex on jute fibre.
2) 2350-2370 cm^{-1} due to the azo group (-N=N-) of benzene diazonium salts. These bands show positive shift because the N atom of azo group forms coordinate bond with the various metal ions.

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