Effect of Processing Variables on Benzoylation of Jute*

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Materials and Methods

All the chemicals used for pretreatment and benzoylation were of CP grade (BDH) and those used for analytical purposes were of Analar grade (BDH). Good quality daisee (Corchorus olitorius) variety jute fibre was used. The sample of jute fibre was prepared from the commercial variety as per the laboratory specifications of the Indian Jute Mills Association Research Institute, Calcutta. The jute fibre was spun in the laboratory into low twist yarns of grist 8 lb (279.6 tex).

Pretreatments—Both the fibre and the yarn were dewaxed and deoiled with alcohol-benzene (1:2, vol/vol.) mixture in a soxhlet apparatus under reflux for 6-8 hr. A portion of the dewaxed and deoiled yarn was further purified by scouring under controlled conditions. A portion of the extracted jute yarn was bleached separately with hydrogen peroxide, sodium hypochlorite and sodium chlorite. Samples of neutralized jute and hydrolyzed jute were also prepared from dewaxed and deoiled yarns.

Benzoylation of jute in liquid phase—The samples of jute were benzoylated under variable reaction conditions in such a manner that the fibrous structure was retained. The procedure adopted, in general, for the benzoylation of jute is as follows. The different fibre materials were dried over P₂O₅ in a vacuum desiccator for 24 hr at room temperature and then imibed in freshly distilled dry pyridine (material to liquor ratio, 1:20) heated to the respective reaction temperature. Benzoyl chloride, also preheated to the requisite

Jute holds a leading position in the Indian textile industry. At present, it is facing heavy competition from other fibres, particularly synthetic fibres. Because of some of its specific physical and chemical characteristics, jute has certain limitations for practical uses. This has necessitated the improvement of some characteristics, such as increasing its resistivity to heat, preventing photochemical discoloration on exposure to light, reducing hygroscopicity, conferring it high immunity to microorganisms, or conferring new characteristics so as to extend its applications.

The chemical structure of jute suggests that its reactivity centres around the hydroxyl groups of alpha-cellulose, carboxyl and hydroxyl groups of hemi-cellulose and phenolic and hydroxyl groups of lignin. The hydroxyl groups of the various constituents of jute are likely to form esters. Fully esterified cellulose, hemicellulose and non-cellulosic derivatives loosen the fibrous structure of jute extensively, leaving no textile value. Therefore, the esterification of the fibre should be done to a limited extent in order not to deprive it of its natural fibrous character and the desirable textile characteristics.

Cross and Bevan¹ did some work on the preparation of benzoylated cellulose. Wohl² carried out the benzoylation of cellulose in pyridine base instead of caustic soda. Early studies were based mostly on benzoylation of cellulose in the non-fibrous form. Arthur et al.³ benzoylated cotton to study certain physical characteristics. An extensive and systematic investigation to see the influence of various variables on the extent of benzoylation of cotton in the fibrous form was done by Chatterjee⁴. But no work has been reported so far on the benzoylation of jute. The present study was undertaken to investigate systematically the influence of different process variables on the extent of benzoylation of jute without affecting its fibrous structure so as to ascertain the optimum conditions of esterification and to evolve a suitable method for the benzoylation of jute. The work was extended to both fibres and yarns with a view to finding out the differences in the extent of reaction.

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* Presented at the 67th session of the Indian Science Congress (1980).
temperature, was then added to the bath in variable amounts. The reaction was performed in a three-necked 250 ml round-bottomed flask fitted with an air condenser, a separating funnel and a thermometer. The reaction temperature was kept constant by placing the vessel in an oil bath fitted with a thermostat. In the beginning, the reaction mixtures were stirred continuously to avoid rise in temperature due to the exothermic nature of the reaction. On completion of reaction after a specific period, the sample was removed, squeezed and rinsed with methanol three to four times at room temperature. This was followed by thorough washing, first in distilled water and then under running tap water, squeezing and drying of the sample in air.

Analysis of benzoylated products—The benzoyl content was estimated by a method given by Genung and Mallatt. This method is based on the alcoholic alkali process for the determination of acyl value. For each estimation, a blank sample, for comparison purpose, was subjected to the conditions of estimation and thus the acyl content of the untreated control jute was taken into account.

Results and Discussion

Effect of benzoyl chloride concentration on the extent of benzoylation—Several samples (2 g each) of dewaxed and deoiled jute fibre and yarn were separately treated with varying amounts of benzoyl chloride (fibre to benzoyl chloride ratio, 1:0.25 to 1:2.5) in the presence of pyridine base at 60 ± 2°C for 45 min as per the general procedure described above. The benzoylated jute was analyzed for increase in benzoyl content. Untreated jute was also analyzed as a control for comparison. The results are presented in Fig. 1.

It is evident from Fig. 1 that the benzoyl content of jute increased progressively with increase in benzoyl chloride concentration. However, the extent of reaction was rather slow at lower concentrations, but increased rapidly at higher concentrations of benzoyl chloride.

Although benzoylation did not disintegrate the fibrous structure at a concentration of 2.5%, the extent of disintegration was reasonably high (50.20%). A further extension of this work to increase the amount beyond this value was not undertaken for the following reasons: (1) Benzoyl chloride forms a complex compound with pyridine, the extent of which increases at higher concentrations of benzoyl chloride and at lower reaction temperatures and hence settles down at the bottom of the vessel. This may result in a non-uniform reaction. (2) The probability of disintegration of the fibrous structure and other desirable characteristics of jute is high at higher concentrations.

A visual examination of the benzoylated samples revealed that the original colour of the dewaxed jute underwent considerable alteration in shade with the formation of yellowish white colour. The whiteness increased with progressive increase in the degree of substitution. It appears that benzoylation was accompanied by a sort of bleaching.

The analysis of the benzoylated products surprisingly showed that both the copper number and the carboxyl content decreased in comparison to those of control samples and the extent of this decrease became progressively lower with increase in the degree of esterification. It is, therefore, likely that there was no major chemical degradation during benzoylation at any concentration.

The jute yarn behaved similarly as the fibre during benzoylation, but a small difference in the extent of substitution is discernible, which is probably due to lower accessibility of the reagent in the former sample. However, the rigidity or the stiffness of the yarn was found to have increased considerably on esterification. Further, the fibre sheddings or droppings from the yarn were more at higher extents of substitution.

The above findings indicate that benzoyl chloride at low concentration (1:0.25) exerts a distinct effect on benzoylation, but the extent is too small to be considered; at high concentration (1:2.5), however, certain practical difficulties are encountered. It appears that the optimum concentration for the benzoylation
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Effect of reaction temperature on the extent of benzoylation—Several dewaxed fibre and yarn samples (2 g each) were separately treated with benzoyl chloride (fibre to benzoyl chloride ratio, 1:2) at different temperatures in pyridine for 45 min as per the general procedure described above. The esterified material was analyzed for benzoyl content and a graph of benzoyl content versus reaction temperature was plotted (Fig. 2).

It is seen from Fig. 2 that increase in temperature causes progressive increase in the extent of benzoylation of jute. The rate as well as the extent of esterification was low at 45°C, but increased rapidly at higher temperatures. Below 45°C, the experiment could not be performed because of the formation of benzoyl chloride-pyridine complex. Another significant observation made was that the benzoylated products suffered greater loss of strength at higher reaction temperatures. The extent of benzoylation of yarn was lower than that of fibre under identical conditions of treatment at lower temperatures, but the differences were reduced with progressive increase in temperature. In fact, at higher temperatures, no such differences were observed. Here again, the lower extent of benzoylation of yarns, compared with that of fibres, at low reaction temperatures seems to be due to the reduced penetration of the reagent in the former. However, fibre droppings increased with increase in the degree of substitution.

Lowering of the temperature below 60°C reduces rapidly the rate and extent of benzoylation, while increase in temperature above 75°C affects adversely the strength as well as the fibre sheddings of the jute yarn. Therefore, the optimum temperature for the esterification of jute should be below 75°C in order to retain the desirable characteristics of the fibre.

Effect of reaction period on the extent of benzoylation—Several samples of dewaxed jute fibre and yarn (2 g each) were separately treated with benzoyl chloride (fibre to benzoyl chloride ratio, 1:2) for different periods in pyridine at 60 ± 2°C as per the general procedure of esterification described earlier. The esterified products were analysed for benzoyl content and a graph of benzoyl content versus reaction period was plotted (Fig. 3).

It is evident from Fig. 3 that extended periods of treatment for both the fibre and the yarn resulted in a progressive increase in the extent of benzoylation. However, the rate of esterification was not uniform; it was rapid during the first 15 min of treatment and then slowed down considerably with increase in the period of reaction. Although the yarn samples behaved similarly as the fibre sample, the extent of benzoylation in the former was much lower with shorter treatment periods. However, such differences in the case of substitution reduced on extending the treatment period. Thus, the same inferences as drawn from the study of the effect of concentration of benzoyl chloride and temperature on the extent of benzoylation can be drawn in this case also. The lower rate of benzoylation of yarn compared to that of the fibre with short treatment periods seems to be because of the lower accessibility of the reagents in the former.

Fig. 2—Effect of reaction temperature on the extent of benzoylation

Fig. 3—Effect of treatment period on the extent of benzoylation

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the above investigation show that the short reaction period, such as 20 min, may produce incomplete and topochemical reaction, whereas a long treatment period has little effect on the extent of further substitution. Therefore, it seems that the optimum period of treatment for benzoylation of jute is 45 min.

Effect of reaction medium on the extent of benzoylation—Samples of dewaxed jute yarn (2 g each) were separately treated with the usual benzoylation mixture in two different reaction media, viz. pyridine and dimethyl formamide, under the optimum conditions of reaction concentration, temperature and reaction period as adopted in the earlier experiments. The benzoylated products were analyzed for benzoyl content, which was found to be 39.05 and 36.75 % in the jute yarns benzoylated in the presence of pyridine and dimethyl formamide respectively.

It is clear from the above findings that the medium of esterification also has a significant influence on the extent of benzoylation. Of the two media used, pyridine is more effective for the benzoylation of jute.

Effect of various pretreatments on the extent of benzoylation—Samples of raw, dewaxed, neutralized, hydrolyzed, scoured and bleached jute yarns were separately benzoylated under the optimum reaction conditions to ascertain the variation in the extent of esterification of the samples. Several hanks of raw, dewaxed, neutralized, hydrolyzed, scoured, and hydrogen peroxide, hypochlorite and chlorite bleached jute yarns (2 g each) were separately reacted with benzoyl chloride (fibre to benzoyl chloride ratio, 1:2) at 60 ± 2 °C in pyridine (material to liquor ratio, 1:20) for 45 min and the benzoylated products were analyzed for benzoyl content. The results are presented in Table 1.

It is seen from Table 1 that dewaxing and deoiling of the raw yarn improved the extent of benzoylation considerably. Since dewaxed yarn was the starting material for all the pretreatments, for discussion, it was taken as a control for comparison. Neutralization of the jute yarn did not affect the extent of esterification, whereas a slight increase was noticed in the case of hydrolyzed jute. This slight increase appears to be due to the liberation of free hydroxyl groups as a result of hydrolysis of lignin-uronic acid ester and acetyl groups occurring in the fibre. However, it was accompanied by a slight loss in the tensile strength of the yarn, as is to be expected.

Scouring of jute yarn reduced the rate of esterification, the reason for which appears to be the removal of some fractions of hemicelluloses. Loss in strength was also observed. Bleaching of jute yarn samples by treatment with three bleaching agents, viz. hydrogen peroxide, sodium hypochlorite and sodium chlorite, affected the extent of benzoylation to varying degrees. The lower degree of benzoylation of chlorite bleached yarn appears to be due to the removal of some portion of lignin from the original yarn. Thus, bleaching did not favour the benzoylation reaction and at the same time a significant loss in tensile strength resulted.

Thus, the pretreatment of the yarn influenced the extent of benzoylation, the degree of substitution being dependent on the nature and kind of pretreatment. In this investigation, dewaxing and deoiling of the jute yarn appears to be an ideal pretreatment process for achieving maximum benzoylation with minimum adverse effect on the tensile strength of the yarn.

Conclusion

Benzoylation of jute is influenced by the concentration of benzoyl chloride, reaction temperature, reaction period, reaction medium and pretreatment of the material. In each case, optimum conditions for the reaction of benzoyl chloride with jute have been established. Although initially the yarn samples exhibit lower extent of benzoylation as compared to fibre samples under identical conditions of reaction, on extending the period of treatment or temperature, the extent of benzoylation increases. A suitable method developed for the benzoylation of jute to varying extents (benzoyl content, 10.01-45.32 %) consists in treating the dewaxed jute with benzoyl chloride of varying concentrations (fibre to benzoyl chloride ratio, 1:1 to 1:2.25) in pyridine (material to liquor ratio, 1:20) at 60 ± 2 °C for a period of 45 min, followed by washing and drying.

References
1 Cross C F & Bevan E J, Researches on cellulose (Longmans and Green, London) 1895-1900, 34.