Modification of jute fibre through vinyl grafting aimed at improved rot resistance and dyeability

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Raw, dewaxed and oxidized jute fibres and those chemically modified with phenol and formaldehyde (treatment done for 3 h at 95° C and pH 8) before or subsequent to oxidation, were subjected to graft copolymerization with methyl methacrylate (MMA) in the presence or absence of some other monomers such as maleic anhydride (MA) or methacrylic acid (MAA) in limited aqueous system using $K_2S_2O_8$ as the initiator under photoconditions with the objective of inducing improved rot resistance and dyeability without loss in tensile strength of the fibre. For preparing oxy-jute, dewaxed and preswollen (dewaxed jute fibre swollen with 10% aqueous urea at 90° C for 2 h) jute fibre were separately subjected to mild oxidation or bleaching using aqueous H_2O_2 and $NaIO_4$ and non-aqueous chlorine (Cl_2 in CCl_4) under specified conditions. Optimum conditions for graft copolymerization have been established by examination of the effect of such variables as monomer concentration, time of polymerization and nature of chemical modification of jute fibre prior to vinyl grafting. Percentage grafting, tenacity (g denier^{-1}), dye fixation (%) and rot resistance (expressed as percentage retention of tensile strength of the fibre after a standard soil burial test) were evaluated and analysed. High rot resistance (80–90% retention of tensile strength after soil burial test) and dye fixation (%) of as high as 86% were readily obtained for grafted jute fibres. Washing fastness and light fastness properties of the dyed fibres (grafted and ungrafted) were also examined and compared.

1. Introduction

Jute, the golden fibre from eastern India and Bangladesh finds widespread applications primarily and conventionally in the packaging field in the form of sacks and hessian. Its other fibre applications include carpets, carpet backings, wall hangings, upholstery, blankets and a reinforcing fibre in laminates and composites. For applications other than packaging, jute is often subjected to bleaching to enhance customer acceptance and sales, over and above imparting technical advantages with respect to processing. However, the direct detrimental consequence of bleaching or oxidation of the fibre is that it becomes poorer in tenacity and devoid of any semblence of rot resistance. By subjecting jute to controlled bleaching, it is possible to retain tenacity to a desired and acceptable level for most fibre applications [1], but in the process, its rot resistance reduces to zero or insignificance. Chemical modification subsequent to the bleaching process leading to substantial enhancement in the rot resistance property of the fibre without materially affecting the tenacity is therefore an essential prerequisite if the fibre is to be considered for long term use in many of the non-packaging applications referred to above. Results based on the modification of raw, dewaxed and bleached jute or some of its chemically modified varieties through vinyl grafting are reported.

2. Experimental procedure

2.1. Materials

Raw jute fibre of grade TD_2 as per Indian standard institution (ISI) specification [2] was used. Chlorine used for oxidation was generated in the laboratory by reacting potassium permanganate and hydrochloric acid together and purifying the liberated chlorine gas by scrubbing successively through water and concentrated sulphuric acid. Monomer methyl methacrylate (MMA) was purified by distillation following a standard procedure [3]. Methacrylic acid was purified by recrystallization and vacuum distillation. Maleic anhydride from Merck was of analytical grade and it was used without any treatment. Acetone used in polymerization was purified by distillation. Other ingredients used in the present investigation were of analytical grade.

2.2. Preparation of the jute fibre prior to graft copolymerization

Dewaxing of the raw jute fibre was done by soxhlet extraction for 6 h using a mixture of benzene and alcohol (2 : 1 v/v); the fibre was then washed with alcohol and distilled water. It was then dried in air and finally under vacuum at 40° C.

Dewaxed fibre thus obtained was treated with a swelling agent (10% aqueous urea solution at 90° C for 2 h) and then subjected to oxidation separately in

aqueous or non-aqueous medium using hydrogen peroxide ($10\,g\,l^{-1}$ aqueous H_2O_2 at $80°\,C$ for 60 min at pH 10), sodium periodate ($10\,g\,l^{-1}$ aqueous $NaIO_4$ at $30°\,C$ for 30 min at pH 7) and with non-aqueous chlorine ($20\,g\,l^{-1}$ chlorine dissolved in CCl_4 at $30°\,C$ for 5 min). The fibre–liquor ratio for oxidation with aqueous H_2O_2 was $1:10$ while that for the other two systems was maintained at $1:50$. Preswelling made the fibre more suited for oxidation [1]. After oxidation, each fibre sample was washed thoroughly with distilled water and dried in air.

The oxidized jute samples were allowed to react initially with excess phenol (based on the aldehyde moieties in jute sample as calculated from its copper number) maintaining phenol:aldehyde molar ratio of $10:1$ and an overall substrate–liquor ratio of $1:50$ using water as the diluent. The medium was kept at pH 8 to begin with, adding requisite volume of 2% sodium carbonate solution. The phenol treatment done at $95°\,C$ under reflux using a magnetic stirrer was arrested after 1.5 h. Formaldehyde in large excess of phenol used in the preceding step (so as to maintain a formaldehyde to phenol molar ratio of $10:1$) was then added into the reaction mixture, which apparently contained the unreacted phenol and the phenol-modified oxy-jute. The second stage reaction with formaldehyde (HCHO) was also done at $95°\,C$ under reflux and stirring conditions for a time period of 1.5 h. Thereafter, the modified jute fibre sample was isolated, washed with distilled water and dried in air.

Raw, dewaxed and oxidized jute fibres and those modified chemically subsequent to oxidation were then used separately as the preformed polymer in graft copolymerization with methyl methacrylate (MMA) in presence or in absence of some other monomers such as maleic anhydride or methacrylic acid, following a procedure given below.

2.3. Graft copolymerization

0.5 g of each of the different jute fibre samples (raw, dewaxed, oxidized and those subsequently modified) was separately taken in a Corning brand borosilicate glass test tube to which freshly prepared aqueous potassium persulphate (3%) solution was added in excess. The jute sample was allowed to be soaked thoroughly for 30 min, after which, the fibre sample was taken out, squeezed to drain out excess water and weighed. From the gain in weight of the fibre at this stage, the amount of persulphate taken up by the fibre was calculated, considering no preferential absorption. The known amount of a squeezed sample was taken in a Corning brand borosilicate glass test tube and known amounts of methyl methacrylate either alone or in combination with maleic anhydride or methacrylic acid were added to the test tube. 1.0 ml of acetone was used in each experiment as a diluent and to dissolve maleic anhydride whenever it was added. The test tubes and the contents were then flushed with purified nitrogen gas, stoppered tightly, placed between a pair of fluorescent tube lamps (40 W, Philips India Limited) and polymerization was allowed to continue for specified time periods at $40 \pm 1°C$. The contents of the test tube was then quantitatively

transferred to a beaker using small volumes of actone to dissolve any vinyl polymer that might stick to the glass surface. Excess methanol was poured into the beaker with stirring so as to completely precipitate the vinyl polymer formed. The precipitate was allowed to settle and the supernatant liquid was decanted out. The collected polymer was washed with more methanol, dried in air and finally at $40°\,C$ under vacuum to constant weight. The dried polymer so obtained will be called "gross polymer".

The gross polymer from each graft copolymerization experiment is likely to contain ungrafted or free vinyl polymer or copolymer, which was removed by subjecting the gross product to acetone extraction for 48 h in a soxhlet apparatus. After acetone extraction, the fibre residue was dried at $50°\,C$ under vacuum to constant weight. Percentage grafting, total percent conversion and grafting efficiency (%) were calculated according to the concept previously described [4].

2.4. Characterization of the ungrafted and grafted jute fibres

Tensile strength of each grafted and ungrafted jute fibre sample was determined in an Instron apparatus (Model No. 1026) and an average of 50 tests was taken
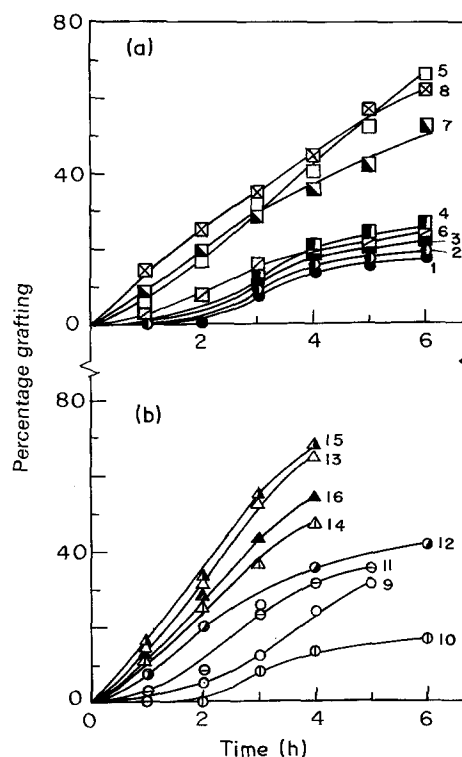

Figure 1 Percentage grafting as a function of time of polymerization and its dependence on the nature of chemical modification of jute fibre prior to vinyl grafting. (a) For graft copolymerization of MMA, data given are nature of fibre and curve No: Raw, 1; dewaxed, 3; Oxidized, 5, 9 and 13 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively); (b) For graft copolymerization of MMA and MA ($1:1$ w/w), data given are fibre nature and curve No: Raw, 2; dewaxed, 4; oxidized, 7, 11 and 15 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively); Oxy-fibre treated with phenol and Formaldehyde, 8, 12 and 16 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). (c) For graft copolymerization of MMA and MAA ($1:1$ w/w), data given are fibre nature and curve No: Oxidized, 6, 10 and 14 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively).
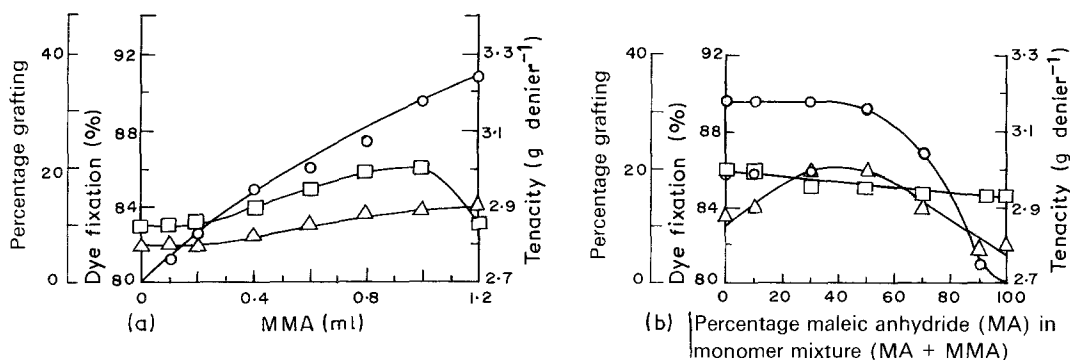
Figure 2 Effect of variation of monomer content using (a) MMA as the monomer and monomer compositions and (b) different mixtures of MMA and MA on percentage grafting (O), dye fixation (%) ($\triangle$) and tenacity (g denier^{-1}) ($\square$) of the oxy-jute fibre (oxidation done with non-aqueous Cl_2).

to calculate the tenacity of the fibre in g denier^{-1} in each case [5]. Tenacity in g denier^{-1} actually expresses mass stress or specific strength at break which therefore becomes grams weight per linear density. In the present studies the linear density used is the denier which is the weight in grams of a 9000 m length of fibre. Dye fixation (%), washing fastness and light fastness for selected fibre samples were determined subsequent to dyeing by a selected dye (mostly malachite green i.e., C.I. Basic green 4, unless otherwise stated) following standard procedures [6, 7]. Rot resistance i.e., resistance to microbiological attack of the selected fibre samples were determined using the standard soil burial test [8] developed for the purpose and is expressed in the form of percentage retention of the tensile strength of the initial fibre (both leached and unleached) in each case. For the soil burial test, a composted soil consisting of a thorough mixture of fertile garden soil, cow dung and sand in 2 : 1 : 1 weight proportions and 20–25% moisture on the overall basis was used. After the soil burial test for 21 days according to IS: 19, 1949, the fibre samples were washed

thoroughly in running water and dried in air. Infra red spectra of the unmodified jute fibre and of those modified by different approaches were studied and compared.

3. Results and discussion

Results are presented graphically in Figs 1–4. A brief description of treatment of jute fibres used for vinyl grafting in relation to different curves in Figs 1, 3 and 4 are given in Table I for convenience.

3.1. Dependence of grafting parameters and conversion on variation of time of polymerization and nature of chemical modification of jute fibre prior to vinyl grafting

Results showing the changes in percentage grafting with time are given in two parts (A and B) in Fig. 1. For raw or dewaxed jute samples in presence of MMA alone or mixture of MMA and maleic anhydride as the monomer, percentage grafting rises slowly with time of polymerization. Percentage grafting reaches a

TABLE I Brief description of treatment of jute fibres used for vinyl grafting corresponding to different curves in Fig. 1, 3 and 4

Figure number*		Nature of jute fibre used for vinyl grafting[†]
1 and 3 Curve No	4 Curve No	
1	1, 1a	Raw[a]
2	2, 2a	Raw[b]
3	3, 3a	Dewaxed [a]
4	4, 4a	Dewaxed [b]
–	5, 5a	Raw fibre treated with C_6H_5OH and HCHO[b]
–	6, 6a	Dewaxed fibre treated with C_6H_5OH and HCHO[b]
5	7, 7a	Oxy-jute fibre[a] (oxidation with non-aqueous Cl_2)
6	8, 8a	Oxy-jute fibre[c] (oxidation with non-aqueous Cl_2)
7	9, 9a	Oxy-jute fibre[b] (oxidation with non-aqueous Cl_2)
8	10, 10a	Oxy-jute fibre (oxidation with non-aqueous Cl_2) Subsequently treated with C_6H_5OH and HCHO[b]
9	11, 11a	Oxy-jute fibre[a] (oxidation with aqueous H_2O_2)
10	12, 12a	Oxy-jute fibre[c] (oxidation with aqueous H_2O_2)
11	13, 13a	Oxy-jute fibre[b] (oxidation with aqueous H_2O_2)
12	14, 14a	Oxy-jute fibre (oxidation with aqueous H_2O_2) Subsequently treated with C_6H_5OH and HCHO[b]
13	15, 15a	Oxy-jute fibre[a] (oxidation with aqueous $NaIO_4$)
14	16, 16a	Oxy-jute fibre[c] (oxidation with aqueous $NaIO_4$)
15	17, 17a	Oxy-jute fibre[b] (oxidation with aqueous $NaIO_4$)
16	18, 18a	Oxy-jute fibre (oxidation with aqueous $NaIO_4$) Subsequently treated with C_6H_5OH and HCHO[b]

*For Fig. 4 only, curve numbers with and without the subscript "a" refer to plot of data corresponding to "leached" and "unleached" fibre samples respectively.
[†] Monomer used for graft copolymerization: a) MMA, b) MMA:MA (1 : 1 w/w) and c) MMA:MAA (1 : 1 w/w).
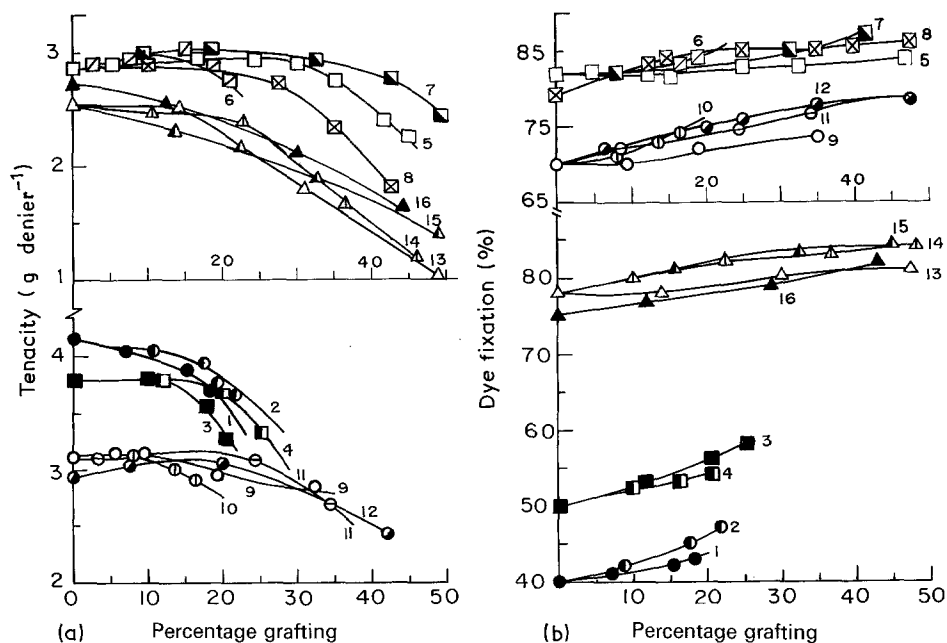
Figure 3 Effect of vinyl grafting on the tenacity (a) and dye fixation % (b) of jute fibres. (a) For graft copolymerization of MMA, data given are nature of fibre and curve No: Raw, 1; dewaxed, 3; Oxidized, 5, 9, 13 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). (b) For graft copolymerization of MMA and MA (1 : 1 w/w), data given are fibre nature and curve No: Raw, 2; dewaxed, 4; Oxidized, 7, 11 and 15 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively); Oxy-fibre treated with phenol and formaldehyde, 8, 12 and 16 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). (c) For graft copolymerization of MMA and MAA (1 : 1 w/w), data given are fibre nature and curve No: Oxidized, 6, 10, and 14 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively).

level of 15–20% in about 6 h. Dewaxing decidedly produces a better grafting effect, Fig. 1a curves 1, 2, 3 and 4.

Oxidation of jute seems to produce improved percentage grafting. Comparing data for oxy-jute samples obtained by using three different oxidizing agents (aqueous H_2O_2, aqueous $NaIO_4$ and non-aqueous Cl_2), the percentage grafting effected under comparable conditions are in the order $H_2O_2 < Cl_2 < NaIO_4$, Figs 1a and b. Analysis of data shows that this order in percentage grafting runs parallel to the order of copper number (–CHO group content) for the three oxy-jute samples used in the experiments. Percentage conversion for the oxy-jute samples also follows the same relative order.

Use of maleic anhydride in equal weight proportions with MMA leads to slightly improved percentage grafting, particularly in the initial stages of graft copolymerization (2–3 h) with each of the three oxy-jute samples, Fig. 1. For the oxy-jute samples from oxidation of jute by non-aqueous chlorine, the percentage grafting–time plot however, tends to level down much more in case of 1 : 1 w/w MMA/MA mixture than in case of MMA alone beyond about 3 h of polymerization. However, for the two other oxy-jute systems (oxidation of jute done with aqueous H_2O_2 and aqueous $NaIO_4$), the improved percentage grafting effect with the MMA/MA mixture over that with pure MMA continues with extended time of reaction. In each system, when the oxy-jute samples were subsequently modified by reaction with phenol and formaldehyde in the manner described in the text, percentage grafting using MMA and MA as the monomer mixture (1 : 1 w/w) gets further improved for jute samples initially oxidized with non-aqueous chlorine or with aqueous

H_2O_2, but the same was measurably lowered for the jute samples initially oxidized with aqueous $NaIO_4$. Substantially higher incorporation of phenol in the last named oxy-jute sample, in view of its substantially high copper number consequent to oxidation earlier, may account for this difference, considering that phenols tend to produce notable retardation effects in vinyl polymerization when present in relatively high concentrations.

Methacrylic acid (MAA) when used as a comonomer with equal weight proportions of MMA on the other hand produces substantially poor grafting in each oxy-jute system over the whole range of the time of polymerization.

For each oxy-jute sample and its phenol-formaldehyde modified product, variation of percentage conversion with time during graft copolymerization follows a trend parallel to percentage grafting. Grafting efficiencies in most of the cases using oxy-jute samples or their derivatives were in the range of 65–85%.

3.2. Effect of variation of monomer concentration on percentage grafting, dye fixation (%) and tenacity (g denier⁻¹) of oxy-jute fibres

Related results are shown in Figs 2a and b. Fig. 2a shows the effect of variation of MMA content, and Fig. 2b the effect of variation of percentage maleic anhydride in a monomer mixture of MMA and MA, keeping total monomer content as 1 g. An oxy-jute sample derived from oxidation of dewaxed jute with non-aqueous chlorine was used for these studies.

From Fig. 2a, it is found that percentage grafting rises quite measurably with increase in the monomer
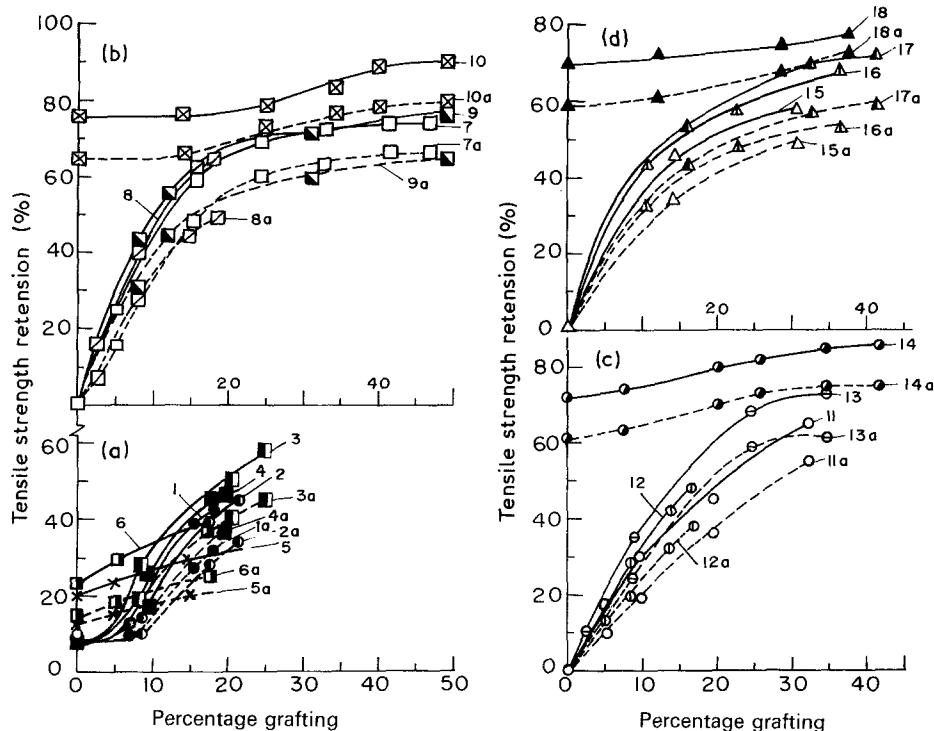
Figure 4 Effect of vinyl grafting on rot resistance (expressed as tensile strength retention (%) after soil burial test) of different jute fibres. (a) For graft copolymerization of MMA, data given are nature of fibre and curve No: Raw, 1; dewaxed, 3; Oxidized, 7, 11, and 15 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). (b) For graft copolymerization of MMA and MA (1 : 1 w/w), data given are fibre nature and curve No: Raw, 2; dewaxed, 4; Oxidized, 9, 13 and 17 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively); Raw fibre treated with phenol and formaldehyde, 5; dewaxed fibre treated with phenol and formaldehyde, 6; Oxy-fibre treated with phenol and formaldehyde, 10, 14 and 18 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). (c) For graft copolymerization of MMA and MAA (1 : 1 w/w), data given are fibre nature and curve No: Oxidized, 8, 12 and 16 (oxidation done with non-aqueous Cl_2, aqueous H_2O_2 and aqueous $NaIO_4$ respectively). Curve numbers with and without the subscript "a" refer to plots of data for corresponding "leached" and "unleached" fibre samples respectively.

(MMA) content; the tenacity $(g\,denier^{-1})$, however, follows a slowly increasing trend up to about 0.8 to 1.0 ml of MMA and a sharp dropping trend thereafter. The dye fixation (%) of the grafted fibres using the basic dye malachite green (C.I. Basic green 4) also follows a slowly increasing trend with increased monomer content, i.e., with enhanced percentage grafting.

From Fig. 2b it is found that percentage grafting remains practically unchanged (32%) with increase in MA content up to 50% in MMA–MA monomer mixture, studied over a period of 3 h for graft copolymerization. Further increase in MA content in relation to MMA content in the monomer mixture, leads to a sharp fall in percentage grafting which is practically zero for 100%, MA and no MMA. About 3% increase in dye fixation (%) was observed by increasing the MA content up to 40–50% in the MA–MMA mixture and thereafter the dye fixation value follows a dropping trend because of progressively lower percentage grafting. Tenacity $(g\,denier^{-1})$ also follows a slowly falling trend with increase in MA content in the monomer mixture. The oxy-jute sample used in this specific study was characterized by a tenacity value of 2.85 $g\,denier^{-1}$, and the corresponding grafted fibres based on MMA only or on MMA–MA mixtures as the monomer system showed a tenacity value greater than or equal to 2.85 g denier, provided that the percentage grafting was controlled within 30%.

3.3. Effect of vinyl grafting on the tenacity $(g\,denier^{-1})$ and dye fixation (%)

Results showing the effect of variation in percentage grafting on tenacity $(g\,denier^{-1})$ and dye fixation (%) are given in Figs 3a and b respectively.

The curves in Fig. 3a reveal the changes in tenacity $(g\,denier^{-1})$ of the various grafted-on jute or modified-jute fibres with increase in percentage grafting in each case. Data for graft copolymerization on raw jute, dewaxed jute and different oxy-jute samples derived through oxidation with aqueous H_2O_2, aqueous $NaIO_4$ and non-aqueous chlorine using MMA alone or a combination of MMA and maleic anhydride (MA) or MMA and methacrylic acid (MAA) as the monomer system are shown. The effect of modification of respective oxy-jute fibres by reacting them with excess of phenol and formaldehyde in successive stages at pH 8 and subsequent vinyl grafting using MMA and MA combination as the monomer system are also shown in Fig. 3a. Results of variation of dye fixation, (%) with increase in percentage grafting on corresponding fibre samples are similarly shown by curves in Fig. 3b.

It may be seen from analysis of the plots in Fig. 3a that changes in tenacity with progressive grafting are very small if not negligible for most of the grafted jute fibres, up to about 15–20% grafting for raw jute and dewaxed jute and up to 20–30% for the oxy-jute or phenol–formaldehyde modified oxy-jute fibres. In respect of tenacity retention with increase in

percentage grafting, jute samples initially oxidized with non-aqueous chlorine and aqueous H_2O_2 show some advantages over other jute fibre (raw, dewaxed or those oxidized with aqueous $NaIO_4$) up to the optimum level of grafting (25–30%). In the presence of methacrylic acid (MAA) as the comonomer with MMA, however, there is a general tendency of a sharp fall in tenacity beyond about 10–15% grafting (Curves 6 and 10, Fig. 3a). This is apparently due to much longer time of polymerization (almost twice) needed in presence of MAA than in its absence for attainment of comparable percentage grafting and consequent severity of hydrolytic degradation of the jute fibre for long contact with the acid monomer. If the time of polymerization needed is lower as for oxy-jute formed by oxidation with aqueous $NaIO_4$, the tenacity lowering effect of MAA is not apparent (curves 13 and 14, Fig. 3a).

As for the dye fixation (%) property, the highest values for the ungrafted sample are given by the jute subjected to oxidation by non-aqueous chlorine (dye fixation equal to 79–82%). In each case, however, the dye fixation value gets improved by 4–6% by vinyl grafting up to about 30% grafting. Use of MA or MAA as the comonomer tends to improve the dye fixation values more than when only MMA is used as the monomer during graft copolymerization. This is expected in view of the dye fixation being studied with the use of the cationic dye, melachite green.

3.4. Examination of rot resistance
The result of rot resistance followed by the standard soil burial test [8] for different jute samples and the effect of increase in percentage grafting on rot resistance are shown in Figs 4a to d for both unleached and leached fibres in each case. Leached fibres were prepared by leaching them with running water for 24 h prior to soil burial test following standard practice [9].

Raw or dewaxed jute samples exhibited 8–10% retention of initial tensile strength determined according to standard procedures [8]. For each of the different oxy-jute samples, the tensile strength retention was nil, the initial tenacity values being 2.85, 3.10 and 2.55 g denier^{-1} for the fibre samples obtained by oxidation with non-aqueous chlorine, aqueous H_2O_2 and aqueous $NaIO_4$ respectively. Treatment of the different oxy-jute fibres subsequently with phenol and formaldehyde at pH 8 for 3 h at 95° C produced little change in their tenacity (g denier^{-1}) value.

Examination of data presented in Fig. 4 in graphical form showing variation in tensile strength retention with increase in percentage grafting clearly reveals that for each fibre sample, both leached and unleached, there are measurable improvements in the rot resistance with vinyl incorporation i.e., on graft copolymerization. For all of the oxy-jute samples the tensile strength retention, shows a substantial gain from 0 to about 40 to 60% or even more, for an extent of 25–30% grafting, beyond which the tensile strength retention curves tend to level off. The corresponding leached samples for each oxy-jute fibres shows about 8 to 10% lower tensile strength retention at the optimum level of grafting (25–30%). Raw and dewaxed

jute samples also produce a similar trend of data on graft copolymerization.

Graft copolymerization on oxy-jute samples using MMA and MA in equal weight proportion as the monomer system produces slightly better rot resistance effect than with only MMA as the monomer system on graft copolymerization. At a comparable level of percentage grafting (say 30%), the oxy-jute samples derived through oxidation with aqueous H_2O_2 and non-aqueous chlorine and the raw and dewaxed jute samples have nearly comparable tenacity values (2.8–3.0 g denier^{-1}) as can be seen from Fig. 3a. Therefore, in terms of rot resistance graft copolymers from the corresponding oxy-jute samples are decidedly superior to those from raw and dewaxed jute samples in view of saving in time of grafting, overall appearance (white or less coloured) and better dyeability for the oxy-jute derived product.

The more interesting case is provided by the phenol–formaldehyde modified oxy-jute fibres. Even before grafting they exhibit high rot resistance (nearly 70–80% tensile strength retention for unleached and 60–65% for leached samples) and with increase in percentage grafting their rot resistance tends to improve further by another 10% in each case (Fig. 4 curves 8, 8a, 12, 12a and 16, 16a).

Treatment of raw and dewaxed jute similarly with phenol and formaldehyde and subsequent vinyl grafting on them using MMA–MA mixture as the monomer system during graft copolymerization produced small improvements in tensile strength retention. For raw and dewaxed jute, the retention is only 8–10%; on phenol–formaldehyde treatment, it goes up to 20–25% for unleached products and on vinyl grafting on the corresponding phenol–formaldehyde modified fibres, the tensile strength retention value further goes up to about only 40% for unleached samples characterized by a percentage grafting of 15–20%. Leaching in each case of the modified fibres results in a drop of nearly 10% in tensile strength retention. Relevant data are not shown in the graphical plots.

3.5. Dyeing with different types of dyes and comparative characterization of the dyed products
Table II, shows comparative data relating to dye fixation (%) and washing and light fastness properties of ungrafted and grafted (grafting done with MMA and MA monomer mixture for 4 h) oxy-jute (dewaxed jute oxidized with aqueous H_2O_2) samples dyed with three different classes of dyestuff, (direct, basic and disperse) following standard procedures of dyeing in each case [10].

As for dye fixation, oxy-jute can be gainfully dyed using basic and direct dyes such as shown in Table II, but disperse dyes are practically useless for jute and even for oxy-jute. Vinyl grafting, however, improves the dye fixation property very substantially using disperse dye (from 10 to 52%) and only to a limited extent in case of dyeing with a basic dye (from 70 to 76%) as shown in Table I. For dyeing with direct dye, however, grafting of a vinyl polymer in jute leads to a

TABLE II Dyeing with different types of dyes and comparative characterization of the dyed products

Exp. No.	Jute sample before dyeing	Data relating to dyeing				
		Percentage grafting	Dyestuff used	Dye fixation (%)	Washing fastness number	Light fastness number
1	Oxy-jute*	0.0	Malachite green crystal HCC (C.I Basic green 4)	70	3–4	4
2	Oxy-jute	0.0	Direct sky Blue 6B (C.I Direct Blue 1)	65	3–4	4
3	Oxy-jute	0.0	Celliton Fast Green 3B (C.I Disperse Green 1)	10	1	1
4	Grafted on oxy-jute†	24.2	Malachite green crystal HCC (C.I Basic Green 4)	76	4–5	6–7
5	Grafted on oxy-jute	24.2	Direct Sky Blue 6B (C.I Direct Blue 1)	55	3	3
6	Grafted on oxy-jute	24.2	Celliton Fast Green 3B (C.I Disperse green 1)	52	4	4

*Oxidation of jute was done with aqueous H_2O_2 ($10 \, g \, l^{-1}$) at $80°C$ for 60 min at pH 10.
†Vinyl grafting on oxy-jute was done using MMA and MA monomer mixture.

measurable lowering (from 65 to 55%) in dye fixation. Similarly, the washing fastness and light fastness characteristics of the dyed fibres can be rated; while ungrafted oxy-jute fibres show good washing and moderate light fastness when dyed with basic and direct dyes, they show poor fastness properties in each case when dyed with a disperse dye. Vinyl grafting substantially, improves the fastness properties for related fibres dyed with basic and disperse dyes. However, the fastness properties are lowered to some extent in case of dyeing with direct dye, much in conformity with the lowering in dye fixation value in this case consequent to vinyl grafting as can be seen and appreciated from Table II.

3.6. Infrared absorption spectra

The IR absorption spectra of samples of dewaxed jute, oxy-jute (before and after modification with phenol and formaldehyde) and a vinyl grafted oxy-jute (obtained by graft copolymerization with MMA on the oxy-jute) are given in Fig. 5. Absorbances at $1745 \, cm^{-1}$ corresponding to $C=O$ stretching get enhanced on oxidation of the jute fibre. The enhancement in the peak absorbance and in the area under the peak is apparently linked with the enhancement in the degree of oxidation which is known to lead to enhanced –COOH and –CHO functional groups in the fibres. On treatment of the fibres with phenol, however, the absorbance in this region gets substantially reduced as expected due to elimination of the aldehyde (–CHO group) in the oxy-jute through condensation with phenol. On the other hand, grafting with polymethylmethacrylate leads to substantial enhancement in the $C=O$ absorption peak (both peak height and peak area) due to incorporation of the ester polymer (to the extent of more than 25% for the grafted fibres chosen for IR study) in to the fibre. The weak absorption bands over the zone 1400–$1650 \, cm^{-1}$, diagnostic of aromatic structures from lignin present in the jute fibre get substantially weakened in the spectrum of

the graft copolymer due to dilution effects caused by vinyl incorporation and also to some minor but basic structural changes in the fibre that take place during graft copolymerization.

4. Conclusions

Raw or dewaxed jute fibres exhibit very low rot resistance (giving tensile strength retention of upto 8–10% only after soil burial test). Oxy-jute fibres obtained by subjecting the raw or dewaxed fibre to mild oxidation using aqueous H_2O_2, aqueous $NaIO_4$ or non-aqueous Cl_2 as the oxidizing agents are still worse in rot resistance (tensile strength retention becoming practically zero after soil burial test) even though the percentage dye fixation shows significant improvement. In respect of tensile strength retention of the fibre subsequent to oxidation, aqueous $NaIO_4$ is less promising than aqueous H_2O_2 or non-aqueous Cl_2. Oxy-jute fibres bearing relatively large numbers of aldehyde groups in their structure show substantial enhancement in rot resistance with little gain in percentage dye fixation on treatment with phenol and formaldehyde.

Vinyl grafting on each type of jute fibre (raw, dewaxed, oxidized, and subsequently phenol-formaldehyde treated) leads to prominent enhancement in their rot resistance. On vinyl grafting, the tensile strength retention values after soil burial test become as high as 35–40% for the raw/dewaxed jute and its treatment with phenol and formaldehyde prior to vinyl grafting makes little difference in the rot resistance of the corresponding grafted fibre. This can be understood in view of very low –CHO groups content or copper number for the raw–dewaxed jute fibre and hence leaving minimum scope for phenol intake in the fibre. For the oxy-jute fibres, however, vinyl grafting improves the rot resistance to a much higher degree (tensile strength retention after soil burial test improving from 0% for the ungrafted oxy-jute fibres to nearly 60–70% for the grafted oxy-jute fibres).
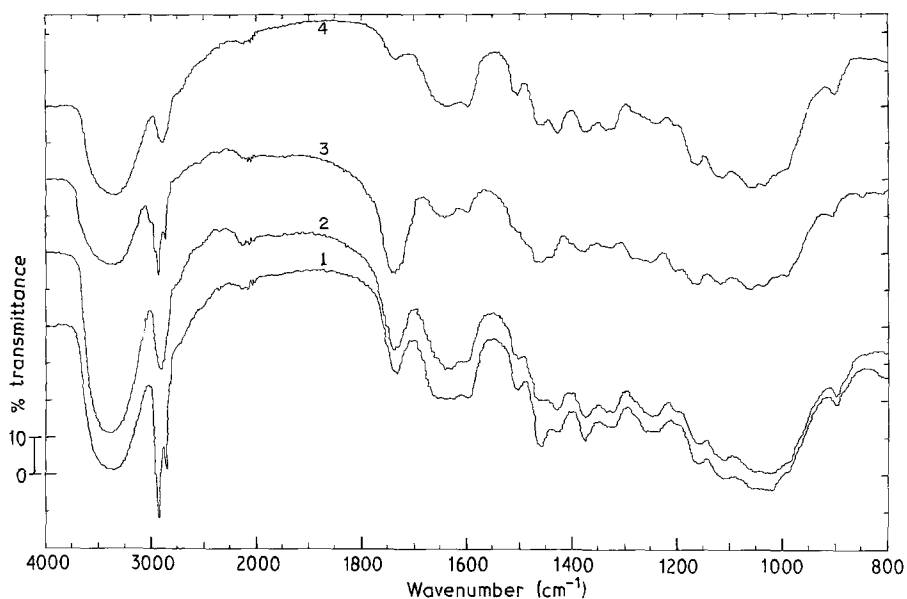
Figure 5 IR spectra of different jute fibre samples. Data given are nature of fibre and curve No: dewaxed, 1; Oxy-jute (oxidation done with aqueous H_2O_2), 2; graft copolymer from MMA and oxy-jute (oxidation done with aqueous H_2O_2), 3; Phenol-formaldehyde treated on oxy-jute (oxidation done with aqueous H_2O_2), 4.

Treatment of the oxy-jute fibres with phenol and formaldehyde enhances the rot resistance of the fibre to a level which is comparable to, if not better than those exhibited by the vinyl grafted oxy-jute fibres. Whatever additional –CHO groups that is formed on the jute fibres during their mild oxidation makes them adequately reactive in respect of phenol–aldehyde condensation and the relatively high incorporation of phenol moieties in the fibre as a consequence of the resinification reaction leads to the enhancement of rot resistance. The phenol–formaldehyde modified oxy-jute fibres show further enhancement in rot resistance (by a margin of another 10% in tensile strength retention after soil burial test) on subsequent vinyl grafting on them.

Vinyl grafting on jute fibres leads to substantial enhancement in their percentage dye fixation and fastness numbers (both washing fastness and light fastness) particularly with a basic dye or a disperse dye, more so, if vinyl grafting is done on the fibre subsequent to its mild oxidation. The above parameters however, suffer adversely, though to a minor extent, if the dyeing is done with a direct dye. Considering all aspects of the grafted fibres, it may be said that vinyl grafting of upto 30% vinyl intake produces the optimum effects. Higher percentage grafting pro-

duces little or marginal difference in the percentage dye fixation and rot resistance properties but tenacity (g denier^{-1}) tends to fall sharply if the percentage grafting is allowed to become more than 30%.

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