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Scanning electron microscopic studies on some chemically modified bast fibres

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The surface morphology of dewaxed jute and of dewaxed and scoured flax and ramie fibres, and the effect of chemically modified morphologies were compared using scanning electron microscopy (SEM). Limited oxidation results in the removal of surface impurities of the bast fibres, producing strands which are clearly distinguishable in the SEM. Treatment of the oxy-fibres with excess phenol (P) and formaldehyde (F) at pH 8 leads to permanent *in situ* deposition of P–F resin moieties, which makes the strands less clearly visible. Modification of the P–F treated oxy-fibres by vinyl grafting leads to further masking of the fibre strands due to measurable vinyl deposition; in the SEM the fibre strands appear closely cemented together by the grafted-on vinyl polymer. On exposure to a standard microbiological degradative environment, damage to the fibre strands takes place in the order jute $\gg$ flat $\geqslant$ ramie; oxy-jute $\ggg$ oxy-flax $\geqslant$ oxy-ramie. Each fibre system suffers little microbiological degradation, thereby showing high rot resistance, when the respective oxy-fibres are modified by P–F treatment and also by vinyl grafting in a subsequent step. At this stage the difference between the three fibre systems in rot resistance becomes slight. The SEM observations are supported by analysis of tensile strength (TS) and retention of TS after exposure to a standard microbiological degradative environment.

1. Introduction

Among the different bast fibres grown seasonally under different climatic conditions, jute, flax and ramie hold positions of importance because of their high volume of production and widespread use in many fields. For practical purposes, and to meet different needs, minor or major modifications of these fibres are often necessary to bring about different degrees and kinds of chemical changes in the fibre, which are also likely to be associated with changes in their surface morphology.

Some of the common treatments relating to these fibres are dewaxing, scouring, swelling with selected agents and some degree of oxidation using selected chemicals under specified conditions. Such treatments bring out changes in the functional group pattern and also delignification to various extents, depending on the nature of the reagent used, and on the conditions employed [1], as well as effecting some leaching of adherent and associated low-molecular-weight or even degraded products, particularly from the surface of the fibres. Changes brought about in the surface of the fibres can be studied by scanning electron microscopy (SEM) [2, 3]. The role of graft copolymerization in bringing about changes in the surface morphology of polymeric materials including fibres has been studied [4]. Most of these reports are sporadic and disjointed, leaving scope for further studies with an integrated approach. The present work was undertaken with this in view. Results of studies on the surface morphology of jute, flax and ramie fibres, and changes due to treatments of the fibres with different chemical reagents under comparable conditions, are presented here. Chemical treatments to which the fibres (initially dewaxed) were subjected are (i) treatment of the dewaxed fibres with an oxidizing agent under controlled conditions; (ii) modification of the oxy-fibres by treatment with phenol and formaldehyde; and (iii) graft copolymerization of a mixture of methyl methacrylate (MMA) and maleic anhydride (MA) on the phenol–formaldehyde modified oxy-fibres.

2. Experimental procedure

2.1. Fibre samples

Raw jute fibre, Indian Standard Institution grade TD_2, was dewaxed by soxhlet extraction for 6 h using a benzene–alcohol solvent mixture (2:1 vol %) [5]. Samples of flax and ramie fibres were obtained courtesy of Jayashree Textiles Ltd. They were subjected to dewaxing following the same method as for jute, and then to scouring with aqueous NaOH (2%) and non-ionic surfactant (0.1%) for 1 h while boiling, with a fibre: liquor ratio of 1:50 (wt %). The dewaxed fibres were used in the present study.

2.2. Chemical treatments and modifications

Dewaxed jute as well as dewaxed and scoured flax and ramie fibre samples, preswollen with 10% aqueous

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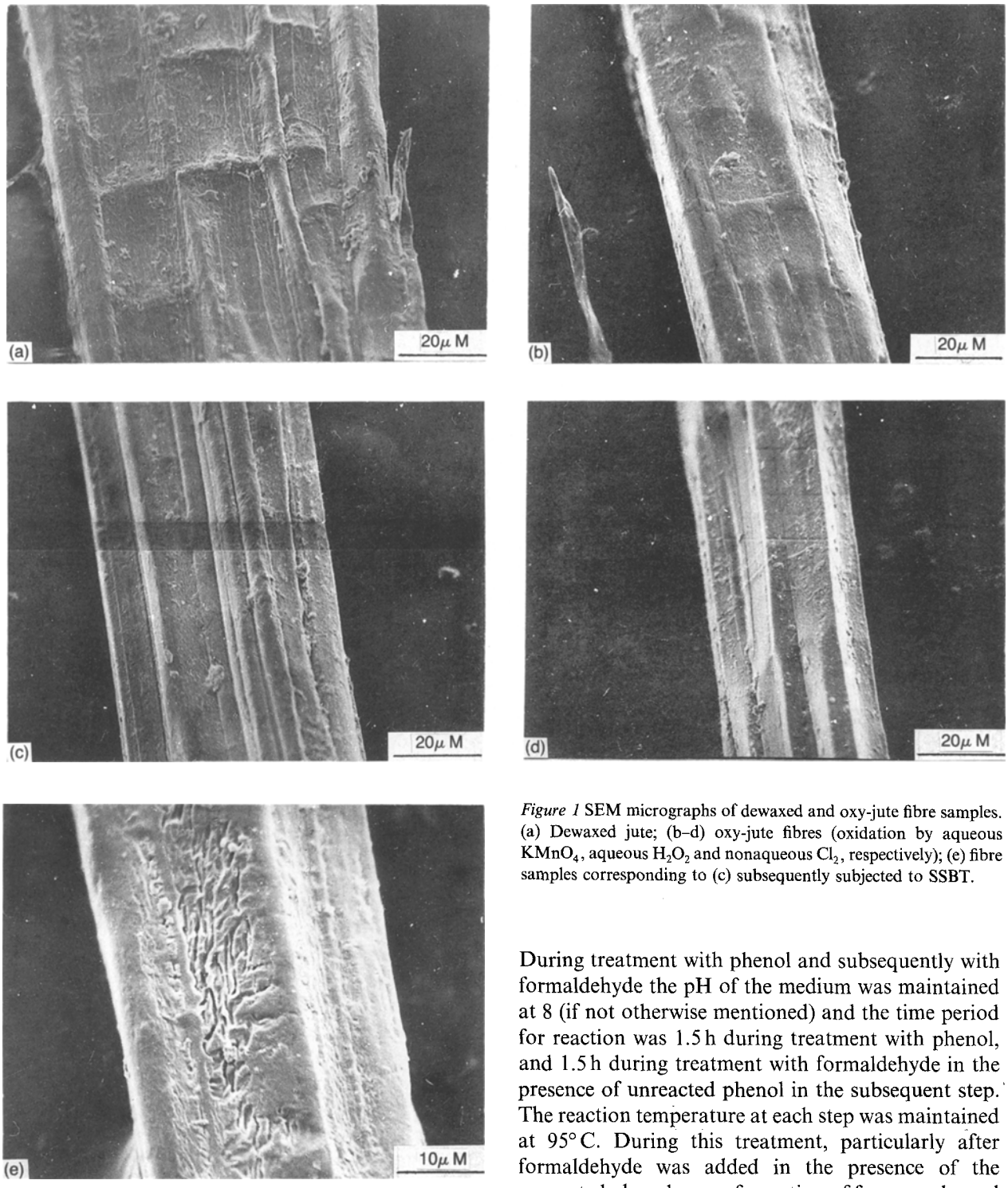
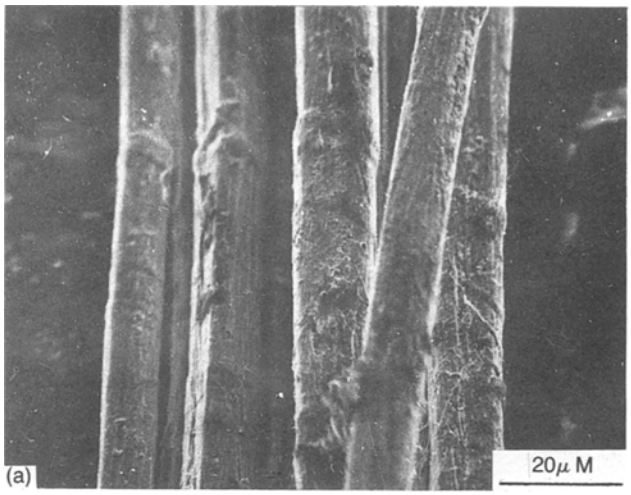


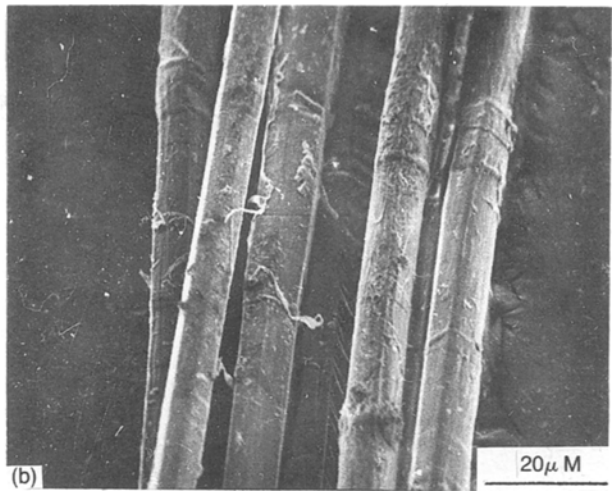
Figure 1 SEM micrographs of dewaxed and oxy-jute fibre samples. (a) Dewaxed jute; (b–d) oxy-jute fibres (oxidation by aqueous $KMnO_4$, aqueous H_2O_2 and nonaqueous Cl_2, respectively); (e) fibre samples corresponding to (c) subsequently subjected to SSBT.

urea solution at 90° C for 2 h (making the fibre more readily suited for oxidation), were subjected to mild oxidation using aqueous H_2O_2 (10 g l^{-1} H_2O_2 for 1 h at 80° C, pH 10) under identical or comparable conditions [1]. Oxidation with aqueous $KMnO_4$ (1.4 g l^{-1} aqueous $KMnO_4$ for 1 h at 60° C, pH 10.5) and with non-aqueous Cl_2 (20 g l^{-1} Cl_2 in CCl_4 for 5 min at 30° C) was also conducted under specified conditions detailed elsewhere [1]. The oxidized fibre sample were then washed with water until free from the oxidizing additives, then dried in air.

Oxidized fibre samples of jute, flax and ramie obtained from oxidation with aqueous H_2O_2 were then separately with excess phenol and subsequently with excess formaldehyde under identical conditions [6]. During treatment with phenol and subsequently with formaldehyde the pH of the medium was maintained at 8 (if not otherwise mentioned) and the time period for reaction was 1.5 h during treatment with phenol, and 1.5 h during treatment with formaldehyde in the presence of unreacted phenol in the subsequent step. The reaction temperature at each step was maintained at 95° C. During this treatment, particularly after formaldehyde was added in the presence of the unreacted phenol, some formation of free or unbound phenol–formaldehyde resins of resinoids of low molecular weight is likely. After the specified period of treatments with phenol and formaldehyde the fibre samples were taken out, washed with a 2:1 (vol %) mixture of alcohol and water to ensure the removal of traces of unbound phenolic resin of resinoid, then washed with distilled water and dried in air.

The oxy-fibre samples modified by treatments with phenol and formaldehyde were further modified by graft copolymerization with a 1:1 (wt %) mixture of MMA and MA using a low concentration of potassium persulphate as the catalyst at 40° C under photoconditions. The reaction mass contained in a borosilicate test tube was placed between a pair of flourescent tube lamps, (40 W; Philips India Ltd) [7]. In each case, 0.5 g of fibre was soaked in an excess of





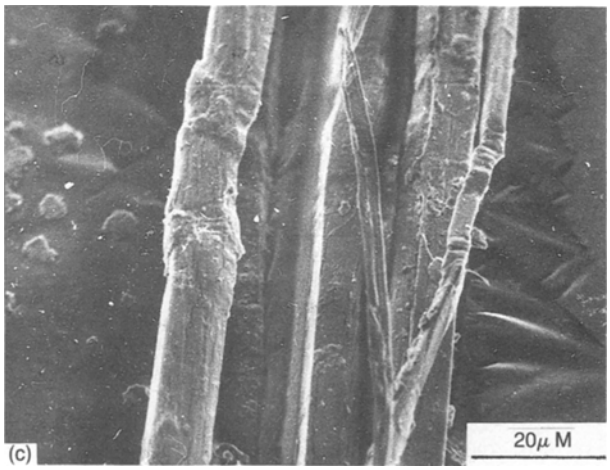


Figure 2 SEM photomicrographs of scoured and oxy-flax fibre samples. (a) Dewaxed and scoured flax; (b) oxy-flax fibre (oxidation by aqueous H_2O_2); (c) fibre sample corresponding to (b) subsequently subjected to SSBT.

3% solution of $K_2S_2O_8$ 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 $K_2S_2O_8$ taken up by the fibre was calculated, considering no preferential adsorption. 0.5 g each of MMA and MA dissolved in 1 ml of acetone was then poured on the moist fibre sample containing the catalyst, and the air in the test tube was flushed out using a nitrogen current. The test tube was then stoppered and the contents were ready for graft copolymerization. After polymerization (under given conditions, over a specified time period) the contents were transferred to a beaker, washed with water and dried at 50° C under a vacuum. Free or ungrafted copolymers of MMA and MA were then removed from the gross product of graft copolymerization by extraction with acetone in a soxhlet apparatus for 48 h. The residue containing the graft copolymers along with the ungrafted fraction of the fibres, if any, was then dried in air and characterized.

2.3. Characterization of fibre samples

The dewaxed fibre samples, as well as those modified by treatments with different chemicals and the vinyl grafted fibres as detailed above, were examined for evaluation of their tensile strength (TS) or tenacity (g denier^{-1}). One of the basic objectives was to infuse in the fibres substantially higher rot resistance or resistance to microbiological attack. For this, the tensile strength of the fibres was also measured after they were separately subjected to a standard soil burial treatment (SSBT) for 21 days, according to Indian Standard Institution specification [8]. The resistance to microbiological attack was measured by the retention of tensile strength of the initial fibre after the specified soil burial treatment. A higher percentage retention of tensile strength indicates higher rot resistance or resistance to micobiological attack.

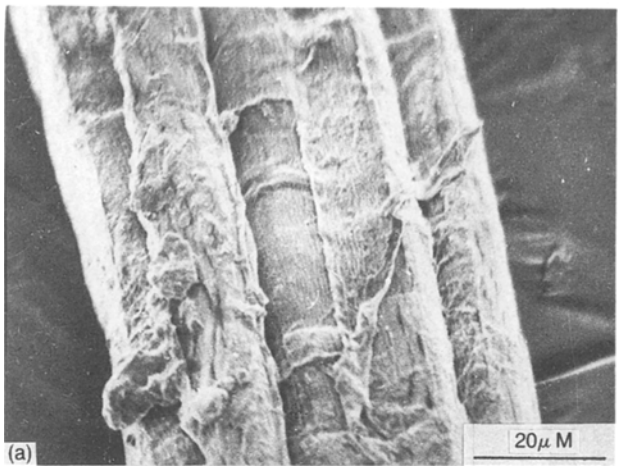
Selected fibre samples were also studied in the SEM (Cambridge, Stereoscan 250, UK) [2] to examine the effect of specific chemical modifications in modifying their surface morphology. The fibre samples were coated with a thin layer of gold–palladium alloy using a sputter coater. For examination in the SEM in the secondary mode, a beam voltage of around 5 kV was used.

3. Results and discussion

The average composition of jute, flax and ramie fibres is given in Table I. In view of the relatively high lignin and hemicellulose content of jute, treatment with alkali with or without oxidative reagents tends to weaken the jute fibre through the removal of a large proportion of hemicellulose and also through delignification (when subjected to oxidative treatments). In this respect, ramie fibre is stable and flax is somewhat more resistant than jute. Thus the

TABLE I Chemical composition of jute, flax and ramie fibres

Chemical constituent	Jute (%)	Flax (%)	Ramie (%)
α Cellulose	55–63	55–60	75–82
Hemicellulose	21–24	13–15	–
Lignin	12–14	2–4	Traces
Fats and waxes	0.8	2.37	0.22
Minerals	0.6–1.2	1.32	2.05
Aqueous extract	1.03	6.02	6.90
Pectins and other intercellular matter	2–3	7.4	5.51
Water	9.93	10.70	8.5



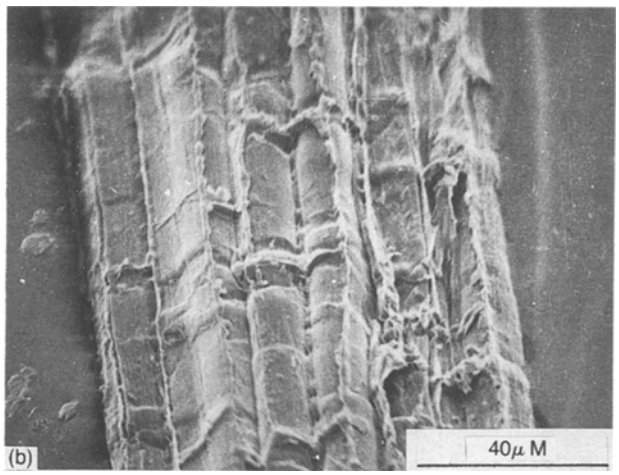


Figure 3 SEM photomicrographs of scoured and oxy-ramie fibre samples. (a) Dewaxed and scoured ramie; (b) oxy-ramie fibre (oxidation by aqueous H_2O_2); (c) fibre sample corresponding to (b) subsequently subjected to SSBT.

pretreatment of jute fibre was limited only to dewaxing, avoiding scouring with a mild alkaline solution in the subsequent step, whereas for flax and ramie the pretreatment also included scouring.

The photomicrographs of different jute fibres with various chemical modifications, including some of those subjected to microbiological attack (soil burial test), are shown in Figs 1 and 4. Selected photomicrographs of treated/modified flax and ramie fibres are shown in Figs 2 and 5, and 3 and 6, respectively.

3.1. Modification of fibre samples by treatment with different oxidizing agents

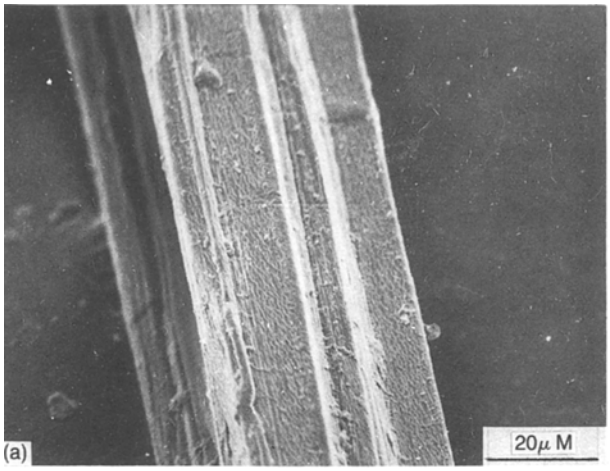
The surface morphology of dewaxed jute fibre, and that of the same fibre subjected to mild oxidation using aqueous $KMnO_4$, aqueous H_2O_2 and nonaqueous Cl_2 are shown in Fig. 1a–d. The dewaxed fibre has a more or less clear surface, showing the presence of knots along the straight strands of the fibre (Fig. 1a).

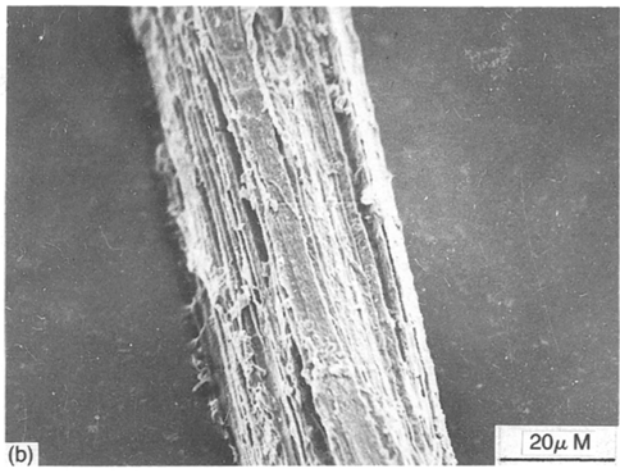
The surface features of jute fibres oxidized with aqueous H_2O_2 (10 g l^{-1} aqueous H_2O_2 at 80° C for 1 h, pH 10) or nonaqueous Cl_2 (20 g l^{-1} nonaqueous Cl_2 at 30° C for 5 min) are similar. The fibre strands are more clearly visible (Figs 1c and d) much as a consequence of further removal of intercellular matter or impurities during the oxidative treatments, the degree of removal being greater for the fibre sample subjected to oxidation with nonaqueous Cl_2 (Fig. 1d). Oxidation with aqueous $KMnO_4$ (1.4 g l^{-1} aqueous $KMnO_4$ at 60° C for 1 h, pH 10.5) results in a different surface morphology. The fibre strands are not as clearly visible, and removal of the intercellular matter is apparently restricted by this oxidative treatment. After the oxidative treatment the fibre appeared black as a consequence of deposition of MnO_2 during the process, which was largely removed by treatment with dilute solution of midly acidic sodium sulphite [1], before making the fibre ready for SEM and other studies. The fibre then appeared light brown, and as seen in Fig. 1b, clearly shows inadequate or incomplete removal of impurities or deposited materials.

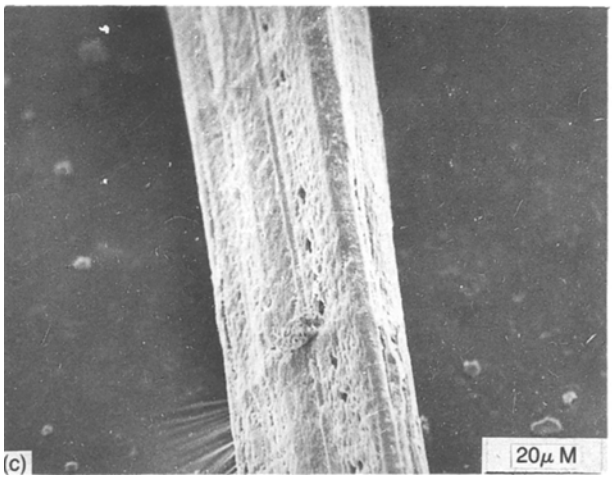
One of the oxy-jute fibre samples (that corresponding to Fig. 1d) was later subjected to micobiological degradation under a specified test condition (SSBT, Indian Standard specification 19,1949) and the result can be seen in Fig. 1e. Extensive damage of the fibre is clearly visible and tensile strength retention of this fibre was found to be zero.

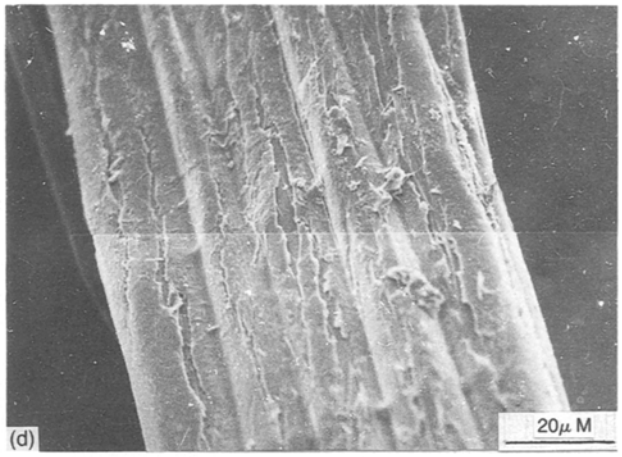
The surface morphologies of dewaxed and scoured flax and ramie fibres are shown in Figs 2a and 3a, respectively. Under mild alkali treatment during scouring, the impurities and intercellular matter in flax are more readily removed, while the removal is rather limited in case of ramie fibre. The fibre strands of flax are distinctly visible with reasonably clear surfaces, but for the ramie fibre the strands are not as clearly visible and apparently the impurities or intercellular matter on the surface of the fibre are still retained.

Following mild oxidation of these two fibres using aqueous H_2O_2, the surface of the fibres becomes still clearer, and the impurities and intercellular matter are further removed (see Figs 2a and b, and Figs 3a and b, respectively). On oxidation, the fibre strands show a clearer surface with more distinct separation of the stands, particularly in the case of flax. Figs 2c and 3c show oxy-flax and oxy-ramie fibres (corresponding to Figs 2b and 3b, respectively) after their exposure to SSBT. Due to the degradative effect consequent on microbiological attack, the fibre surfaces are apparently split and broken at different points and the clarity of the fibre strands initially visible (prior to this treatment) are not as readily visible now. But the









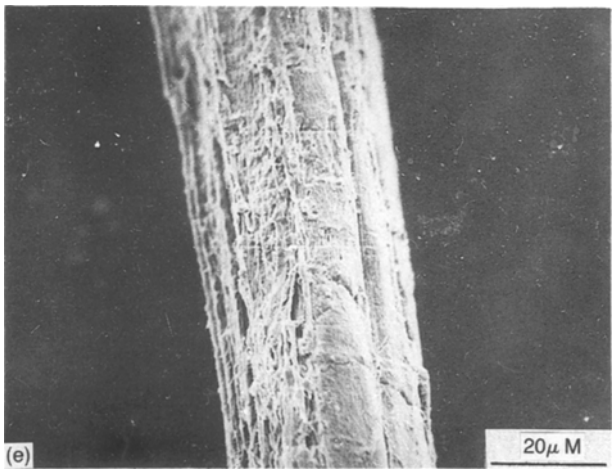


Figure 4 SEM photomicrographs of oxy-jute after selected chemical modifications. (a) Oxy-jute fibre (oxidation by aqueous H_2O_2) modified by treatment with phenol and formaldehyde at pH 8; (b) oxy-jute fibre (oxidation by aqueous H_2O_2) modified by treatment with phenol and formaldehyde at pH 4.5; (c) fibre sample corresponding to (a) subsequently subjected to SSBT; (d) fibre sample corresponding to (a) subsequently vinyl grafted (24%); (e) fibre sample corresponding to (d) subsequently subjected to SSBT.

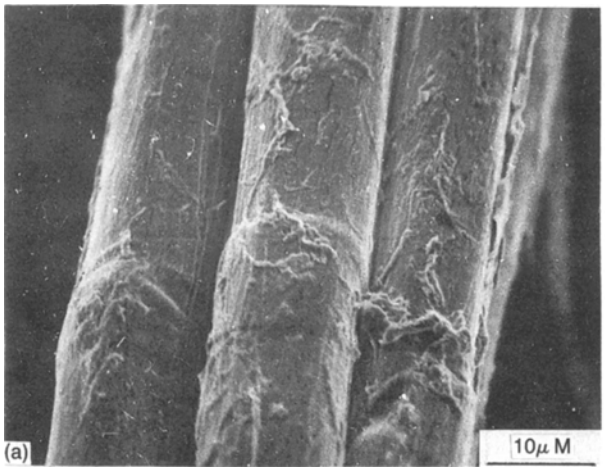
damage due to SSBT in oxy-fibres from flax and ramie is not as extensive as in the case of oxy-jute fibres (Fig. 1e). The oxy-fibres from flax and ramie show relatively high tensile strength retention (40–45%) after SSBT (Table II).

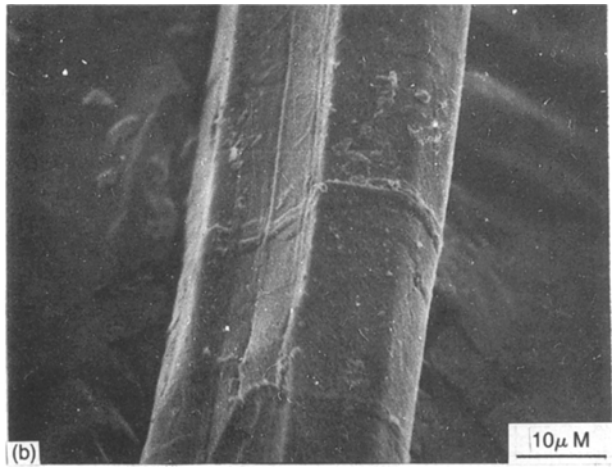
3.2. Modification of oxy-fibres by treatment with phenol and formaldehyde and subsequent vinyl grafting

Some selected oxy-fibres from jute, flax and ramie were subsequently subjected to further treatment with excess phenol and fomaldehyde in successive steps as detailed elsewhere [6]. In each case, the pH of the solution during the treatment of the oxy-fibres was maintained at pH 8. The photomicrographs of phenol–formaldehyde treated oxy-fibres (mild oxidation with aqueous H_2O_2) from jute, flax and ramie are shown in Figs 4a, 5a and 6a, respectively. Deposited phenol formaldehyde resin is chemically linked to the fibre molecules through the –CHO groups formed on them in relatively enchanced numbers as a consequence of the oxidative treatments. Deposition of resin, however small, is clearly indicated in the photomicrographs, the fibre strands being less clearly visible when compared with the corresponding fibre samples prior to treatment with phenol and formaldehyde (Figs 1c, 2b and 3b, respectively). In the case of jute, the oxy-fibre was treated with phenol and formaldehyde at pH 4.5 (Fig. 4b) resulted in severe damage of the fibre, despite good phenolic resin formation on it. Thus modification of oxy-jute with phenol and formaldehyde at an acidic pH is not recommended, as it leads to a fibre of very poor strength or tenacity (2.00 g denier^{-1}, as opposed to a tenacity of 2.95 g denier^{-1} for modification of the same fibre with phenol and formaldehyde at pH 8; Table II).

TABLE II Properties of jute, flax and ramie after varying degrees of chemical modification

Fibre type	Sample number	Chemical treatment/ modification	Tenacity (g denier^{-1})	TS retention after SSBT (%)	Surface morphology		Figure
					Before SSBT A	After SSBT B	
Jute	J1	Dewaxed	3.8	8	Clear surface and presence of knots along straight strands		1a
	J2	Oxy-jute; oxidation by					
		aqueous $KMnO_2$	2.95	–	Fibre strands clearly visible showing removal of impurities	Extensive damage clearly visible	1b–d
		aqueous H_2O_2	3.00	–	Fibre strands clearly visible showing removal of impurities	Extensive damage clearly visible	
		non-aqueous Cl_2	2.85	–	Strands less visible due to deposition of MnO_2	Extensive damage clearly visible	1e
	J3	Oxy-jute; oxidation by aqueous H_2O_2, modified with P–F treatment	2.95	61	Fibre strands less clearly visible due to *in situ* deposition of P–F resin on the fibre	Fibre strands retain their individual structure intact; high rot resistance	4a 4c
	J4	Grafted with MMA and MA (1:1 wt %) on J3	2.95	73	Deposition of vinyl polymer distinctly visible; fibre strands more closely held or cemented together by grafted-on vinyl polymer	Fibre strands still remain intact; limited surface damage indicating high rot resistance	4d 4e
Flax	F1	Dewaxed and scoured	5.35	35	Fibre strands distinctly visible with clear surface		2a
	F2	Oxy-flax; oxidation by aqueous H_2O_2	4.85	43	Fibre strands clearer due to oxidative treatment	Fibre surfaces split showing limited damage in comparison with oxy-jute	2b 2c
	F3	Oxy-flax modified with P–F treatment	4.90	67	Fibre strands less clearly visible due to *in situ* deposition of P–F resin moieties in the fibre		5a
	F4	Grafting with MMA and MA (1:1 wt %) on F3	5.00	73	Deposition of vinyl polymer indicated; fibre strands more closely held or cemented together by grafted-on vinyl polymer	Fibre strands still intact; limited surface damage indicating high rot resistance	5b 5c
Ramie	R1	Dewaxed and scoured	5.45	42	Individual fibre strands visible, without any interstrands		3a
	R2	Oxy-ramie; oxidation by aqueous H_2O_2	5.00	46	Individual fibre strands more clearly visible with improved surface structure	Fibre strands appear split, broken and blurred	3b-c
	R3	Oxy-ramie modified with P–F treatment	4.90	75	Fibre strands less clearly visible due to *in situ* deposition of P–F resin moieties on the fibre		6a
	R4	Grafting with MMA and MA (1:1 wt %) on R3	4.70	78	Deposition of vinyl polymer distinctly visible; fibre strands more closely held or cemented together by grafted-on vinyl polymer	Fibre strands remain intact; limited surface damage indicating high rot resistance	6b 6c





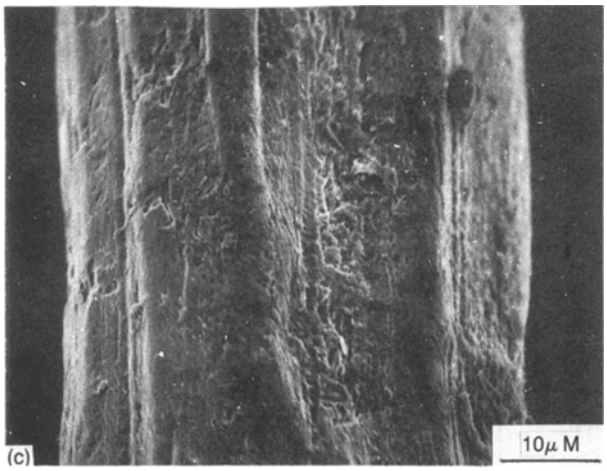


Figure 5 SEM photomicrographs of oxy-flax after selected chemical modifications. (a) Oxy-flax fibre (oxidation by aqueous H_2O_2) modified by treatment with phenol and formaldehyde; (b) fibre sample corresponding to (a) subsequently vinyl grafted (30%); (c) fibre sample corresponding to (b) subsequently subjected to SSBT.

The oxy-fibres modified by treatment with phenol and formaldehyde at pH 8 were subsequently subjected to vinyl grafting using a 1:1 (wt %) mixture of MMA and MA in limited aqueous media according to a procedure detailed elsewhere [7]. The grafted jute fibre (25% grafting), flax fibre (30%) and ramie fibre (40%) are shown in Figs 4d, 5b and 6b, respectively. Further deposition of the vinyl polymer on the phenol–formaldehyde modified oxy-fibres is distinctly visible in each case, and the fibre strands are more closely held or cemented together by the grafted polymer.

The vinyl-grafted jute, flax and ramie fibres (oxy-fibres treated with phenol and formaldehyde) were subsequently subjected to SSBT to evaluate their ability to resist microbiological attack. The changes in the surface morphology of the grafted fibres consequent to microbiological attack can be understood by comparing photomicrographs before (Figs 4d, 5b and 6b for jute, flax and ramie fibres, respectively) and

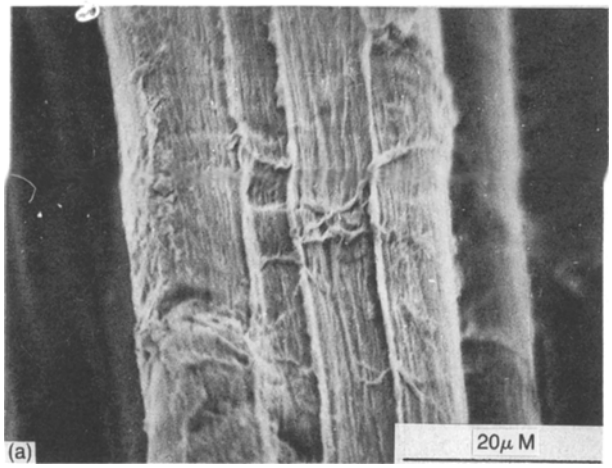
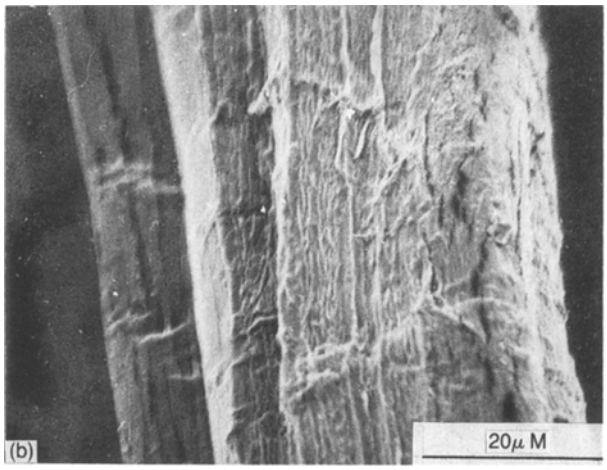
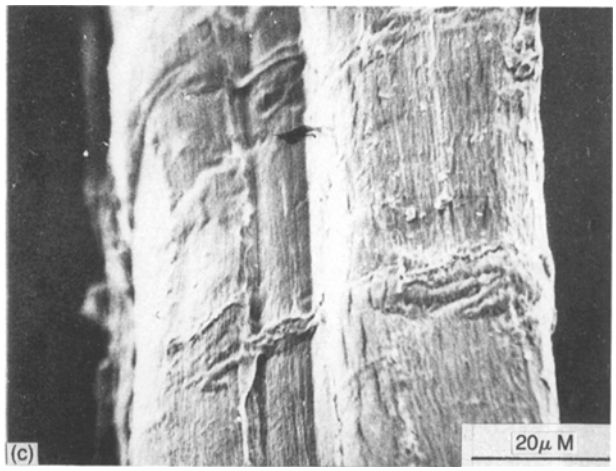


Figure 6 SEM photomicrographs of oxy-ramie after selected chemical modifications. (a) Oxy-ramie fibre (oxidation by aqueous H_2O_2) modified by treatment with phenol and formaldehyde; (b) fibre sample corresponding to (a) subsequently vinyl grafted (40%); (c) fibre sample corresponding to (b) subsequently subjected to SSBT.





after (Figs 4e, 5c and 6c, respectively) the soil burial test.

The grafted fibre samples exposed to SSBT clearly show the deposition of vinyl polymers on the fibres, but the fibre strands are still retained intact and damage in structure of the fibre strands does not appear to be extensive, in contrast to the extensive damage observed for an oxy-jute fibre on SSBT (Fig. 1e). The oxy-jute fibres show little resistance to microbiological attack (Fig. 1e). But if the oxy-jute fibre is subsequently modified by treatment with phenol and formaldehyde under slightly alkaline conditions (pH 8) and then subjected to SSBT, it shows enchanced resistance to microbiological degradation, the fibre strands retaining their individual structure largely intact (Fig. 4c).

4. Conclusions

After a limited degree of oxidation, fibre strands of jute, flax and ramie become more clearly distinguishable, much as a consequence of the removal of surface impurities and intercellular matters. In view of the higher proportions of lignin and hemicellulose in jute fibre in comparison with flax and ramie fibres, jute behaves somewhat differently when subjected to mild oxidation. Considerable amounts of lignin and hemicellulose are removed from the jute fibre during its mild oxidation; the fibre is weakened in tenacity and more importantly its resistance to microbiological attack is reduced: the oxy-jute fibres of any mild degree of oxidation studied here show little rot resistance. Flax and ramie fibres, however, are superior to jute in this respect and these oxy-fibres show a high level of rot resistance.

Treatment of the oxy-fibres with phenol and formaldehyde made them sufficiently resistant to microbiological degradation, and this resistance is further improved (though to a limited extent) when the respective phenol–formaldehyde modified fibres were further modified by vinyl grafting. Examination of tensile strength data and analysis of the SEM photomicrographs revealed that all the bast fibres studied here behave similarly in this respect.

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