Graft copolymerization of methyl methacrylate on jute using the aqueous IO_4^-–Cu^{2+} combination as the initiator system and evaluation of the graft copolymers

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The graft copolymerization of methyl methacrylate (MMA) on jute was studied using a combination of $NaIO_4$ and $CuSO_4$ as the initiator in an aqueous medium. Concentrations of $IO_4^- = 0.005$ mol dm^{-3} and $Cu^{2+} = 0.001$ mol dm^{-3} gave optimum grafting conditions and percentage conversion at 50°C. IO_4^- and Cu^{2+} when used separately failed to induce either homopolymerization or graft copolymerization of MMA in the presence of jute. The effects of variation of time, temperature, monomer concentration and pH of the medium on grafting parameters and percentage conversion were also studied and reported. Progressive removal of lignin and hemicellulose from jute separately produced significant improvements in the percentage grafting and the percentage conversion without greatly affecting the grafting efficiency. A mechanism for the graft copolymerization reaction has been proposed. Grafting of poly(methyl methacrylate) (PMMA) to the extent of 20–25% was found to improve certain properties, including fibre strength and modulus, moisture regain, rot resistance, whiteness index, light-fastness and resistance to thermal degradation. I.r. spectra and X-ray crystallinity of the fibre samples with different degrees of grafting have been compared. Surface morphology, as studied using scanning electron microscopy, indicates that PMMA grafting occurs on surfaces and in the intercellular regions of the multicellular jute fibre.

(Keywords: graft copolymerization; lignocellulosic fibres; PMMA grafting)

INTRODUCTION

Jute is a multicellular lignocellulosic bast fibre. The axially oriented overlapping bundle of cellulosic cells, called the ultimate cells, in a single jute fibre remains cemented together in the intercellular regions by lignin and hemicellulosic constituents[1,2].

Properties of jute fibre can be modified and tailored to different degrees by chemical modifications, including graft copolymerization with a vinyl monomer under controlled selective conditions[3–8]. The multicellular and multiconstituent nature of jute poses problems in modifying it by graft copolymerization. Selection of catalysts or initiator systems for graft copolymerization reactions is critical, bearing in mind the tendency of jute towards oxidative and hydrolytic degradation.

The IO_4^- ion has been reported to act as an aqueous initiator for graft copolymerization of a vinyl monomer on cellulose[9] and wool[10]. We thought it of interest to examine the suitability of IO_4^- ion as an initiator on its own or in combination with an activating agent for graft copolymerization of methyl methacrylate (MMA), a vinyl monomer, on jute and to examine how the graft copolymerization contributed to modification in its properties.

EXPERIMENTAL

Raw jute fibre (*Corchorus olitorius*), obtained locally, was extracted with an ethyl alcohol–benzene mixture (1:2, v/v) for 6 h under reflux, washed successively with ethyl alcohol and distilled water and finally dried under vacuum at 40°C. This gave dewaxed jute (DJ).

Bleached jute (BJ) was obtained by treating the raw jute fibre or the scoured (using 2% detergent solution at 60°C for 1 h) jute fabric with H_2O_2 (ref. 11).

Progressive removal of lignin from DJ was effected by treating a part of DJ with 0.7% $NaClO_2$ solution at 98 ± 1°C at pH 4 using a fibre to liquor ratio of 1:50 (w/w)[12] for specified time periods (*Table 1*). The fibre was then washed with excess of distilled water, treated with 2% (w/w) sodium metabisulfite solution at 50°C for 30 min and finally washed with distilled water and dried in air.

Progressive removal of hemicellulose from DJ was effected by treating the fibre with NaOH solutions[13] of specified strength at specified temperatures for 60 min using a fibre to liquor ratio of 1:50 (w/w) (*Table 1*). This was followed by washing with distilled water, neutralization with 1% acetic acid solution, further

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Table 1 Composition of major chemical constituents of dewaxed jute (DJ) and some chemically treated DJ samples (oven dried)

	DJ	Delignified DJ[a]			DJ treated for removal of hemicellulose[b]		
Major constituents	(A)	(B)	(C)	(D)	(E)	(F)	(G)
α-Cellulose (%)	61.0	61.1	60.7	61.2	61.1	60.9	60.7
Hemicellulose (%)	23.0	22.9	22.6	22.1	19.0	15.9	6.8
Lignin (%)	13.9	9.8	5.2	0.8	13.1	13.0	12.1

[a] Time of delignification: B, 10 min; C, 40 min; D, 120 min. Temperature 98°C; [$NaClO_2$] = 0.7%

[b] Data for hemicellulose removal ([NaOH], time, temperature): E, 1%, 60 min, 30°C; F, 5%, 60 min, 30°C; G, 7%, 60 min, 98 ± 1°C

washing with distilled water to an acid-free condition and drying.

Table 1 shows the composition of the major chemical constituents of DJ (column A) and of DJ fibre samples subjected to progressive removal of lignin (columns B, C, D) and of hemicellulose (columns E, F, G). Lignin and hemicellulose contents were determined by standard methods[12,14].

Monomer MMA was purified by washing with dilute alkali and vacuum distillation following standard procedures[15]. Analytical grade $NaIO_4$ and $CuSO_4 \cdot 5H_2O$ (E. Merck) and other chemicals and solvents of reagent grade were used as received. Water, distilled twice in an all-glass distillation unit, was used in polymerization experiments.

Graft copolymerization

Appropriate quantities of distilled water, purified monomer (MMA) and copper sulfate solution (0.01 mol dm^{-3}) were added successively to an appropriate jute sample of known mass in a stoppered borosilicate glass ampoule which was then placed in a thermostatted bath for 5 min. The ampoule was then flushed with a slow stream of nitrogen for 5 min and an appropriate volume of $NaIO_4$ solutions (0.05–0.2 mol dm^{-3}) was added under a N_2 blanket. The ampoule was then stoppered with an air-tight stopper and graft copolymerization was allowed to proceed at a specified temperature (30–60°C) in a thermostatted bath. After a specified time period (0.5–6.0 h), the overall polymer product was quantitatively transferred in a beaker, filtered, washed successively with distilled water, dilute (0.01 M) HCl (to remove adsorbed $CuSO_4$), distilled water, methanol and petroleum ether, dried under vacuum at 40°C and weighed (w_1). Removal of free, homopolymeric poly(methyl methacrylate) (PMMA), formed during graft copolymerization was effected by extracting the dried gross product with benzene for 48 h in a Soxhlet apparatus under reflux. The residue was washed with methanol, dried in air and finally under vacuum at 40°C and weighed (w_2). Grafting parameters and percentage conversion values were calculated as follows:

$$\%\text{Grafting} = \frac{w_2 - w}{w} \times 100$$

$$\text{Grafting efficiency } (\%) = \frac{w_2 - w}{w_1 - w} \times 100$$

$$\%\text{Conversion} = \frac{w_1 - w}{w_3} \times 100$$

where w and w_3 are the mass of the vacuum-dried jute sample and the monomer used for graft copolymerization, respectively.

Independent blank experiments using jute separately in the presence of water only, aqueous monomer, $CuSO_4$ (0.0005–0.006 mol dm^{-3}) and $NaIO_4$ (0.001–0.1 mol dm^{-3}) at 50°C showed mass losses of 0, 0, 0.2–0.3% (after washing with dilute HCl) and 1–2%, respectively, over a time period of 5 h, and in each case the mass loss was negligible up to 1 h. Again, when jute was used in the presence of the two initiator components ($CuSO_4$ and $NaIO_4$) over a pH range of 2–12, it showed a mass loss of 0.5–2%; however, in this case, in the presence of the monomer, there was always a mass gain due to graft copolymerization of the monomer on jute. It is most likely that polymers formed initially on the fibre during graft copolymerization would act as a barrier against mass loss. Any correction for blanks on the grafting parameters and on percentage conversion is therefore considered uncertain if not unnecessary and so was not attempted.

Characterization

DJ with different degrees of chemical modification through PMMA grafting was examined using an i.r. spectrophotometer (Shimadzu, model IR 440) and an X-ray diffractometer (Philips, model 1700 using PW 1710 system for computation) for evaluation of the effects of vinyl grafting. The surface morphology of the jute fibres with different degrees of grafting was examined using a scanning electron microscope (Hitachi, model S 430); standard procedures were followed in each evaluation. The effect of PMMA grafting on the thermal properties of the fibres was also studied using thermogravimetry (Mettler TA 4000 system) and differential scanning calorimetry (d.s.c.) DuPont model 9900). The moisture regain (average of five tests)[16], light-fastness (average of five tests)[17] and whiteness index (average of 100 tests)[18] properties of the jute and of the grafted jute fibres were determined. The tensile properties of the fibres based on an average of 50 tests[19,20] were determined using an Instron universal testing unit (model 1148) with a test length of 10 mm and a cross-head speed of 5 mm min^{-1}. The rot resistance of grafted and ungrafted DJ was assessed by subjecting the fibres to a standard soil burial test (SSBT)[21].

RESULTS AND DISCUSSION

The aqueous graft copolymerization of MMA on to jute cannot be initiated using either IO_4^- or Cu^{2+} separately as the initiator. Aqueous IO_4^-, however, is known[9] to act as a polymerization initiator of MMA in the presence or absence of cellulose, even though it fails to do so in the presence of jute fibre (raw, DJ or BJ). IO_4^-, however, can readily polymerize MMA in the presence of a jute sample which has been largely delignified, thus yielding the graft copolymer. A combination of copper sulfate and sodium periodate (i.e. Cu^{2+} and IO_4), however, can initiate the graft copolymerization of MMA on jute under aqueous conditions. The jute may be dewaxed or further modified chemically by delignification and/or subjected to the removal of hemicellulose etc. The results are shown in *Figures 1–5*.

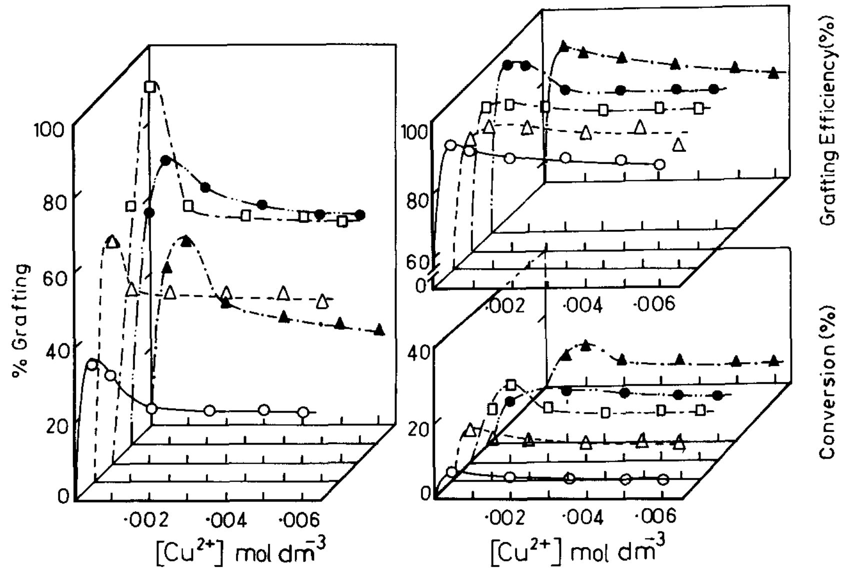


Figure 1 Effect of variation of [Cu^{2+}] and [IO_4^-] on grafting parameters and percentage conversion in graft copolymerization of MMA on DJ. DJ, 0.2 g; MMA, 1 cm^3; fibre to liquor ratio, 1:50 (w/w); temperature, 50°C; time, 4 h. [IO_4^-] (mol dm^{-3}): ○, 0.001; △, 0.003; □, 0.005; ●, 0.01; ▲, 0.05

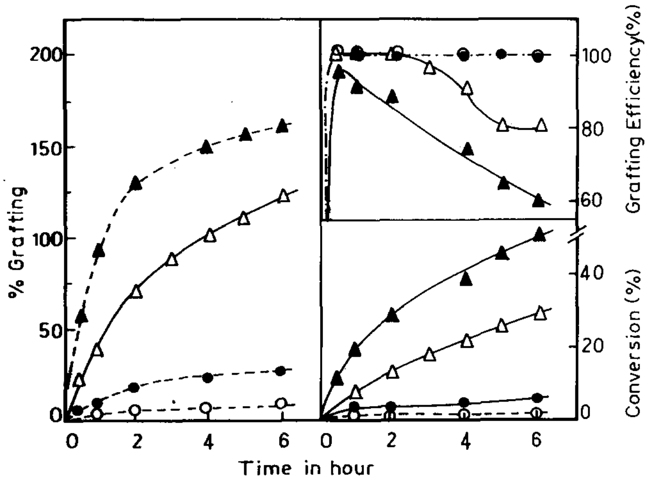


Figure 2 Effect of varying time and temperature on grafting and percentage conversion in the graft copolymerization of MMA on DJ. DJ, 0.2 g; MMA, 1 cm^3; fibre to liquor ratio, 1:50 (w/w); [IO_4^-] = 0.005 mol dm^{-3}; [Cu^{2+}] = 0.001 mol dm^{-3}. Temperature: ○, 30°C; ●, 40°C; △, 50°C; ▲, 60°C

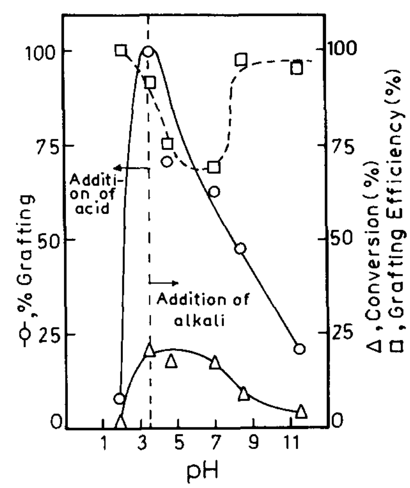


Figure 4 Effect of variation of pH of the reaction medium on grafting parameters and percentage conversion in graft copolymerization of MMA on DJ. DJ, 0.2 g; MMA, 1 cm^3; fibre to liquor ratio, 1:50 (w/w); temperature, 50°C; time 4 h; [IO_4^-] = 0.005 mol dm^{-3}; [Cu^{2+}] = 0.001 mol dm^{-3}

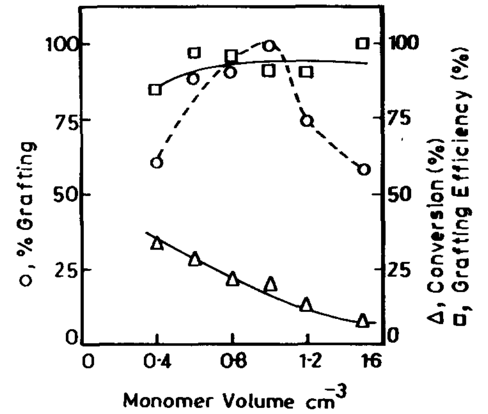


Figure 3 Effect of variation of monomer (MMA) content on grafting parameters and percentage conversion in graft copolymerization of MMA on DJ. DJ, 0.2 g; fibre to liquor ratio, 1:50 (w/w); temperature, 50°C, time, 4 h; [IO_4^-] = 0.005 mol dm^{-3}; [Cu^{2+}] = 0.001 mol dm^{-3}; total volume (water + monomer) = 10 cm^3

Effect of varying initiator concentration

The effect of varying [Cu^{2+}] (0.005–0.006 mol dm^{-3}) at five different fixed values of [IO_4^-] (0.001–0.050 mol dm^{-3}) on the grafting parameters and the percentage conversion at 50°C for polymerization for 4 h is shown in *Figure 1*. For a given [IO_4^-] in the range of 0.001–0.050 mol dm^{-3} a [Cu^{2+}] of 0.005–0.001 mol dm^{-3} produced a maximum in grafting parameters and also in percentage conversion. For graft copolymerization of MMA on jute (DJ) using the IO_4^-–Cu^{2+} combination as initiator, the grafting efficiency was usually high (>85%).

Effect of varying temperature and time of polymerization

When the graft copolymerization of MMA on DJ was carried out at 30 and 40°C, the percentage conversion and percentage grafting were low for a given time of polymerization (*Figure 2*), but they improved substantially when grafting was done at 50 and 60°C and

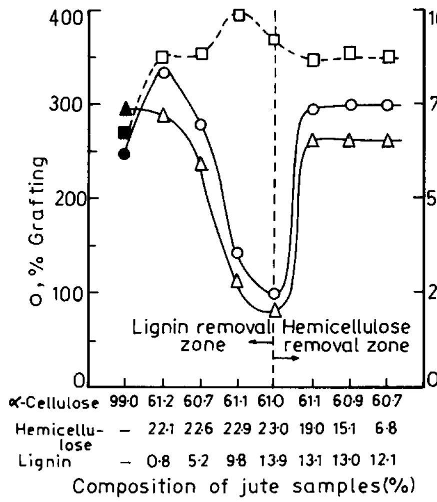


Figure 5 Effect of progressive removal of lignin and hemicellulose from jute on grafting parameters and percentage conversion in graft copolymerization of MMA on DJ. DJ, 0.2 g; MMA, 1 cm^3; fibre to liquor ratio, 1:50 (w/w); temperature, 50°C; time, 4 h; $[IO_4^-]=0.005$ mol dm^{-3}; $[Cu^{2+}]=0.001$ mol dm^{-3}. Solid symbols give the corresponding data for graft copolymerization on α-cellulose (scoured cotton) under comparable conditions. Dotted vertical line corresponds to the composition of DJ

the values increased with increase in the time of polymerization. Values for the degree of grafting of the order of 100 and 150% were readily obtained at 50 and 60°C, respectively, for 4 h of graft copolymerization. The corresponding values for conversion were about 20 and 40%. The grafting efficiency is nearly 100% at lower temperatures (30–40°C) and the percentage conversion is very low (<6%). The grafting efficiency follows a decreasing trend with increase in temperature beyond 40°C and also with time of polymerization at higher temperatures. This is apparently due to the fact that at higher temperatures (>40°C), homopolymer formation assumes increasing prominence. Also, the grafted-on polymer, formed substantially on the fibre surface at the early stages of the reaction, acts as a physical barrier to further monomer penetration in the fibre structure in the later stages, thereby restricting further formation of graft copolymer while formation of the homopolymer in the aqueous medium continues unhindered throughout.

Effect of varying monomer concentration

From the results shown in *Figure 3*, it is apparent that increasing the monomer concentration from 4 to 15% (v/v) at 50°C using the optimum initiator concentration causes the degree of grafting to pass through a maximum corresponding to a monomer concentration of 10%. Conversion, however, follows a decreasing trend with increase in monomer concentration (possibly because of poor solubility of MMA in water). Grafting efficiency remains above 80% at 50°C over the range of monomer concentrations studied.

Effect of varying pH of the reaction medium

Changes in the pH of the reaction medium (which is 3.6 at 50°C using the optimum initiator concentration, $[IO_4^-]=0.005$ mol dm^{-3} and $[Cu^{2+}]=0.001$ mol dm^{-3}) was effected by addition of small volumes of either 0.5% H_2SO_4 or 0.2% NaOH solution to the reaction medium. The results, presented graphically in *Figure 4*, indicate that lowering or increasing the pH of the reaction medium from the initial instantaneous pH value of 3.6 results in different orders of lowering of percentage grafting and conversion values. Grafting efficiency, however, follows a decreasing trend with increase in pH up to pH 7, beyond which it shows a sharp increase followed by levelling off at around 90–95%. Thus, addition of acid or alkali causing changes in pH of the medium is believed to alter the nature, oxidizing power and solubility of the initiating species based on or derived from $NaIO_4$ (ref. 22) and also of the solubility of $CuSO_4$ used, thereby causing changes in the course and extent of the polymerization reaction in a manner that results in appreciable drop in overall formation of PMMA.

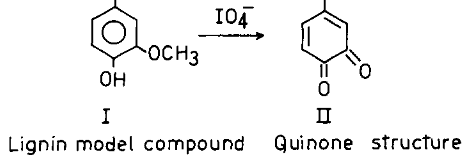
Mechanism

IO_4^- is known to induce graft copolymerization of MMA on cellulose[9]. The initiation of graft copolymerization is attributed to radicals derived from cellulose through complexing between aqueous periodate ions and the anhydroglucose units of cellulose molecule followed by oxidation of the latter at the 1,2-glycol positions[9,23].

In the case of jute fibre, the oxidative attack of IO_4^- on the lignin and hemicellulose constituents of the fibre also assumes importance in the radical reactions. IO_4^- is reported[24] to react with lignin at phenolic–OH sites resulting in formation of quinone structures (*Scheme 1*) which cause prominent inhibition during graft copolymerization. This is also evidenced by the i.r. spectrum of the $NaIO_4$-treated jute (*Figure 6*, *curve 3*) which features a weak peak at 1715 cm^{-1} assigned to quinone structures. In addition, there is broadening of the –C=O stretching band at 1740–1750 cm^{-1}.

The sluggish and subdued nature of graft copolymerization induced by aqueous IO_4^- in the presence of jute on the one hand, and ready initiation of graft copolymerization by the same initiator system in the presence of delignified jute, point to the strong radical scavenging role of the lignin constituents of jute. The present observations support the radical scavenging role reported for lignin[25].

When $CuSO_4 \cdot 5H_2O$ is used in combination with $NaIO_4$, a large part of Cu^{2+} (~85%) is instantaneously adsorbed onto jute. The pH of the reaction medium drops from 5.6 (when only IO_4^- was present) to 3.6. The adsorbed Cu^{2+} apparently complexes with the phenolic moieties of lignin and shields them from oxidative attack of IO_4^-. The chance of formation of quinone structures is thereby eliminated or restricted substantially, as would be evident from i.r. spectra (*Figure 6*) of relevant fibre samples (DJ, IO_4^--treated jute and PMMA-grafted jute samples). The (Cu^{2+}–IO_4^-)-initiated grafted fibre samples do not show the weak peak (1715 cm^{-1}) assigned to quinone structures. In the presence of Cu^{2+}, the scope for formation of quinone moieties recedes to inconsequence and IO_4^- is almost exclusively used



Scheme 1

up in radical-forming reactions involving cellulosic/hemicellulosic constituents of jute, thereby allowing ready formation of graft copolymers of MMA on jute (*Scheme 2*).

Polymer formation is also likely to be initiated by $\dot{H}$ and $\dot{O}H$ generated in the system by reactions between Cu^{2+} and IO_4^- as shown below (refs 26, 27):

$$Cu^{2+} + IO_4^- + H_2O \rightarrow Cu^+ + IO_3^- + H^+ + \tfrac{1}{2}O_2 + \dot{O}H$$

$$Cu^+ + H^+ \rightarrow Cu^{2+} + \dot{H}$$

$$Cu^+ + IO_4^- + H_2O \rightarrow Cu^{2+} + IO_3^- + OH^- + \dot{O}H$$

$$\dot{O}H \text{ (or } \dot{H}) + M \rightarrow \text{Polymer (homopolymer)}$$

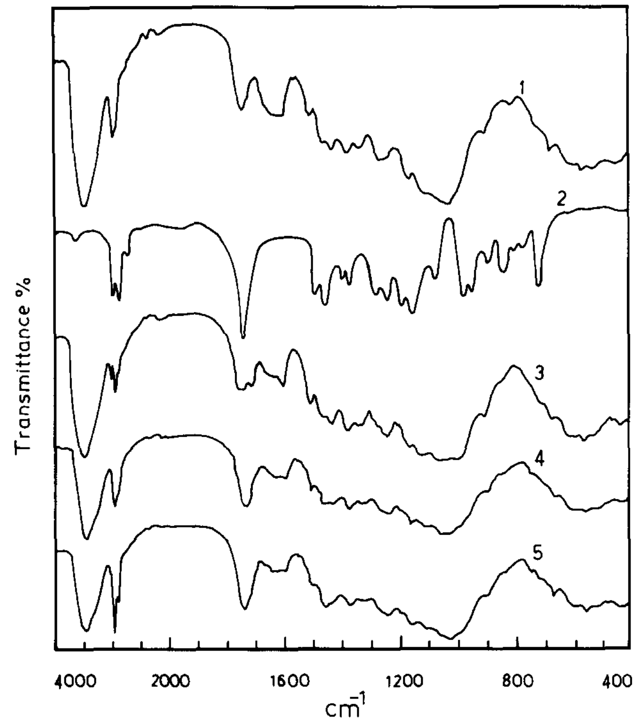


Figure 6 I.r. spectra of jute fibres of different types and degrees of modification and of PMMA: 1, DJ; 2, PMMA; 3, $NaIO_4$-treated DJ; 4, 25% PMMA-grafted DJ; 5, 50% PMMA-grafted DJ. For graft copolymerization, the conditions given in *Figure 3* were employed

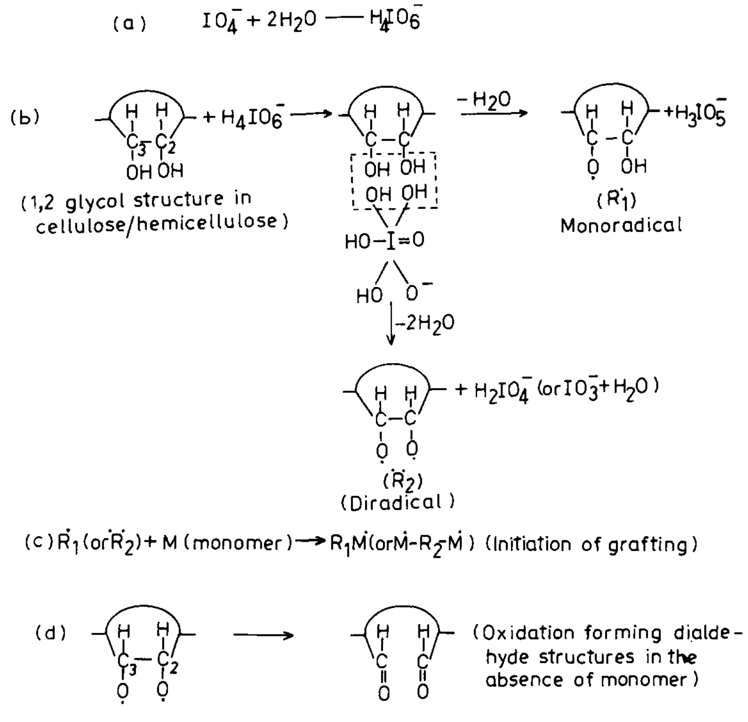
The lignin and hemicellulosic constituents of jute, however, have a measurable influence on the polymerization process initiated by the Cu^{2+}–IO_4^- combination and, on progressive removal of lignin from jute, the degree of grafting is seen to follow an increasing trend. On progressive removal of hemicellulose, the degree of grafting also increases, sharply in the initial stage and marginally thereafter (*Figure 5*). While the effect of lignin removal is understandable, that due to hemicellulose removal appears to result from a combination of factors. These are especially significant during the initial stage of hemicellulose removal[28,29]. The sequence involves removal of the reducing and the methoxyl groups of jute, rupture of the lignin–hemicellulose ester linkages in jute and increase in specific surface area of jute.

X-ray crystallinity

DJ shows X-ray crystallinity of the order of 58%. PMMA-grafted DJ fibres, however, exhibit a much lower overall percentage crystallinity (*Table 2*), which follows a decreasing trend with increase in degree of grafting. However, when the degree of crystallinity is calculated on the basis of equal amounts of jute in each case, little difference in percentage crystallinity is indicated among the grafted and the ungrafted jute, implying that the fine structure of DJ remains virtually unaffected by PMMA grafting and that the grafted PMMA is located overwhelmingly in the amorphous regions of the jute fibre.

Study of surface morphology by scanning electron microscopy

Scanning electron microphotographs of $NaIO_4$-treated DJ and PMMA-grafted jute samples in *Figure 7* reveal



Scheme 2

Table 2 Effect of PMMA grafting[a] on the properties and fine structure of dewaxed jute (DJ) and bleached jute (BJ)

					Grafted fibre, % grafting								
			IO_4^--treated fibre		10%		20%		25%		30%		40%
Properties	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ
Specific stress[b] (cN tex^{-1})	38.4	36.3	32.2	33.1	41.3	36.0	42.6	36.8	41.1	40.2	34.8	40.9	31.2
Breaking extension (%)	1.75	1.68	1.38	1.40	1.60	1.56	1.49	1.50	1.43	1.47	1.40	1.45	1.28
Initial modulus (cN tex^{-1})	2194	2161	2333	2364	2562	2308	2859	2453	2839	2721	2486	2820	2437
Moisture regain (%)	13.4	–	–	–	12.16	–	11.22	–	10.51	–	9.82	–	–
Retention of specific stress (%) after 21 days of SSBT	Nil	–	–	–	35.0	–	39.0	–	40.1	–	43.0	–	–
X-ray crystallinity[c] (%)	58.1	–	57.6	–	51.1 (58.0)	–	46.0 (57.5)	–	43.0 (57.3)	–	40.5 (57.8)	–	–
Whiteness index	–	61.0	–	40	–	51	–	54.0	–	56.0	–	58.0	–
Light-fastness rating	–	1–2	–	1	–	2	–	3	–	3–4	–	3–4	–

[a] Grafting was done at 50°C for 1 h using aqueous $[IO_4^-]=0.005\ mol\ dm^{-3}$ and $[Cu^{2+}]=0.001\ mol\ dm^{-3}$ combination as initiator; fibre to liquor ratio, 1:50 (w/w); concentration of MMA was varied from 4 to 15% (v/v) to effect different degrees of grafting

[b] Specific stress = breaking load (cN)/linear density (tex); 1 tex $= 10^{-6}\ kg\ m^{-1}$

[c] Figures with and without parentheses indicate percentage crystallinity of the grafted fibres calculated on the basis of jute (DJ) content and on overall basis, respectively

increasing deposition of the grafted polymer on the surface of the fibre with increase in the degree of grafting. 30% PMMA grafting (*Figure 7c*) results in almost complete masking of the surface features of DJ.

Tensile properties

From the results given in *Table 2*, it is apparent that PMMA grafting brings about moderate to significant changes in the tensile properties of both DJ and BJ fibres. Specific stress and initial modulus values of DJ increase by about 7–10% and 17–30%, respectively, for 10–25% PMMA grafting. For a grafting level of >25%, however, both specific stress and initial modulus of DJ follow decreasing trends. For BJ, measurable improvement in specific stress on PMMA grafting is apparent only at a relatively high degree of grafting (>20%). The initial modulus value follows an increasing trend with increasing grafting right from the initial stage. The breaking extension (BE) values of both DJ and BJ, however, follow decreasing trends with increase in degree of grafting. The observed improvements in specific stress and initial modulus values with simultaneous lowering in BE values of the fibres are consequences of the filling of voids, particularly in the intercellular matrix region of the multicellular jute fibre, by the grafted PMMA chains. The matrix regions in the initial fibres, partly filled with amorphous lignin and hemicellulose constituents, are reinforced through the cementing action of the grafted PMMA chains. This results in densification and stiffening of the matrix regions leading to more efficient transfer of stress between the ultimate cells, thereby causing improvements in the overall fibre strength.

The higher specific surface area[11] and lower strength of BJ in comparison to DJ, and the oxidative treatment received by the former, may account for the differences in the tensile behaviour of the two on PMMA grafting. The fall in the specific stress value of DJ for PMMA grafting beyond 25% is apparently due to accumulation of stresses and strains in excess of a threshold level consequent to non-uniform anchorage and overgrowth of the grafted-on PMMA chains in the fibre structure during polymerization in the heterogeneous system.

Moisture regain and rot resistance

The results given in *Table 2* indicate that the moisture regain of DJ at 65% relative humidity and 27°C follows a decreasing trend with increase in degree of grafting. This is expected in view of the hydrophobic nature of the grafted PMMA chains.

The rot resistance of jute, as measured by a standard soil burial test for 21 days[21], is nil. However, rot resistance of jute improves considerably on PMMA grafting and follows an increasing trend with increase in degree of grafting, as evident from data given in *Table 2*.

Whiteness index and light-fastness

From the data given in *Table 2* it is apparent that whiteness index value of BJ suffers a substantial initial fall on PMMA grafting (from 61 to 51 on 10% grafting) but then improves slowly with increase in degree of grafting. Loss in whiteness index of BJ with low degrees of PMMA grafting is a consequence of the action of the major initiator component, i.e. IO_4^- on lignin present in BJ. A very low value of whiteness index is obtained for BJ treated by IO_4^- alone. On PMMA grafting, the surface of BJ becomes progressively masked by the grafted-on PMMA, resulting in improved whiteness index.

The light-fastness rating of BJ also improves on PMMA grafting as a consequence of the masking of the surface of BJ by grafted-on PMMA, which provides, to some extent, a protective shield for BJ against the action of light[30]. The light-fastness rating improves from a value

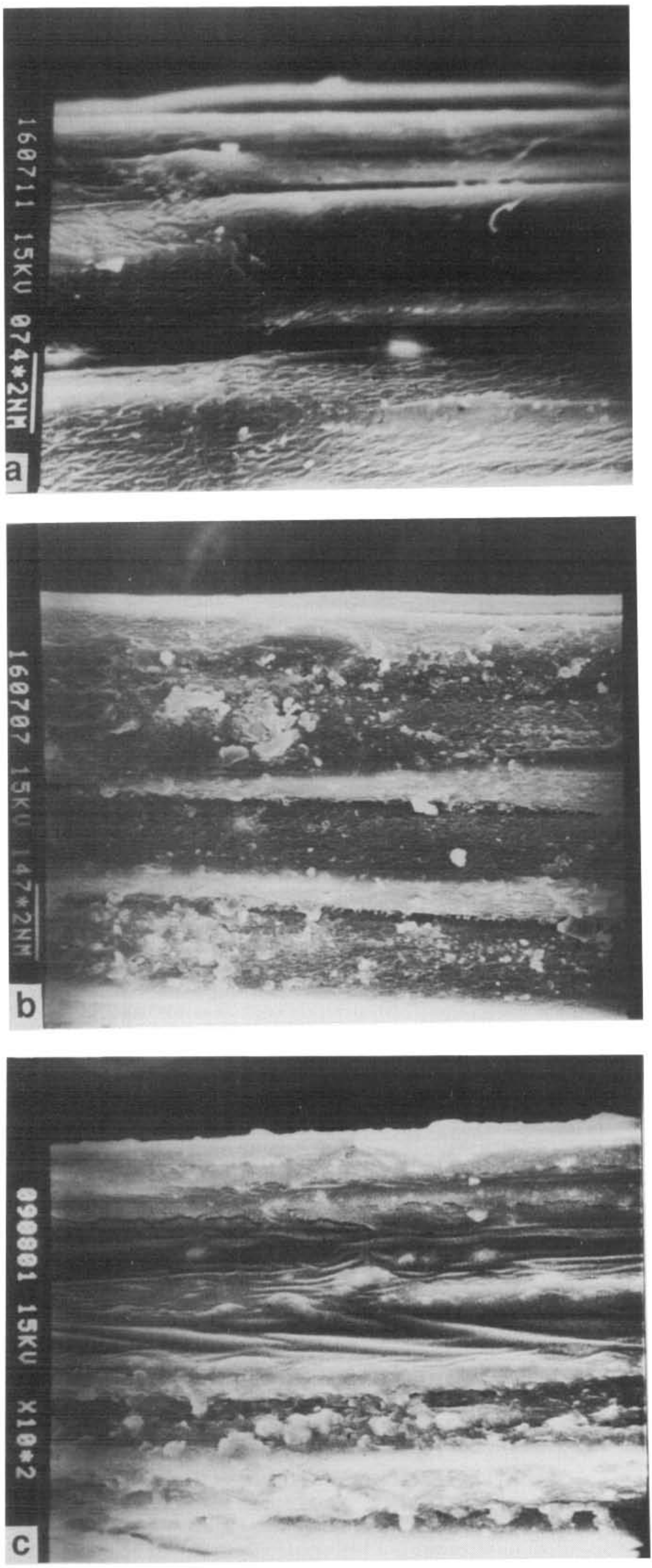


Figure 7 SEM micrographs showing surface morphology of different fibre samples: (a) $NaIO_4$-treated DJ; (b) 15% PMMA-grafted DJ; (c) 30% PMMA-grafted DJ

of 1–2 for BJ to a value of 3–4 for 30% PMMA-grafted BJ (*Table 2*).

Thermal behaviour

Thermogravimetric analysis (under flowing N_2). Three distinct zones can be identified in the thermogravimetric curves (*Figure 8*) of DJ with different extents of PMMA grafting (0, 25 and 50%) and of homopolymer PMMA extracted with benzene from a gross polymer product of graft copolymerization. The initial zone corresponds to a small weight loss due to evaporation of absorbed water. The middle zone corresponds to major weight loss due to thermal decomposition of the test sample (onset temperature, T_1) and a third or final zone appears on conclusion of the major thermal decomposition process; over this zone a more or less steady weight of a carbonized residue is retained. The observed onset temperatures (T_1)

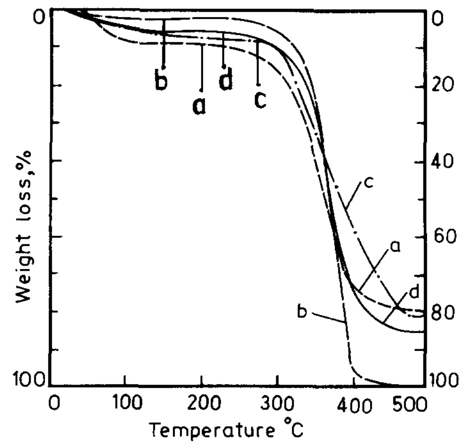


Figure 8 Thermogravimetric (percentage weight loss *versus* temperature) traces of fibre/polymer samples: a, --, DJ; b, ——, PMMA homopolymer; c, –·–·, 25% PMMA-grafted DJ; d, ——, 50% PMMA-grafted DJ. Heating rate 10°C min^{-1}; sample weight, 10 mg; tests carried out under flowing nitrogen

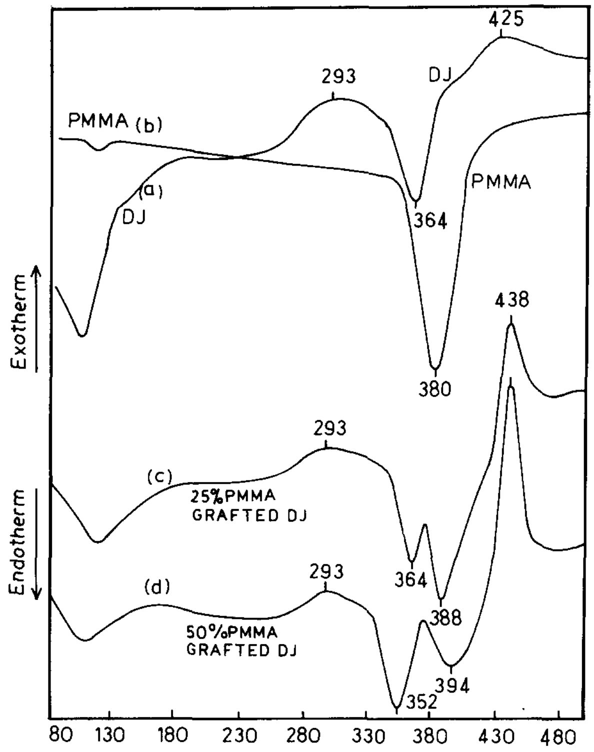


Figure 9 D.s.c. thermograms of fibre/polymer samples under flowing nitrogen: a, DJ; b, PMMA homopolymer; c, 25% PMMA-grafted DJ; d, 50% PMMA-grafted DJ. Heating rate 10°C min^{-1}, sample weight 10 ± 1 mg

of decomposition for DJ, PMMA homopolymer, 25% PMMA-grafted DJ and 50% PMMA-grafted DJ are 215, 240, 240 and 225°C, respectively.

PMMA is known[31] to degrade thermally giving 100% monomer as volatiles leaving no residue beyond 450°C. PMMA-grafted jute fibres therefore liberate higher proportions of volatiles than the ungrafted jute although the onset temperatures (240 and 225°C for 25 and 50% grafting of PMMA, respectively) for the grafted fibres are higher than that of ungrafted jute. A degree of PMMA grafting over 25–30% makes the grafted fibre weaker. This is due to the accumulation of stresses and strains resulting from random overgrowth of layers of the vinyl polymer (PMMA) on the fibre as grafted-on chains; this is also reflected in a measurable drop in thermal stability (T_1 value) for the grafted fibre with a still higher degree of grafting (50%).

Since jute is a multicellular and multiconstituent fibre, its modification by PMMA grafting results in complex chemical changes with respect to both location and distribution of the grafted PMMA chains, with the result that interpretation of the observed changes is complicated.

D.s.c. analysis. D.s.c. curves of selected fibre and polymer samples are shown in *Figure 9*. A small endothermic peak at around 100°C is caused by evaporation of absorbed water in each case. The d.s.c. curve of jute is characterized by two weak exotherms at around 293 and 425°C, due to decomposition of hemicellulose and lignin constituents, respectively, and a strong endotherm at around 364°C, due to degradation of cellulosic constituents[32]. The d.s.c. curve of PMMA is characterized by a strong endothermic peak at around 380°C. PMMA grafting of jute leads to notable sharpening of the exotherm assigned to the lignin constituents of the fibre and also to a shift in the exotherm peak to a slightly higher temperature (from 425 to 438°C). Liberation of monomer MMA in the preceding endotherm zone due to decomposition of PMMA (peak around 380°C), interaction of the liberated monomer with lignin constituents and some shift to a higher temperature of the endothermic peak corresponding to PMMA decomposition (388–394°C, caused presumably by the pronounced endothermic decomposition of the cellulosic constituents in the immediately preceding step, peak at 364°C) may have combined to contribute to the shift and sharpening of the final exotherm corresponding to lignin decomposition. Changes of a similar nature in the thermal response of cellulose due to the presence of some other associated polymer in the systems have been reported earlier[33].

It is also interesting to note that the endotherm corresponding to cellulose decomposition for DJ with a fairly high degree of grafting (50% PMMA) has its peak at a relatively low temperature (352°C) as compared to the expected 364°C for DJ (0–25% PMMA grafting). This indicates that a higher degree of grafting (>25% PMMA) on jute makes the grafted fibre less thermally stable because of the accumulation of stress in the fibre system consequent to overgrowth of the vinyl polymer as grafted-on chains. Observations, presented in an earlier section, of trends in the variation of tensile properties of the fibres with increasing degree of grafting are compatible with these observations of their thermal response.

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