

Effects of grafted methyl methacrylate on the microstructure of jute fibres

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The effects of grafting methyl methacrylate (MMA) by radiochemical methods on the microstructure of bleached jute fibres have been investigated by X-ray diffraction techniques. The fractional crystallinity (X_{cr}), crystallite size $L(hkl)$ perpendicular to the (hkl) planes, overall isotropic temperature factors, and lattice distortions caused by grafting have been determined. The disordered regions between (040) planes are more favourable sites for introducing monomers than those between (120) planes. At 8.6% wt MMA, strong secondary bonds between crystalites perpendicular to the (040) planes and monomers appear to align these particles along the (040) direction. At the same time, X_{cr} assumes the minimum value of 0.50 suggesting that the monomers enter the disordered region between (040) planes. At 10.6% wt monomer, secondary bonds between particles perpendicular to the (120) planes and monomers align these particles, and it is suggested that hydrogen bonds between $L(120)$ particles increase X_{cr} to 0.64. Above 10.6% wt monomer, disordered regions are overcrowded so that $L(hkl)$ values are minimal and X_{cr} slowly decreases.

INTRODUCTION

Chemical modification of jute, and other natural and synthetic fibres, by grafting has received considerable attention in recent years¹⁻⁴. With the availability of a wide variety of vinyl and other monomers, grafting presents a powerful technique for the modification of fibre properties.

Polymerization can be achieved by the formation of radicals both from polymer and monomer, giving graft and block copolymers, and homopolymers, respectively⁵. In practice, homopolymerization can be avoided if a system is chosen for which radicals from polymer are in large excess of those from monomer. In γ -irradiated jute fibres, various side reactions lead to oxidation and oxidative degradation of cellulose molecules and produce carbonyl and carboxyl groups^{6,7}. It was suggested that alkoxy radicals were produced, due to rupture of glycoside linkages at C(1) or C(4) positions and radical formation by hydrogen abstraction from the C(1) position of the glucose unit⁸. This work aims to elucidate the effects of grafting methyl methacrylate (MMA) on the microstructure of bleached jute fibres using wide angle X-ray diffraction techniques. Recently, the crystal-defect concept of polymer structure has received much attention. Crystallinities for differently grafted jute fibres have been determined by Ruland's method, using the crystal-defect concept^{9,10}. Lattice distortions caused by grafting have also been investigated^{11,12}.

EXPERIMENTAL

Radiochemical method

Raw white jute fibres (*Corchorus capsularis*) were washed thoroughly, dewaxed and finally bleached. These were then soaked in purified MMA solution. The samples were degassed by repeated evacuation through freezing with liquid nitrogen

and melting cycles. The specimens were subjected to γ -irradiation using a ⁶⁰Co source at 0.1 Mrad h⁻¹ for 15 h in a nitrogen environment. The grafted specimens thus prepared are designated as MMA_{xo}(yo) where xo denotes the weight percentage of monomer in the solution and yo denotes the weight percentage of monomer incorporated into the bleached jute fibres (dry basis).

X-ray diffraction

X-ray diffractometer data were obtained using CuK α radiation which was monochromatized by a curved quartz crystal after transmission through the specimen. There is negligible incoherent scattering in such a set up¹³. Specimens were cut finely and rotated to reduce the preferred orientation effect. Absorption was negligible. Average intensity data were corrected for background and polarization.

RESULTS

Crystallinity

The new theory of polymer structure that is emerging may be designated as the crystal-defect concept. Ruland's^{9,10} pioneering work based on this concept defines the fractional crystallinity X_{cr} as:

$$X_{cr} = \frac{1}{R} K \quad (1)$$

where:

$$\frac{1}{R} = \int_{s_0}^{s_p} s^2 I_{cr}(s) ds \int_{s_0}^{s_p} s^2 I(s) ds \quad ;$$

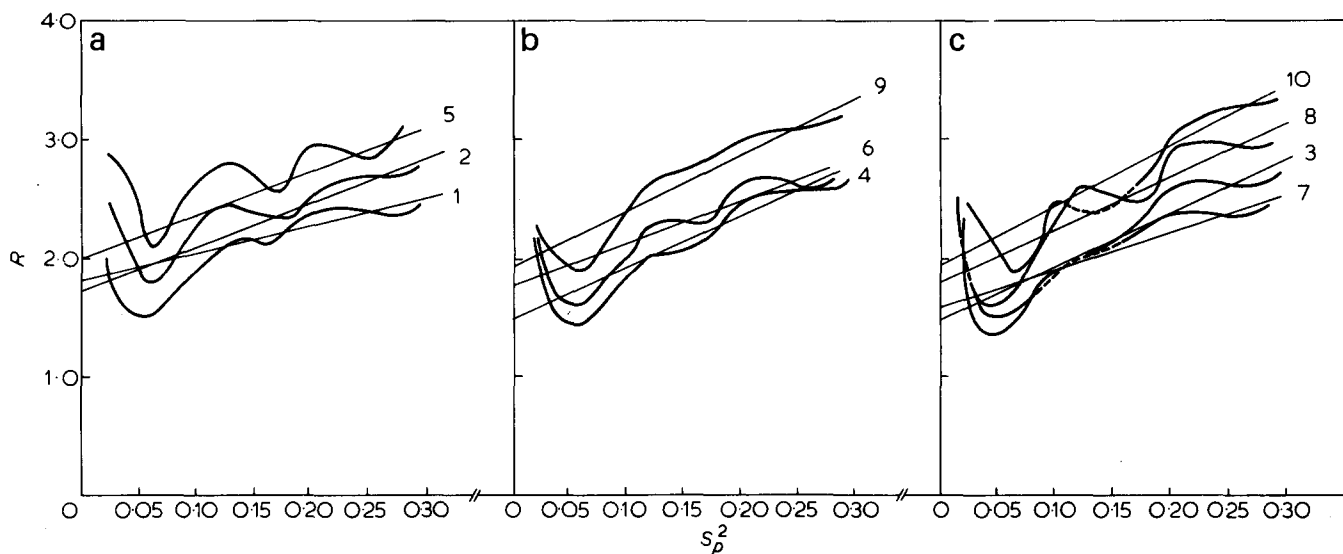


Figure 1 (a) Graphs for R versus s_p^2 for raw, bleached and $MMA_{5,0}$ (8.6) jute fibres numbered as 1, 2 and 5 respectively; (b) graphs for R versus s_p^2 for $MMA_{10,0}$ (10.6), MMA_0 (0), $MMA_{11,0}$ (12.6) and $MMA_{15,0}$ (18.5) jute fibres numbered as 7, 3, 8 and 10 respectively; (c) graphs for R versus s_p^2 for $MMA_{2,5}$ (4.7), $MMA_{7,5}$ (9.6) and $MMA_{12,5}$ (16.0) jute fibres numbered as 4, 6 and 9 respectively

Table 1 Data for percentage crystallinity

Specimen	K from graph	$\frac{\int_{s_0}^{s_p} \bar{f}^2 s^2 ds}{\int_{s_0}^{s_p} \bar{f}^2 s^2 D ds}$	$\frac{1}{R} = \frac{\int_{s_0}^{s_p} I_{cr} s^2 ds}{\int_{s_0}^{s_p} I s^2 ds}$	$X_{cr} = \frac{1}{R} K$	X_{cr} from equation (3)
MMA_0	3.40	1.60	0.39	0.62	0.62
$MMA_{2,5}$ (4.7)	3.40	1.60	0.39	0.62	0.62
$MMA_{5,0}$ (8.6)	3.50	1.60	0.31	0.50	0.50
$MMA_{7,5}$ (9.6)	3.50	1.60	0.37	0.59	0.56
$MMA_{10,0}$ (10.6)	3.90	1.66	0.40	0.66	0.62
$MMA_{11,0}$ (12.6)	4.90	1.80	0.33	0.59	0.56
$MMA_{12,5}$ (16.0)	4.90	1.80	0.30	0.54	0.52
$MMA_{15,0}$ (18.5)	5.20	1.90	0.30	0.55	0.52
Raw jute	2.70	1.40	0.42	0.59	0.56
Bleached jute	4.30	1.70	0.35	0.60	0.59

$$K = \int_{s_0}^{s_p} s^2 \bar{f}^2 ds \int_{s_0}^{s_p} s^2 \bar{f}^2 D(s) ds \quad ;$$

and:

$$D(s) = 2 \exp(-2K's^2) / (1 + \exp(-2K's^2)) \quad (2)$$

where $I_{cr}(s)$ is the part of the intensity in the crystalline peaks at the end of the reciprocal lattice vector $s = 2 \sin \theta / \lambda$ (for Bragg angle θ and wavelength λ); $I(s)$ is the total coherent scattering at the point s ; s_0 and s_p are the limits of integration; and K' is the overall distortion factor due to temperature and lattice distortions.

One of the problems in evaluation X_{cr} is the large amount of calculation involved, particularly in selecting the interval until X_{cr} is constant. Vonk¹⁴ has described a simplified method. A plot of $R(s_p)$ against s_p^2 should oscillate about a straight line defined by:

$$y = \frac{1}{X_{cr}} + (K'/2X_{cr})s_p^2 \quad (3)$$

Plots of $R(s_p)s_p^2$ from $\theta = 4^\circ$ to $\theta = 25^\circ$ for raw, bleached and grafted jute fibres are shown in Figures 1a, 1b and 1c. Various data for crystallinity in this investigation are given in Table 1.

Crystallite size

In cases where multiple order reflections are not available, the apparent particle size $L(hkl)$ perpendicular to the (hkl) planes can be measured from the broadening of the diffraction pattern by^{15,16}:

$$L(hkl) = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta} \quad (4)$$

where $\beta_{1/2}$ is the corrected breadth at half maximum intensity. In view of the uncertainty of the real nature of the

Table 2 Data for crystallite sizes $L(002)$, $L(120)$, $L(040)$ perpendicular to the planes (002), (120), (120) and (040) respectively

Jute specimens	(002) Plane				(120) Plane				(040) Plane			
	β_1 (C) (deg)	β_2 (G) (deg)	$\beta = \sqrt{\beta_1\beta_2}$ (deg)	$L(002)$ (Å)	β_1 (C) (deg)	β_2 (G) (deg)	$\beta = \sqrt{\beta_1\beta_2}$ (deg)	$L(120)$ (Å)	β_1 (C) (deg)	β_2 (G) (deg)	$\beta = \sqrt{\beta_1\beta_2}$ (deg)	$L(040)$ (Å)
Raw jute	3.14	3.45	3.30	25	0.84	1.08	0.95	85	0.51	0.75	0.61	137
Bleached jute	3.57	3.80	3.68	22	0.84	1.08	0.95	85	0.84	1.08	0.95	88
MMA ₀ (0)	1.39	1.60	1.50	54	1.05	1.29	1.17	69	1.05	1.29	1.17	71
MMA _{2.5} (4.7)	1.86	2.15	2.02	40	1.03	1.28	1.15	70	1.08	1.31	1.19	70
MMA _{5.0} (8.6)	2.36	2.68	2.50	32	0.97	1.21	1.08	75	0.23	0.46	0.325	257
MMA _{7.5} (9.6)	2.49	2.80	2.64	31	0.84	1.08	0.95	85	0.51	0.75	0.618	135
MMA _{10.0} (10.6)	2.49	2.80	2.64	31	0.41	0.64	0.51	158	0.73	0.97	0.84	99
MMA _{11.0} (12.6)	2.49	2.81	2.64	31	0.88	1.14	1.01	80	0.71	0.95	0.82	102
MMA _{12.5} (16)	2.91	3.20	3.05	27	1.27	1.51	1.38	59	0.62	0.86	0.73	114
MMA _{15.0} (18.5)		2.80	2.64	31	1.27	1.51	1.38	59	0.62	0.86	0.73	114

C ≡ Cauchy correction applied; G ≡ Gaussian correction applied; β s are breadths at half maximum intensity

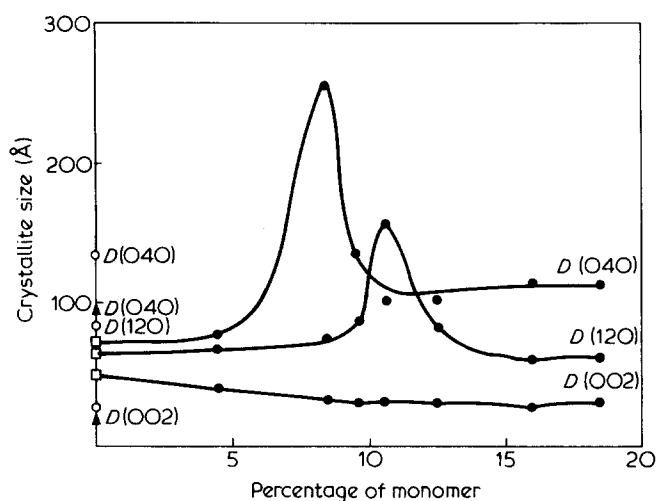


Figure 2 Graphs for crystallite size versus percentage of monomer by weight incorporated in bleached jute fibres. ○, raw jute fibre; ●, grafted jute fibre; ▲, bleached jute fibre; □, radiation subjected jute fibre

correction needed, the geometric mean of the Cauchy (C) and Gaussian (G) corrections was considered and paracrystalline lattice distortions were neglected in deriving the crystallite sizes (Table 2)¹⁷. Variations of crystallite sizes perpendicular to the planes (040), (002) and (120), designated by $L(040)$, $L(002)$ and $L(120)$, respectively, with percentage weight of monomer incorporated are shown in Figure 2.

Paracrystalline lattice distortions

Distortions of the second kind are more important in jute fibres as evident by the broadened peaks and absence of high order reflections¹¹. A similar situation was found in ramie¹⁸. A method for separating the line widths due to particle size β_p and paracrystalline lattice distortions β_d from the observed line breadth β_{pd} is given by^{12,18}:

$$\beta_{pd}^2 = \beta_p^2 + \beta_d^2 = \frac{1}{L^2(hkl)} + \frac{(\pi g_{II} m)^4}{d^2(hkl)} \quad (5)$$

where $d(hkl)$ is the repeat distance in the direction perpendicular to the (hkl) plane, and g_{II} is the relative distance fluctuation, $(\Delta d)_{II}/\bar{d}$ for several m orders of reflections.

In cases where multiple order reflections are not present, assuming negligible lattice distortions for maximum particle size, β_p can be approximated¹⁸ to $1/L(hkl)_{max}$. The factor

Table 3 Fractional crystallinity (X_{cr}), K' , K_D and $g_{II}\%$ for (040) plane for raw, bleached and radiochemically treated jute fibres

Specimens	X_{cr}	K'	K_D	$g_{II}\%$ for (040) plane
Raw jute	0.58	2.70	1.45	1.01
Bleached jute	0.60	4.30	3.05	1.28
MMA ₀ (0)	0.62	3.40	2.15	1.48
MMA _{2.5} (4.7)	0.62	3.40	2.15	1.48
MMA _{5.0} (8.6)	0.50	3.50	2.25	0
MMA _{7.5} (9.6)	0.58	3.50	2.25	1.01
MMA _{10.0} (10.6)	0.64	3.90	2.65	1.22
MMA _{11.0} (12.6)	0.58	4.90	3.65	1.21
MMA _{12.5} (16.0)	0.53	4.90	3.65	1.14
MMA _{15.0} (18.5)	0.54	5.20	3.95	1.14

g_{II} for particles perpendicular to the (040) planes are found with this approximation.

DISCUSSION

Designating the thermal component of K' as K_T and the component due to lattice imperfections as K_D one may write¹⁰:

$$K' = K_T + K_D \approx 0.5B + K_D \quad (6)$$

where B is the isotropic temperature factor. The component due to lattice distortions may be calculated² taking $B = 2.5 \text{ \AA}$ which is the minimum value from similar structure¹⁹. The values for X_{cr} (average), K' , K_D and $g_{II}\%$ for (040) planes are given in Table 3.

Increase in crystallinity for bleached jute fibre by 2% from that of the raw one is possibly due to the removal of some amorphous content by bleaching. Also bleaching should break many hydrogen bonds causing an increase in the lattice distortion factor (K_D).

Bleaching reduces particle sizes perpendicular to (040) and (120) planes; these are further reduced by γ -irradiation. However, in MMA₀(0), γ -irradiation increases particle sizes perpendicular to the (002) plane. This possibly occurs by hydrogen bonding, causing a slight increase in the crystallinity and a considerable decrease in the lattice distortion ($K_D = 2.15$).

Electron microscopy revealed elementary fibrils of 70 to 90 Å diameter in degraded fibres²⁰. The elementary fibrils are made up of crystalline core that is flattened parallel to

the (101) plane. Tendency towards growth in the (101) plane was found greater than in the direction perpendicular to it, so that distortions may be introduced easily between (101) planes. The lack of resolution between (101) and (10 $\bar{1}$) reflections suggests the presence of a considerable amount of type II distortions in the particles perpendicular to the (101) plane. The variation of g_{II} with monomer incorporated could not be studied for particles perpendicular to (101) plane and this has been evaluated for particles perpendicular to the (040) plane for comparison with $g_{II} = 1.44\%$ for ramie¹⁸. The lattice distortion factor (K_D) increases as more and more monomers are incorporated into the fibres. This is in agreement with Ruland's results for nylons having hydrogen bonding in the chain which was affected by quenching and annealing¹⁰.

A plausible explanation for the changes in crystallite size and crystallinity with the percentage weight of monomer is attempted. Bleaching and γ -irradiation reduce particle size perpendicular to the (040) plane, due to rupture of glycoside linkage at C(1) or C(4) positions⁸. The radicals thus formed possibly initiate block copolymerization at 8.6% wt monomer. It is unlikely that the monomers would enter the crystalline region without giving rise to any marked change in the diffraction pattern. Monomers dissolving crystalline regions should require more energy than their entry into the disordered regions. Thus the decrease of X_{cr} from about 0.60 to 0.50 at 8.6% wt of monomer suggests the possibility that the monomers enter into the disordered region mainly between (040) planes. It is also possible that the monomers form stronger secondary bonds with the $L(040)$ particles, thereby aligning these around their perpendicular direction and increasing $L(040)$ to their maximum value at 8.6% wt of monomer.

As more and more monomers are introduced, disordered regions between (120) planes become more favourable at 10.6% wt of monomer, and crowding in the region between (040) planes causes a decrease in $L(040)$. At 10.6% wt monomer, secondary bonds between $L(120)$ particles and monomer possibly become the strongest and thereby $L(120)$ particles assume the maximum value of 158 Å. As the width of the disordered regions between (120) planes is much smaller than that between (040) planes, the alignment of particles perpendicular to (120) planes by secondary bonds

might also initiate a large number of hydrogen bonding which increases X_{cr} to 0.64. Above 10.6% wt disordered regions between (040) and (120) planes are overcrowded, thereby decreasing X_{cr} , $L(040)$ and $L(120)$.

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