Pressure induced graft-co-polymerization of acrylonitrile onto *Saccharum cilliare* fibre and evaluation of some properties of grafted fibre

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Abstract. In the present work, graft co-polymerization of acrylonitrile (AN) onto *Saccharum cilliare* fibre has been carried out in the presence of potassium persulphate and ferrous ammonium sulphate (FAS–KPS) as redox initiator. The reactions were carried out under pressure in an autoclave. Various reaction parameters such as pressure, time, pH, concentrations of initiator and monomer were optimized to get maximum graft yield (35·59%). Grafted and ungrafted *Saccharum cilliare* fibres were then subjected to evaluation of some of their properties like swelling behaviour in different solvents, moisture absorbance under different humidity levels, water uptake and resistance towards chemicals such as hydrochloric acid and sodium hydroxide. The characterization of the graft copolymers were carried out by FTIR spectrophotometer, X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies.

Keywords. *Saccharum cilliare* fibre; acrylonitrile; graft copolymer; redox initiator; chemical resistance.

1. Introduction

Graft copolymerization presents one of the finest methods for modifying the cellulose molecules through the creation of branches of synthetic polymers, which impart certain desirable properties to the cellulose without destroying its basic properties. Several oxidant systems such as photoactive quinines, ozone hydroxyl radicals, ceric ammonium nitrate, potassium bromate etc have been used to generate free radicals on cellulose molecules to initiate graft copolymerization. On the other hand, beating, grinding and swelling of cellulose in the solvents also increase grafting rate. The polymerization of vinyl monomers may be initiated by free radicals or certain ions. Depending upon the monomer, one or the other type of initiator may be preferred. The grafting process depends upon the reactivity of the monomer used, the type of initiation, and cellulose accessibility (Habish and Mehta 1967, 1968). Most of the grafting processes involve the creation of free radicals on the cellulose molecules. Free radicals are produced by gamma radiation (Krassto and Stannet 1965; Guthrie and Han 1974) and by chemical methods (Philips *et al* 1972). If a vinyl monomer is polymerized onto cellulose in the presence of free radical, a hydrogen atom may be abstracted from the cellulose by a growing chain radical or by a free radical formed by the polymerization catalyst (initiator), which leaves free electron on the cellulose

chain that is capable of initiating grafting. As cellulose is a very poor transfer agent (Mino and Kaizerman 1958), very little copolymer results from the abstraction of hydrogen atoms by a growing chain radical. The only way by which a chain transfer reaction between a growing chain radical and cellulose can be made to succeed is by first introducing into the cellulose molecule certain atoms or groups, that are readily abstracted by radicals. Therefore, in most cases a radical produced by the initiator is responsible for the formation of the graft copolymer (Kaizerman *et al* 1962; Schwob *et al* 1962). It has been observed that incorporation of nitrogen, phosphorous or halogens containing organic and inorganic compounds provide flame retardation to polymeric backbone. Various workers have carried out studies on the thermal degradation behaviour of cellulose and other properties of graft copolymers (Hurdue and Scheider 1970; Verma and Narsimha 1972; Yang and Kokot 1996; Chauhan *et al* 2000). Most of the graft co-polymerization studies have been made by varying the temperature conditions. In the present communication, we report for the first time the graft co-polymerization of *S. cilliare* fibre under pressure. The advantage of pressure induced grafting has been that unlike grafting in air very less changes take place in the texture of the fibre. Literature survey has revealed that there has been no work on graft co-polymerization of this precious wealth of the nature especially under pressure. The graft copolymers after their characterization have been further subjected to evaluation of their physico-chemical properties.

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2. Experimental

2.1 *Purification of materials*

Natural fibre (*Saccharum cilliare*) was treated with 5% sodium bisulphate under pressure for 3–4 h to remove lignin contents. Then the fibre was dried in a hot air oven at 50°C. Purification of acrylonitrile (AN) was done by initially washing with 5% sodium hydroxide and then drying over anhydrous Na_2SO_4 followed by distillation (Kaith *et al* 2003). Ferrous ammonium sulphate (FAS) was recrystallized from hot water and potassium persulphate (KPS) was used as received. Weighing of samples was done on Libror AEG-220 (Shimadzu) electronic balance.

2.2 *Graft co-polymerization*

The natural fibre (*S. cilliare)* (0·5 g) was masticated to create active sites onto the polymeric backbone and was then immersed in a known amount of distilled water for 24 h. A known amount of initiator (FAS–KPS) and monomer (AN) were then added to the flask containing fibre at suitable pH and the reaction was carried out for 120 min in an autoclave. Optimum conditions of pressure, solvent, time, initiator (FAS–KPS ratio), pH and monomer concentration were worked out so as to get maximum graft yield (table 1). The homo-polymer formed during graft co-polymerization was removed by extraction with dimethyl formamide (DMF). The graft copolymer was then dried at 50°C to a constant weight. The percentage grafting (P_g) and percentage efficiency (P_e) were calculated as per the procedure reported earlier (Kaith *et al* 2003).

2.3 *Swelling, moisture absorbance, chemical resistance and water uptake studies*

Swelling of grafted and ungrafted fibres was studied in different solvents such as dimethyl formamide (DMF),

Table 1. Optimization of various reaction parameters for maximum graft co-polymerization of acrylonitrile onto *S. cilliare* fibre.

Sl no.	Solvent (ml)	Monomer (mol/L × 10⁻³)	FAS–KPS ratio	Time (min)	Pressure (kg/cm²)	pH	Grafting (%)	Efficiency (%)
1.	100	6·78	1 : 1	120	0·5	4	08·90	2·22
2.	125	6·78	1 : 1	120	0·5	4	11·60	2·90
3.	150	6·78	1 : 1	120	0·5	4	13·70	3·42
4.	175	6·78	1 : 1	120	0·5	4	12·50	3·12
5.	200	6·78	1 : 1	120	0·5	4	10·00	2·50
6.	150	6·78	1 : 1	120	1·0	4	20·00	5·00
7.	150	6·78	1 : 1	120	1·5	4	21·00	5·25
8.	150	6·78	1 : 1	120	2·0	4	18·00	4·50
9.	150	6·78	1 : 1	120	2·5	4	04·30	1·07
10.	150	6·78	1 : 1	30	1·5	4	–	–
11.	150	6·78	1 : 1	60	1·5	4	01·70	0·42
12.	150	6·78	1 : 1	90	1·5	4	11·60	2·90
13.	150	6·78	1 : 1	150	1·5	4	08·20	2·04
14.	150	6·78	0·125 : 1	120	1·5	4	15·00	3·75
15.	150	6·78	0·250 : 1	120	1·5	4	22·00	5·50
16.	150	6·78	0·5 : 1	120	1·0	4	21·30	5·32
17.	150	6·78	1·250 : 1	120	1·5	4	04·80	1·20
18.	150	6·78	1·50 : 1	120	1·5	4	02·00	0·50
19.	150	6·78	0·250 : 1	120	1·5	2	13·50	3·37
20.	150	6·78	0·250 : 1	120	1·5	6	06·50	1·62
21.	150	6·78	0·250 : 1	120	1·5	8	Nil	Nil
22.	150	6·78	0·250 : 1	120	1·5	10	Nil	Nil
23.	150	4·52	0·250 : 1	120	1·5	4	14·20	5·32
24.	150	6·78	0·250 : 1	120	1·5	4	22·00	5·50
25.	150	9·03	0·250 : 1	120	1·5	4	25·40	4·76
26.	150	11·30	0·250 : 1	120	1·5	4	28·47	4·27
27.	150	13·55	0·250 : 1	120	1·5	4	35·59	4·45
28.	150	15·83	0·250 : 1	120	1·5	4	17·89	1·92

Optimized conditions: solvent, 150 ml; time, 120 min; pressure, 1·5 kg/cm²; pH, 4·0; FAS : KPS, 0·250 : 1 and monomer, $13·55 × 10^{-3}$ mol/L.

Table 2. X-ray diffraction analysis of raw fibre, fibre free from lignin and graft co-polymers.

2θ		14·860		23·195		
Sl. no.	Sample code (P_g)	$d\alpha'_1$ [A]^0	I [%]	$d\alpha'_1$ [A]^0	I [%]	D_{cr}
1.	F_{raw}	5·9575	36·8	3·8374	98·5	67·5
2.	F_{lig}	5·9868	16·2	3·8770	100·0	64·8
3.	Cotton	5·9568	37·6	3·8317	100·0	67·6
4.	Sc-19 (20%)	5·1426	34·3	3·9562	100·0	59·98
5.	Sc-20 (22%)	5·1439	30·2	3·8980	100·0	57·78
6.	Sc-21 (21%)	5·2637	54·7	3·8997	100·0	58·24
7.	Sc-22 (13·5%)	5·2761	100	3·9115	100·0	63·25
8.	Sc-23 (13·7%)	5·9688	35·3	3·887	100·0	63·12
9.	Sc-24 (35·59%)	5·2575	51·8	3·9641	100·0	56·83

d, d spacing; I, relative intensity; D_{cr}, degree of crystallinity.

water, methanol and isobutyl alcohol as per the method reported earlier (Kaith *et al* 2003). Moisture absorbance study at various humidity levels was carried out as per the method reported earlier (Singha *et al* 2002). Water uptake capacity of grafted and ungrafted fibres was studied by making small wicks of diameter 5 mm, which were then dipped in the beaker containing 25 ml of water. Rise of water through capillary action in each fibre wick was noted at different time intervals and water uptake (P_w) was calculated as follows

$$P_w = \frac{T_f - D_t}{T_f} \times 100,$$

where T_f is total fibre length and D_t the distance travelled by water in the fibre wicks. Chemical resistance of grafted and ungrafted fibres was studied by inserting definite amounts of ungrafted and grafted fibres in 100 ml of 1N HCl and 1N NaOH. The loss in weights of the grafted and ungrafted fibres was then studied at different time intervals and percentage of chemical resistance (PC_r) was calculated as follows

$$PC_r = \frac{T_i - T_f}{T_i} \times 100,$$

where T_i is initial weight and T_f the final weight of the sample.

The IR spectra of raw fibre, fibre without lignin and grafted fibres were recorded on Perkin–Elmer spectrometer. Scanning electron micrographs of raw fibre, lignin free fibre and its graft copolymer were recorded on Leo 435 VP. X-ray diffraction analysis of raw fibre, lignin free fibre and its graft copolymer was carried out on PW 1710 BASED machine. On comparing the XRD results, it has been observed that graft co-polymerization decreases the degree of crystallinity (table 2).

2.4 *Evidence of grafting*

The IR spectra of raw *Saccharum cilliare* fibre showed a broad peak at 3370 cm^{-1} due to bonded OH groups and at 2922·4, 1438 and 1043 cm^{-1} due to –CH$_2$, C–C and C–O stretching, respectively. Whereas in the case of grafted fibre one additional peak at 2245·4 cm^{-1} was obtained due to the presence of C≡N group of acrylonitrile.

2.5 *Scanning electron micrographs (SEM) of raw fibre, lignin free fibre and its graft copolymers*

On comparing the scanning electron micrographs of raw fibre, lignin free fibre and its graft copolymers (figures 1–4), it has been found that upon graft co-polymerization, a considerable amount of monomer gets deposited onto the fibre backbone which causes morphological changes in the fibre. The deposition of monomer has been found to be more when grafting has been done in air as compared to the grafting carried out under pressure. Further it has been observed that grafting under pressure gives more smoothness to the surface as compared to grafting in air.

3. Results and discussion

It has been observed that polymeric materials containing cellulose, C$_2$, C$_3$ and C$_6$ –OH groups and C–H sites are the active centres for grafting of polymeric chains onto polymeric backbone. Potassium persulphate takes part in the redox reaction with Fe^{2+}, as given below

$$Fe^{2+} + {}^-O_3S-O-O-SO_3^- \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^-*.$$
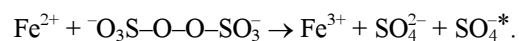
Interaction of SO$_4^-$* with H$_2$O generates OH free radicals and these free radicals are responsible for carrying out graft co-polymerization onto *S. cilliare* fibre.

3.1 *Optimization of different reaction parameters for grafting of acrylonitrile onto S. cilliare fibre*

The optimization of various reaction parameters such as amount of the solvent, reaction time, pressure, pH, ratio of the initiator (FAS–KPS ratio) and concentration of the monomer were carried out for graft co-polymerization of

acrylonitrile onto *S. cilliare* fibre. The optimum conditions for maximum graft yield (35·59%) are given in table 1.

3.2 *Effect of monomer concentration*

Grafting increases with increase in monomer concentration and after reaching the maximum P_g of 35·59%, further increase in monomer concentration results in decrease of graft yield (figure 5). This may be due to the formation of more homopolymers as compared to graft copolymer at higher monomer concentration. Moreover, due to homopolymerization, viscosity of the reaction medium increases which creates hindrance in the movement of the

free radicals towards active sites, thereby resulting in less graft yield.

3.3 *Effect of solvent*

With increase in amount of solvent (figure 6), the P_g has been found to increase. The maximum grafting took place when 150 ml solvent was used. Further increase in solvent results in decreased graft yield. This probably occurs due to the dilution of reaction medium which lowers the concentration of monomer radical per unit volume and hence less grafting takes place.
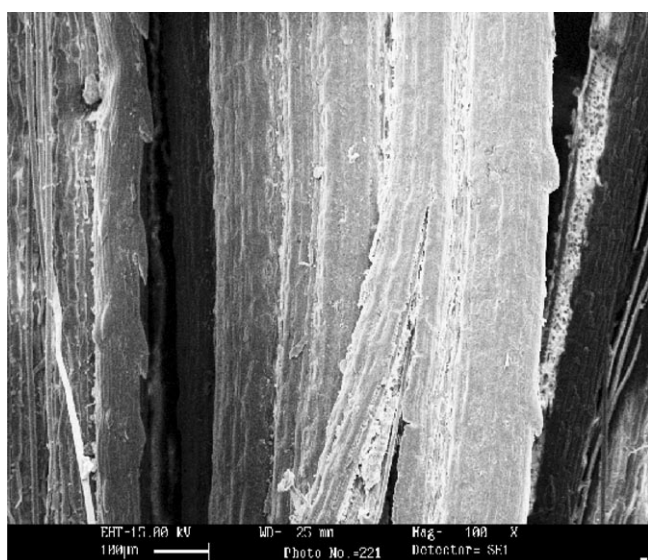
Figure 1. SEM of raw fibre.
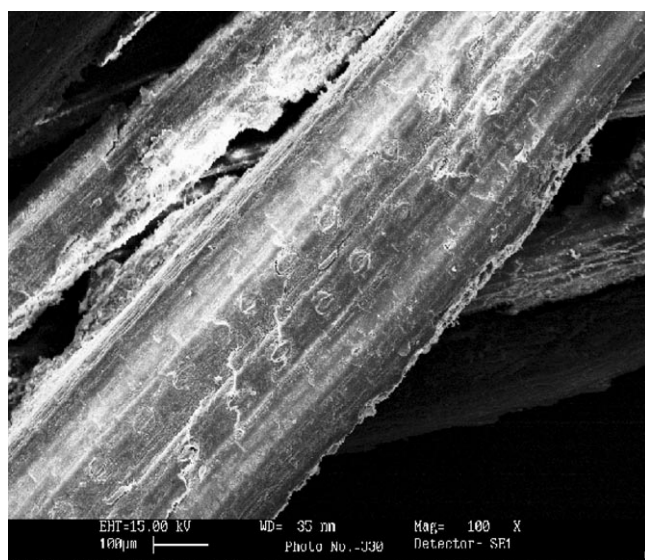
Figure 3. SEM of grafted fibre (under pressure).
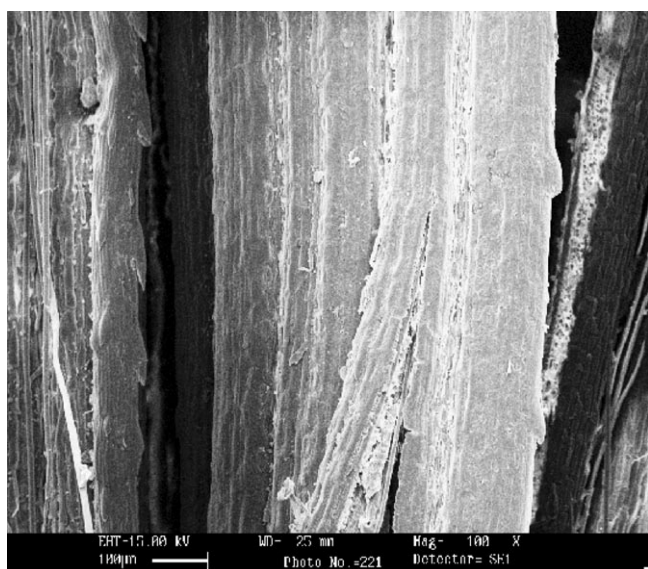
Figure 2. SEM of lignin free fibre.
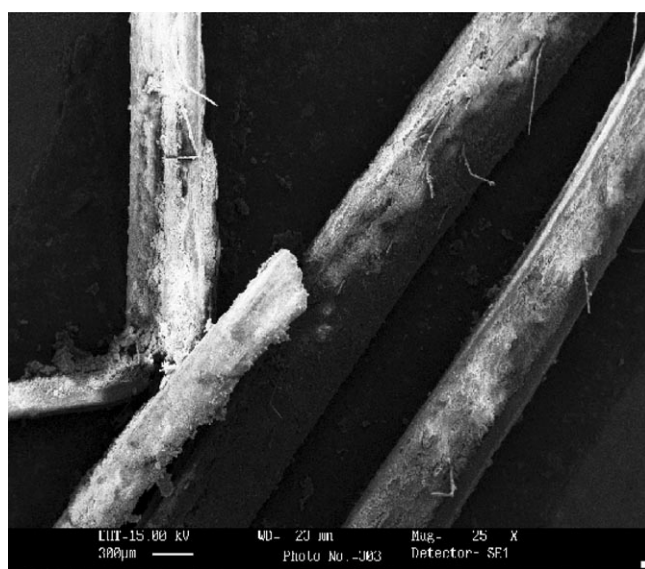
Figure 4. SEM of grafted fibre (in air).

3.4 *Effect of time*

The optimum reaction time has been found to be at 120 min (figure 7). With further increase in time, a decline in P_g has been observed. This probably happens due to the occurrence of various hydrogen abstraction reactions along with some other side chain reactions as well as excessive homo-polymerization.

3.5 *Effect of pressure*

Pressure has been found to affect the grafting (figure 8). The rate of grafting increases till a pressure of 1·5 kg/cm^2

is not attained. Beyond this pressure the grafting has been found to decrease due to the predominance of homo-polymer over graft copolymer at elevated pressure.

3.6 *Effect of initiator*

The molar ratio of initiator (FAS–KPS) plays an important role in obtaining higher graft yield (figure 9). The optimum molar ratio for the maximum graft yield has been found to be 0·250 : 1. It has been observed that with further increase in molar ratio, the P_g was found to decrease. This is attributed to generation of more Fe^{3+} ions at higher molar ratio, which results in the termination of
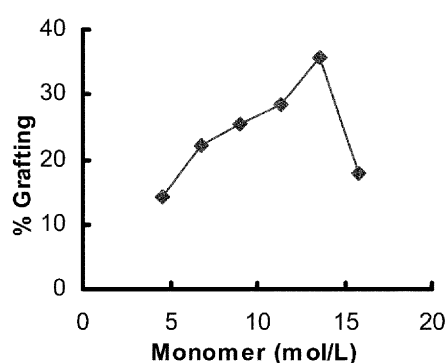
Figure 5. Variation of grafting with monomer.
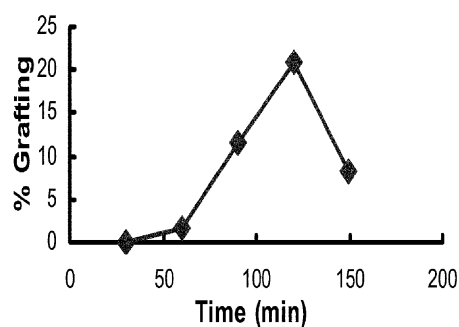

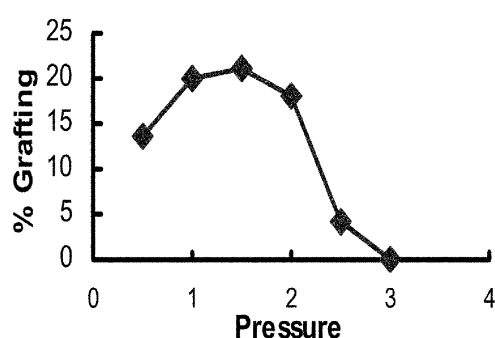**Figure 8.** Variation of grafting with pressure.

Figure 6. Variation of grafting with solvent.

Figure 9. Variation of grafting with FAS–KPS ratio.

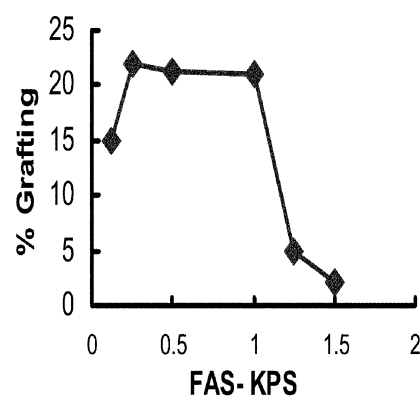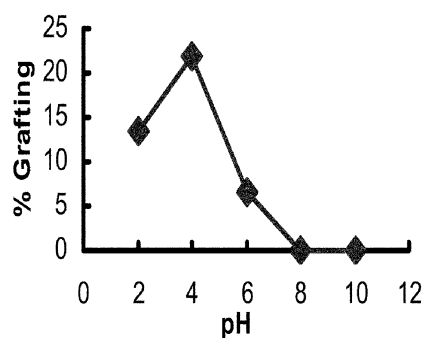**Figure 7.** Variation of grafting with time.

Figure 10. Variation of grafting with pH.

growing chains. Further, it has been observed that if the FAS–KPS molar ratio is lower than the critical value, then there is decrease in P_g because of lesser generation of OH free radicals.

3.7 *Effect of pH*

With the increase in pH of reaction medium, grafting process increases up to a pH value of 4, but beyond pH 4

Figure 11. Effect of grafting on swelling behaviour.

Figure 12. Effect of grafting on moisture absorbance behaviour.

Figure 13. Effect of grafting on chemical resistance against 1 N NaOH.

there is decrease in graft yield (figure 10). This may be due to the fact that at higher pH, the *OH are generated in basic medium which combine with the back-bone free radicals to terminate the chain reaction.

3.8 *Swelling studies*

Grafted and ungrafted fibre show different swelling behaviours in different solvents (figure 11). The swelling behaviour of ungrafted fibre in different solvents follows the trend: $H_2O > CH_3OH > iso\text{-}BuOH > DMF$. Whereas in grafted fibre, it varies as a function of P_g and follows the trend: $DMF > CH_3OH > H_2O > iso\text{-}BuOH$. This trend in ungrafted fibres may be due to greater affinity of water for OH groups present in the raw *S. cilliare* fibre which results in more penetration of water into the polymeric backbone as compared to other solvents. In case of grafted fibres containing acrylonitrile monomer chains, water and alcohols do not interact with the same extent as with raw fibre. This may be due to blockage of active sites on main polymeric backbone by poly acrylonitrile chains which causes change in the sorption behaviour of different solvents. Further polyacrylonitrile chains on grafted fibre get more solvolysed by dipolar aprotic solvent (DMF) as compared to water or alcohol, hence resulting in more swelling in DMF as compared to other solvents.

3.9 *Moisture absorbance studies*

It has been found that moisture absorbance (M_{abs}) decreases with the increase in P_g (figure 12). The raw fibre shows more M_{abs} than the grafted fibres. This behaviour of grafted fibres can be explained on the basis that with the increase in P_g, the active sites responsible for maximum moisture absorbance on raw fibre get replaced by the grafted polyacrylonitrile chains having lesser affinity towards water as compared to the raw fibre.
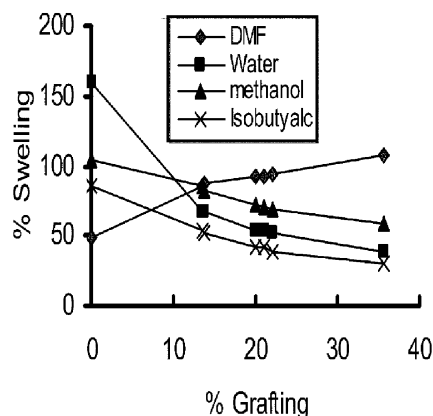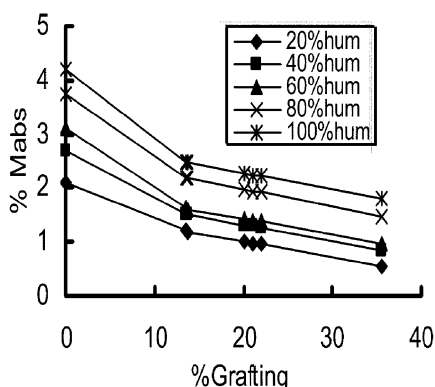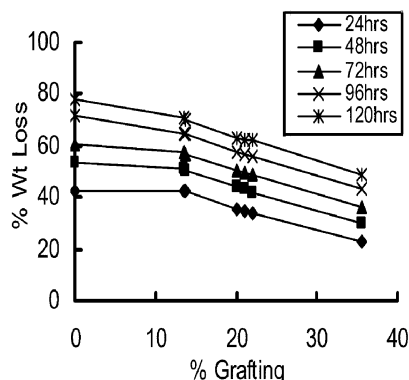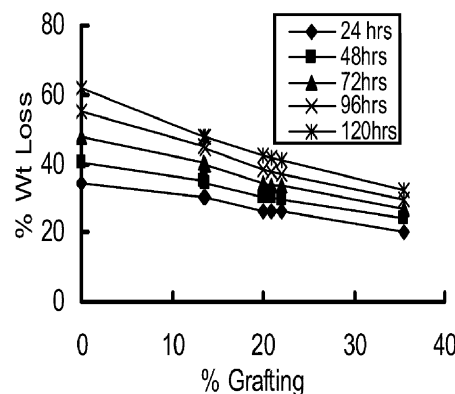

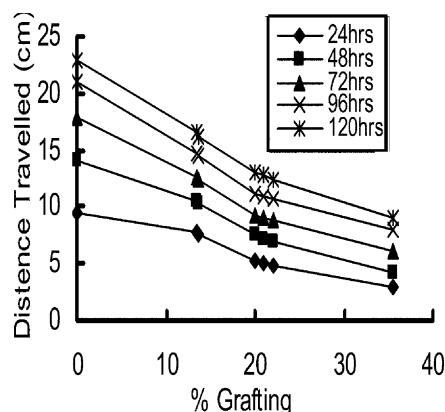**Figure 14.** Effect of grafting on chemical resistance against 1 N HCl.

Figure 15. Effect of grafting on water uptake behaviour.

3.10 *Chemical resistance studies*

Further it has been observed that resistance of the fibre towards chemicals like 1N sodium hydroxide and 1N hydrochloric acid increases with the increase in grafting (figures 13–14). This probably occurred due to blockage of active sites vulnerable to the chemical attack on polymeric backbone by grafted polyacrylonitrile chains.

3.11 *Water uptake studies*

Water uptake capacity of graft copolymers has been found to decrease with increase in grafting (figure 15). The reasons for this behaviour could be the same as explained above.

3.12 *X-ray diffraction studies*

X-ray diffraction studies on grafted and ungrafted fibres have been shown in table 2. Since cellulosic materials generally contain both crystalline and amorphous regions so it is evident that X-ray diffraction patterns of such materials will show both the region in the form of sharp peaks and diffused patterns (Singha *et al* 2006). Degree of crystallinity was calculated by Segal's formula (Segal *et al* 1959). As evident from the tables the degree of crystallinity decreases with an increase in grafting. This

change in diffraction pattern occurs due to the creation of disorder in the crystalline pattern of the main polymeric backbone by the grafted units of the polyacrylonitrile chains.

4. Conclusions

It has been found that upon graft co-polymerization of acrylonitrile onto natural fibre *Saccharum cilliare,* properties like moisture absorbance, chemical resistance and water uptake varies directly with the degree of grafting. It has been observed that through grafting it is possible to increase water resistance, chemical resistance and swelling behaviour of the raw fibre. When grafting is carried out under pressure, then a decrease in grafting has been observed as compared to grafting in air.

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