Graft Copolymerization with a New Class of Acidic Peroxo Salt IV. Grafting of Acrylamide onto Jute Fiber Using Potassium Monopersulphate: Catalyzed by Fe(II)

Rajani K. SAMAL,* Himansu S. SAMANTARAY, and Rabi N. SAMAL

Macromolecular Research Laboratory, Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India

ABSTRACT: Graft copolymerization of acrylamide (AM) onto jute fibers has been studied in aqueous solution using a new class of acidic peroxosalt "potassium monopersulphate" as the initiator, under the catalytic influence of Fe(II) in a nitrogen atmosphere. It was observed that the graft yield was influenced by the reaction time, temperature, and concentration of the monomer, initiator, and base polymer. The grafting reaction has also been studied in the presence of a number of salts and organic solvents. The maximum graft yield (75.3%) was observed at 25°C at the concentrations of monomer (1.2 M), initiator (12.9×10^{-3} M), and catalyst (1.0×10^{-3} M) for a reaction time of 4 hours. From the experimental results a suitable mechanism for graft initiation and termination has been suggested. The graft copolymers have been characterized and their improved properties have been tested.

KEY WORDS Tailoring / Monomer : Polymer-Ratio Effect / $KHSO_5$ Effect / Catalyst Effect / Temperature Effect / Solvent Effect /

Graft copolymerization of vinyl monomers onto cellulose, lignocellulose and their derivatives has been the subject of extensive studies since 1946.[1] Modification of polymers *via* graft copolymerization has been the subject of much interest and has paramount contribution towards their improved industrial and biomedical applications. Chemical modifications of preformed polymers both natural and synthetic can provide a potential route for significantly altering the physical and mechanical properties. The grafting process possesses great potential for tailoring material properties to a specific ends. Jute, a lignocellulosic polymer is the most abundant renewable agricultural raw material and is transformed into multifarious products affecting every phase of our daily life due to its wide applications for making the coarse woven fabrics such as gunny sacks and bagging where cheapness is the prime factor. Recently, efforts are being made in India and Bangladesh for commercial utilization of jute fibres[2] to meet total fabric requirements of the country as well as to minimize the import of synthetic fibres. Although jute fibres possess high dimensional stability, certain unfavourable textile properties such as high stiffness, very low elasticity, susceptibility towards sunlight etc. have tremendously limited their use.[3] With a view to minimizing their undesirableness and enhancing their effectiveness for intensified textile use, graft copolymerization onto jute fibres has recently been attempted using chemical methods of initiation with higher valency transition metal ions such as V(V), Mn(VII), and Ce(IV).[4-6] However, no reports seem to be available on the use of potassium monopersulphate as the initiator in

---

* To whom all correspondence should be addressed.

R. K. SAMAL, H. S. SAMANTARAY, and R. N. SAMAL

affecting graft copolymerization onto jute fibres. Potassium monopersulphate is an acidic peroxo salt of recent origin. Kenedy et al.[7] recognized the oxidizing ability of $KHSO_5$ in the oxidation of a multitude of organic substrates for preparative purpose. Samal et al. have recently studied the chemistry of $KHSO_5$ in connection with its mode of decomposition in solution under the catalytic influence of metal salts, complexing agents, and metal salt/complexing agent couples and evaluated the efficiency of ideal components in causing a high rate of initiation in vinyl polymerization and graft copolymerization.[8-19] The present report is a continuation of their work on graft copolymerization onto natural fibers using $KHSO_5$ as the initiator.

EXPERIMENTAL

Materials

Jute fibers (Corchorus Capsularis) were purified by treating them with hot ethanol and benzene in a 1:2 (v/v) mixture in a Soxhlet apparatus. They were then washed well with alcohol and air dried. Acrylamide (AM) (E. Merck) was purified by recrystallization from acetone and dried at room temperature under vacuum. A 4M stock solution of AM in triple distilled water was used.

Potassium monopersulphate ($KHSO_5$) was a gift sample from Du Pont Co., U.S.A. and used without further purification. A stock solution of 12.9×10^{-2} M of the initiator was used for all experiments and the strength of the stock solution was determined by iodometry. All other reagents were of B.D.H. (AR) grade and used after purification by standard methods.

Graft copolymerization was carried out in a specially designed reaction vessel with an outlet and inlet system for deaeration. Defatted jute fibers (0.2—1 g) were immersed in a mixture containing water, required amounts of acrylamide (AM) and the initiator. The reaction vessels were kept in a freezing mixture and

deaerated by (passing) oxygen free nitrogen for one hour, and sealed air tight. The vessels were then kept in a constant temperature bath and the grafting reaction was carried out for the desired time. The homopolymers were extracted by repeated washings with warm water followed by warm methanol.

From the weight of the graft copolymer, homopolymer and base polymer, the percent grafting and grafting efficiency were calculated using the following formula,

$$\text{Percent grafting} = \frac{X - Y}{Y} \times 100$$

$$\text{Grafting efficiency } (\%) = \frac{X - Y}{X - Y + Z} \times 100$$

where,

X = weight of the graft copolymer,
Y = weight of the original base polymer,

and

Z = weight of the homopolymer.

RESULTS AND DISCUSSION

Acrylamide was graft copolymerized with defatted jute fibers using potassium monopersulphate as the initiator either alone or under the catalytic influence of a number of salts. The results of percent grafting for the individual initiating systems are presented in Table I.

The results of Table I indicate that in the presence of salts such as $MnSO_4$, $CoSO_4$, $ZnCl_2$, KBr, and Na_2SO_4, the reaction mixture retards the percent graft-on, whereas in the presence of $MgSO_4$, $CuSO_4$, $FeSO_4$, $FeCl_3$, $Cu(OAc)_2$, and $Cr_2(SO_4)_3$ the reaction mixture accelerates the percent graft-on in the order, $FeSO_4 > FeCl_3 > Cu(OAc)_2 > MgSO_4 > Cr_2(SO_4)_3 > CuSO_4$. The accelerating effects may be attributed to increase in the concentration of free radicals and highly reactive unstable metal ions which increase the number of active free radical sites on the backbone of jute fibers.

Table I. Results of graft percent in the $KHSO_5$ initiated graft copolymerization of acrylamide onto jute fibres in the presence of various metal and non-metal salts

(jute, 0.2 g; [AM] = 1.0 M; [$KHSO_5$] = 12.9 × 10^{-3} M; [Salts] = 25 × 10^{-5} M; temp, 40°C; time, 2 h).

Salts	Percent grafting
—[a]	11.2
$MnSO_4$	7.3
$MgSO_4$	16.7
$CuSO_4$	14.0
$CoSO_4$	1.6
$ZnCl_2$	9.6
KBr	4.3
$FeSO_4$	47.7
$FeCl_3$	36.7
$Cu(OAC)_2$	17.7
Na_2SO_4	10.8
$Cr_2(SO_4)_3$	14.5

[a] In the absence of salts.

The retarding effects in rest of the metal salts may be attributed to (i) the generation of primary free radicals at a greater rate from the facile redox reaction between the initiator and metal salts, which in turn attack the reacting monomer leading to hompolymerization and (ii) premature termination of the growing grafted chains by higher valency unstable metal ions such as Mn(III) from Mn(II) and Co(III) from Co(II) produced during the redox process.

The promising activity of Fe(II) under the existing experimental conditions in enhancing the percent grafting may be attributed to the homologous Fe(II)–$KHSO_5$ adduct formation that disproportionates in an unimolecular fashion at the fiber surface producing jute radicals at a faster-rate.

Effects of Monomer/Polymer Ratios

The effects of variation of the monomer/polymer ratio on the grafting of acrylamide onto jute fiber were studied in a series of monomer concentration from 0.1 to 1.2 M at six initiator concentrations between 3.225 × 10^{-3}—25.8 × 10^{-3} M and at a fixed weight
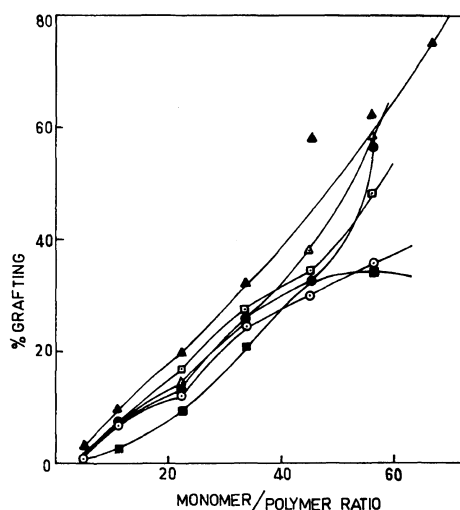
Figure 1(a). Variation of graft percent at fixed times: effects of monomer/polymer ratio at various initiator ($KHSO_5$) concentrations.
Jute, 0.2 g; [$FeSO_4$] = 10 × 10^{-4} M; temp, 25°C; time, 4 h.
Plots: (○) [$KHSO_5$] = 3.225 × 10^{-3} M;
(●) [$KHSO_5$] = 6.45 × 10^{-3} M;
(△) [$KHSO_5$] = 9.675 × 10^{-3} M;
(▲) [$KHSO_5$] = 12.9 × 10^{-3} M;
(⊡) [$KHSO_5$] = 19.35 × 10^{-3} M;
(■) [$KHSO_5$] = 25.8 × 10^{-3} M.
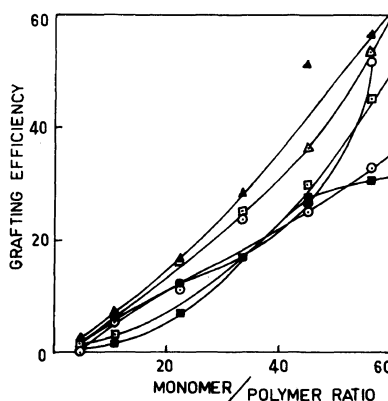
Figure 1(b). Variation of grafting efficiency at fixed times: effects of monomer/polymer ratio at various initiator ($KHSO_5$) concentrations.
Jute, 0.2 g; [$FeSO_4$] = 10 × 10^{-4} M; temp, 25°C; time, 4 h.
Plots: (○) [$KHSO_5$] = 3.225 × 10^{-3} M;
(●) [$KHSO_5$] = 6.45 × 10^{-3} M;
(△) [$KHSO_5$] = 9.675 × 10^{-3} M;
(▲) [$KHSO_5$] = 12.9 × 10^{-3} M;
(⊡) [$KHSO_5$] = 19.35 × 10^{-3} M;
(■) [$KHSO_5$] = 25.8 × 10^{-3} M.

of jute fiber (0.2 grams). The percent grafting was found to increase steadily with monomer concentration (Figure 1a). The grafting efficiency was also been found to increase in a similar manner (Figure 1b). The enhancement of percent graft-on and grafting efficiency with increase of monomer/polymer ratio may be attributed to increase of the monomer concentration at the reaction site and complexation of jute with AM enhancing the reactivity of (AM) owing to the formation of a donor-acceptor complex in which the uncomplexed AM, though initially an electron acceptor, behaves as a donor relative to the complexed AM which is converted to a strong acceptor. Similar explanations for enhancement in grafting have been suggested by Gaylord[20] and Hebeish et al.[21]

Effects of Initiator Concentration

The effects of initiator concentration were studied at various initiator concentrations $(3.225 \times 10^{-3}$—25.8×10^{-3} M) with a series of monomer/polymer ratio varying from 5.61 to 56.1 and are shown in Figure 2. It was observed that the percent grafting increases as the initiator concentration increases to 12.9 $\times 10^{-3}$ M beyond which it decreases. The enhancement of percent grafting may be attributed to increase in the number of active sites on the backbone of jute fibers, arising from the attack of the diffused $KHSO_5$ molecule into the polymer matrix. The retarding effects of the graft-on percent at higher concentration $(>12.9 \times 10^{-3}$ M) of $KHSO_5$ may be ascribed to (i) the predominancy of homopolymerization over grafting, (ii) the termination of the growing grafted chain by primary free-radicals resulting from the decomposition of the excess of the initiator and (iii) production of excess Fe(III) ions which interact with the growing grafted chains leading to the cease of their growth.

Effects of Catalyst Concentration

Increase in the concentration of $FeSO_4$ from
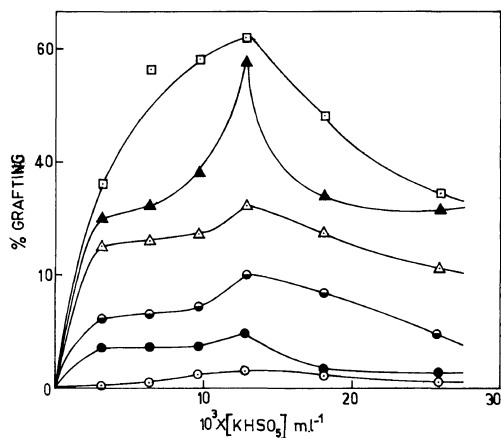
Fgure 2. Variation of graft percent at fixed times: effects of $[KHSO_5]$ at various monomer (m)/polymer (p) ratios. Jute, 0.2 g; $[FeSO_4] = 10 \times 10^{-4}$ M; temp, 25°C; time, 4 h. Plots (○) m/p = 5.61; (●) m/p = 11.22; (◓) m/p = 22.44; (△) m/p = 33.66; (▲) m/p = 44.88; (□) m/p = 56.1.
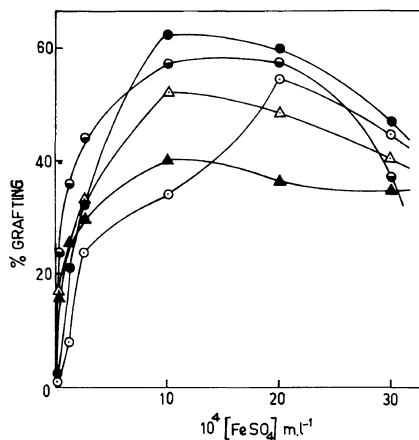
Figure 3. Variation of graft percent at fixed times: effects of $[FeSO_4]$ at several temperatures.
Jute, 0.2 g; $[AM] = 1.0$ M; $[KHSO_5] = 12.9 \times 10^{-3}$ M; time, 4 h.
Plots: (○) $T = 20°C$; (●) $T = 25°C$; (◓) $T = 30°C$; (△) $T = 35°C$; (▲) $T = 40°C$.

0.25×10^{-4} M to 20.0×10^{-4} M increased the percent grafting after which the rate decreased (Figure 3). The increase in the percent grafting with increase in Fe(II) concentration may be attributed to the increase in concentration of the Fe(II)–$KHSO_5$ transient adduct which undergoes forced decomposition at the film

surface resulting in production of jute radicals at a faster rate.

The decrease in percent graft beyond 20.0×10^{-4} M of Fe(II), may be attributed to a detrimental factor arising from excess Fe(III) ions produced on oxidation of Fe(II). The premature termination of growing grafted chains has been observed by Rogovin et al.[22] and Mishra et al.[23] in graft copolymerization initiated with an H_2O_2/Fe(II) system beyond certain concentrations of Fe(II).

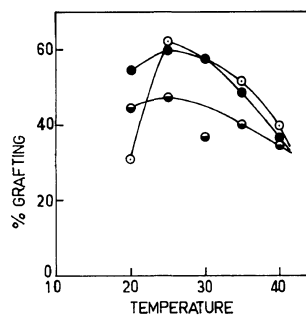### Effects of Temperature

Graft copolymerization of acrylamide onto jute fibers has been studied at temperatures ranging from 20 to 50°C as shown in Figure 4. The graft percent increased to 25°C at fixed concentrations of monomer (1.0 M) and KH-SO₅ $(12.9 \times 10^{-3}$—30.0×10^{-4} M) beyond which it decreased. The increase in percent grafting up to 25°C may be ascribed to (i) increase in the rate of production of active free-radicals which increase the number of grafting sites at a higher rate. The rate of graft initiation by jute radicals is thereby increased, (ii) increase in temperature increases the rate of diffusion of acrylamide into the fiber matrix where grafting is also initiated by (on) complexed monomers. Similar phenomena were observed by Samal et al.[24,25] in the grafting of acrylamide onto nylon 6 and silk fibres.

The decrease in percent grafting beyond 25°C may be attributed to (i) the increase in activation energy i.e., increase in the rate of homopolymerization and (ii) premature termination of growing grafted chains by excess Fe(III) ions produced on oxidation of Fe(II) ions. Premature termination by higher valency transition metal ions has been observed by Bamford et al.[26] and Samal et al.[27]
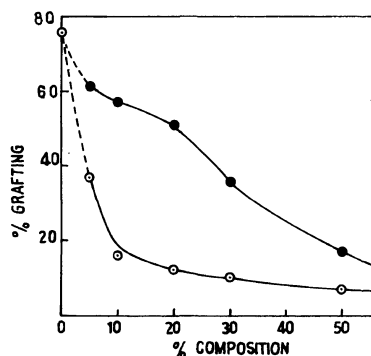
Effects of Solvent Composition

The effects of water soluble organic solvents such as acetic acid and methanol of various composition (5:95 to 50:50) on the grafting reaction were studied at 25°C at fixed concen-

Figure 4. Variation of graft percent at fixed times: effects of temperature at various [FeSO₄].
Jute, 0.2 g; [AM] = 1.0 M; [KHSO₅] = 12.9×10^{-3} M; time, 4 h.
Plots: (○) [FeSO₄] = 10.0×10^{-4} M; (●) [FeSO₄] = 20.0×10^{-4} M; (◕) [FeSO₄] = 30×10^{-4} M.

Figure 5. Variation of graft percent at fixed times: effects of solvent composition.
Jute, 0.2 g; [AM] = 1.2 M; [KHSO₅] = 12.9×10^{-3} M; [FeSO₄] = 1.0×10^{-3} M; temp, 25°C; time, 4 h.
Plots: (○) CH₃COOH; (●) CH₃OH.

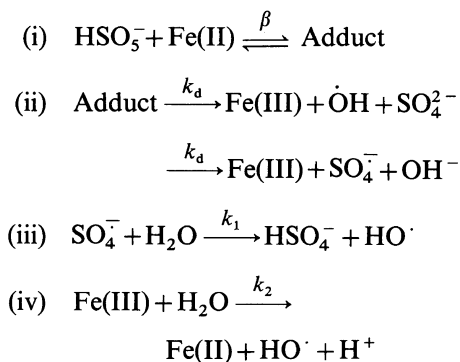trations of AM (1.2 M), KHSO₅ $(12.9 \times 10^{-3}$ M), FeSO₄ $(1.0 \times 10^{-3}$ M), and jute (0.2 g) (Figure 5). All proportions of solvent composition the percent grafting was significantly affected by both organic solvents. The graft-on percent was studied from control values 75.3% to 7.15% and 17.05% in acetic acid and methanol, respectively. This rapid decrease of percent grafting may be ascribed to (i) the rapid reaction of the initiator radical with solvent molecules to other products like glycolic acid and formaldehyde, thereby seriously impending jute radical formation.

The oxidation of acetic acid to glycolic acid by $KHSO_5$ was recognized,[7] and (ii) the rate of homopolymer initiation by the intermediate solvent radical predominates over macro-jute radical formation.
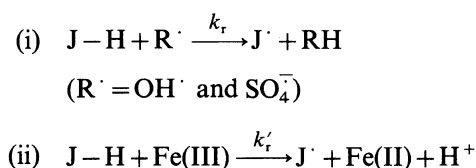
MECHANISM

The mechanism of graft copolymerization of acrylamide onto jute fibers initiated by $KHSO_5$ in the presence of $FeSO_4$, may be pictured as involving generation of macro-jute radicals resulting from the attack of the free-radical species ($OH\cdot$, SO_4^-) and to some extent by Fe(III) ions on jute fibers. The free-radical species and Fe(III) ions are produced from the redox reaction between $KHSO_5$ and Fe(II). The macroradicals so formed subsequently attack the monomer leading to chain initiation. The termination of graft copolymerization may be due to the interaction with Fe(III) ions or mutual combination of grafted chains on different backbones.

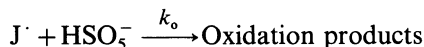### Primary Radical and Fe(III) Production

(i) $HSO_5^- + Fe(II) \overset{\beta}{\rightleftharpoons} Adduct$

(ii) $Adduct \xrightarrow{k_d} Fe(III) + \dot{O}H + SO_4^{2-}$

$\xrightarrow{k_d} Fe(III) + SO_4^- + OH^-$

(iii) $SO_4^- + H_2O \xrightarrow{k_1} HSO_4^- + HO\cdot$

(iv) $Fe(III) + H_2O \xrightarrow{k_2}$
$Fe(II) + HO\cdot + H^+$

Formation of Macrojute Radicals

(i) $J-H + R\cdot \xrightarrow{k_r} J\cdot + RH$
($R\cdot = OH\cdot$ and SO_4^-)

(ii) $J-H + Fe(III) \xrightarrow{k_r'} J\cdot + Fe(II) + H^+$

Oxidation

$J\cdot + HSO_5^- \xrightarrow{k_o} Oxidation\ products$

Initiation

(i) Graft Copolymerization

$J\cdot + M \xrightarrow{k_i} J-M\cdot$
(M = Monomer)

(ii) Homopolymerization

$R\cdot + M \xrightarrow{k_i'} R-M\cdot$

$Fe(III) + M \xrightarrow{k_i''} M\cdot + Fe(II) + H^+$

Propagation

(i) $J-M\cdot + M \xrightarrow{k_p} J-M_2\cdot$
$J-M_{n-1}\cdot + M \longrightarrow J-M_n\cdot$

(ii) $M\cdot + M \xrightarrow{k_p'} M_2\cdot$
$M_{n-1}\cdot + M \longrightarrow M_n\cdot$

Termination

(i) $J'-M_n\cdot + Fe(III) \xrightarrow{k_{t_1}}$
Graft copolymer + Fe(II) + H$^+$

$J-M_n\cdot + J-M_m\cdot \xrightarrow{k_{t_2}}$
Graft copolymer

(ii) $M_n\cdot + Fe(III) \xrightarrow{k_{t_1}'} Homopolymer$

$M_n\cdot + M_m\cdot \xrightarrow{k_{t_2}'} Homopolymer$
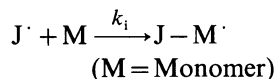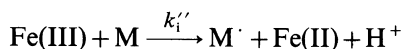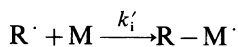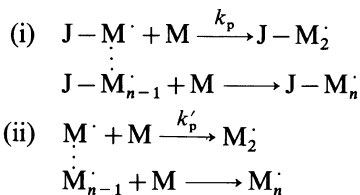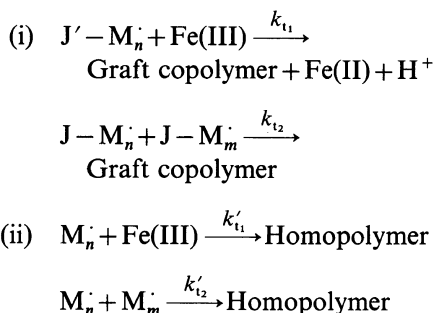
Dimerization

Two macrojute radicals might couple to yield a dimerized product.

$2J\cdot \xrightarrow{k_c} Dimerized\ polymer.$
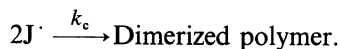
Applying the steady state conditions and considering that graft copolymerization predominates over hompolymerization and dimerization of macrojute radi-

cals, the rate of graft copolymerization (R_p) was evaluated as

$$R_p = \frac{\beta k_d k_r k_i k_p [\text{Fe(II)}] \, [\text{HSO}_5^-] \, [\text{J}] \, [\text{M}]^2}{k_{t_1} [\text{Fe(III)}] (k_i [\text{M}] + k_o [\text{HSO}_5^-])}$$

Further if the reaction exhibits massive oxidation of Fe(II) to Fe(III), *i.e.*,

$$[\text{Fe(II)}] \simeq [\text{Fe(III)}]$$
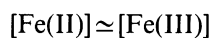
and

$$k_o [\text{HSO}_5^-] \gg k_i [\text{M}]$$

eq 8 can take form eq 9

$$R_p = \frac{\beta k_d k_r k_i k_p}{k_o k_{t_1}} [\text{J}] \, [\text{M}]^2$$

PROPERTIES OF THE GRAFTS

Acrylamide grafted jute fibers have the following properties.

(a) the absorption of water and water vapour increases.

(b) the luxture of the fiber increases.

(c) resistance towards the attack of mineral acid and alkali increases.

(d) *Tensile properties*: The tensile properties of grafted jute fibers were determined through determination of tenacity and stiffness following the method of Huque *et al.*[28] The tenacity was expressed as grams/denier. After conditioning the jute samples, they were combed and the fiber aggregates of uniform length were taken and weight and length determined. The tensile strength was determined by a Zeueigles strength Tester.

Stiffness or tensile modulus at break was determined from the value of tenacity and elongation at break using the following relation.

$$\text{Stiffness at break} = \frac{\text{Tenacity at break}}{\text{Elongation at break}}$$

The results of the tensile properties are recorded in Table II, where it is understood that grafting of polyacrylamide onto jute fibers

Table II. Effects of graft percent on tensile properties of acrylamide grafted jute fibers

Sample	Grafting	Elongation at break (B.L.)	Tenacity	Tensile modulus at break
	%	%	g/denier	
Jute/PAN	20.3	1.28	1.70	132.86
Jute/PAN	32.2	1.36	2.02	148.6
Jute/PAN	62.1	1.45	2.27	156.7

enhances their tensile strength which increases with graft percent.

REFERENCES

1. S. N. Ushakov, *Fiz-Mat. Nauk*, **1**, 35 (1946).
2. A. C. S. Symposium Series, **187**, 73 (1982).
3. Arther D. Little, Inc. "The Engineering Properties of Fibers," Cambridge, Massachusetts, 1966.
4. S. Jena, Ph.D. thesis, Utkal University (1984).
5. S. S. Tripathy, Ph.D. thesis, Utkal University (1984).
6. Md. Habibuddowla, *A. C. S. Symposium Series*, **187**, 73 (1982).
7. R. J. Kenedy and A. M. Stock, *J. Org. Chem.*, **25**, 1901 (1960).
8. R. K. Samal, P. K. Sahoo, R. N. Samal, and H. S. Samantaray, *J. Mol. Catal.*, to be published in 1985.
9. R. K. Samal, P. K. Sahoo, S. Send, and S. P. Bhattacharjee, *J. Ind. Chem. Soc.*, accepted.
10. R. K. Samal, R. R. Das, M. C. Nayak, D. P. Das, G. V. Suryanarayan, and G. Panda, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2751 (1981).
11. R. K. Samal, M. C. Nayak, and D. P. Das, *Eur. Polym. J.*, **18**, 313 (1982).
12. R. K. Samal, S. C. Satrusallya, and B. L. Nayak, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 409 (1982).
13. R. K. Samal, S. C. Satrusallya, and B. L. Nayak, *J. Macromol. Sci. Chem.*, **A19**, 475 (1983).
14. R. K. Samal, P. K. Sahoo, and S. P. Bhattacharjee, *J. Mol. Catal.*, **33**, No 2, 225 (1985).
15. R. K. Samal, P. K. Sahoo, H. S. Samantaray, and S. Send, *J. Polym. Material*, **1**, 210 (1984).

16. R. K. Samal, P. K. Sahoo, S. C. Satrusallya, and B. K. Patnaik, *Polym. J.*, **17**, 453 (1985).

17. R. K. Samal, P. K. Sahoo, and S. P. Bhattacharjee, *Eur. Polym. J.*, **21**, 499 (1985).

18. R. K. Samal, P. K. Sahoo, H. S. Samantaray, and R. N. Samal, *Colloid Polym. Sci.*, communicated.

19. R. K. Samal, H. S. Samantaray, and R. N. Samal, *J. Polym. Material*, **2**, 158 (1985).

20. N. G. Gaylord, *J. Polym. Sci., C*, **37**, 153 (1972).

21. A. Hebeish, M. I. Khalil, and M. H. El-Rafie, *Angew. Makromol. Chem.*, **37**, 149 (1979).

22. B. P. Morin and Z. A. Rogovin, *Polym. Sci. USSR*, **A18**, 20, 2451 (1976).

23. B. N. Misra, R. Dogra, J. Kaur, and J. K. Jassal, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1861 (1979).

24. R. K. Samal, P. L. Nayak, and M. C. Nayak, *Angew. Makromol. Chem.*, **80**, 95 (1979).

25. R. K. Samal, S. C. Satrusallya, B. L. Nayak, and C. N. Nanda, *J. Appl. Polym. Sci.*, 1311 (1983).

26. C. H. Bamford, A. D. Jenkins, and H. Johnston, *Proc. R. Soc. London, Ser. A*, **239**, 214 (1957).

27. R. K. Samal, P. L. Nayak, and T. R. Mohanty, *Macromolecules*, **10**, 489 (1977).

28. M. M. Haque and Md. Habibuddowla, *J. Sci. Ind. Res. (Bangladesh)*, **15**, 64 (1980).