

# Graft Copolymerization of Acrylic Acid onto Jute Fibers Initiated by Quinivalent Vanadium

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## Synopsis

Graft copolymerization of acrylic acid onto jute fibers was carried out with quinivalent vanadium as initiator in an aqueous sulphuric acid medium under nitrogen atmosphere. The graft yield was influenced by reaction time, temperature, concentrations of acid, monomer, initiator, reaction medium, and base polymer. Grafting has also been carried out in presence of various organic solvents. It has been observed that the maximum graft yield 56.7% was obtained at 50°C for  $[AA] = 1.453 \text{ M}$ ,  $[V^{+5}] = 15 \times 10^{-3} \text{ M}$ , acid (2.12 M) and for a reaction time of 6 h. The tensile properties, dye-uptake ability, and absorption of water and water vapours of the grafts have also been studied.

## INTRODUCTION

Graft copolymerization of vinyl monomers onto lignocellulosic and related fibers has been the subject of extensive studies since 1946.<sup>1</sup> Jute, a lignocellulosic fiber is the most abundant renewable agricultural raw material and is transformed into multifarious products affecting every phase of our daily life. Recently efforts are being made in India and Bangladesh for commercial utilization of jute fibers in the textile industries to meet the total fabric requirements of the country as well as to minimize import of synthetic fibers. Although jute fibers possess high dimensional stability, certain unfavourable textile properties such as high stiffness, very low elasticity, susceptibility towards sunlight, and common chemical reagents have tremendously limited its use. Therefore to minimize the undesirableness and enhancing their effectiveness for intensified textile uses, graft copolymerization onto jute fibers has been done using radiation induced and chemical method of initiation involving a number of initiators such as Ce(IV), Mn(VII),  $K_2S_2O_8$ ,  $KHSO_5$ , etc.<sup>2</sup> Among the chemical initiators quinivalent vanadium has a separate identity of its own and is reported to oxidise a multitude of organic substrates via free radical path.<sup>3</sup> With polymeric substrates containing pendent,  $-OH$ ,  $-CHO$ ,  $-NH_2$ ,  $-SH$ ,  $-COOH$ , etc., it easily creates free-radicals on their backbones that attack vinyl monomers leading to graft copolymers with minimum homopolymer formation.<sup>4,5</sup> Recently Singh and coworkers<sup>6-8</sup> have studied the graft copolymerization of methyl methacrylate onto modified jute fibers initiated by quinivalent vanadium/

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cyclohexanon and V(V)/cyclohexanol redox system. The graft copolymers showed improved thermal stability, dye-ability, and the grafting resulted the light eastness of jute fibers.

The present report includes graft copolymerization of acrylic acid onto jute fibers initiated by V(V) in aqueous sulphuric acid under variable reaction condition and studies on various properties of the grafts.

## EXPERIMENTAL

### Materials

Jute fibers (*Corchorus Capsularies*) were purified by treating with hot ethanol and benzene in 1 : 2 (V/V) mixture in a soxhlet apparatus. They were then washed well with alcohol and air dried. Acrylic acid (G.S.C) was purified by distillation under reduced pressure and middle fraction was collected and used for all experiments. A stock solution of the initiator "V(V)" (0.1 M) was prepared by dissolving 2.925 gms of the  $\text{NH}_4\text{VO}_3$  in 5 M  $\text{H}_2\text{SO}_4$ . The strength of stock solution was determined by "vanadometry." 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 carrying outlet and inlet systems, for deaeration. The defatted jute fibers (0.2–1.0 gms) were immersed in a mixture containing water required amount of acrylic acid (AA) and acid. The reaction vessels were deaerated by passing oxygen free nitrogen for 1 h and were than sealed airtight by rubber capping. The vessels were then kept in a constant temperature bath till the mixture attained thermal equilibrium after which required amount of the initiator was injected through rubber capping, and the reaction was carried out for desired time. The homopolymers were extracted by repeated boiling of the grafts in distilled water and warm methanol till washings did not yield any precipitate.

From the weight of the grafts and parent fiber the percent grafting was calculated as follows:

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

Where  $X$  = Wt. of the graft copolymer

$Y$  = Wt. of the original base polymer.

## RESULTS AND DISCUSSION

Acrylic acid was graft copolymerized with defatted jute fibers initiated by V(V) at varying acid concentrations. The results of such polymerizations are presented in Table I. From Table I it is observed that the increase of acid concentration in the reaction mixtures enhances the percent grafting. This may be attributed to increase in the oxidation potential of quinquivalent vanadium resulting in the production of more active  $\text{VO}_2^+$  species and/or  $\text{V}(\text{OH})_3^{2+}$ . These vanadium species have been proved to be potential oxidisers of a large number of organic substrates, the oxidation of which proceed through

TABLE I  
Results of Graft Percent in the V(V) Initiated Graft Copolymerization of Acrylic Acid  
Onto Jute Fibers in the Presence of Different Acid Concentration

[H <sup>+</sup> ]	Percent of grafting
0.88	9.55
1.1	10
1.4	29.45
1.6	34.05
1.9	49
2.1	56.7

Jute = 0.2 gm; [AA] = 1.453 M; [V<sup>+5</sup>] =  $15 \times 10^{-3}$  (M); Temp. = 50°C; Time = 6 h.

free radical path.<sup>3</sup> In the present case the said vanadium species probably attacks jute backbone at a faster rate resulting in the production of a large number of grafting sites to which monomer addition takes place. The important observation which was noted in the present studies is that beyond 1.6 M of the concentration of sulphuric acid, the grafted samples were brittle. The brittleness of the grafted samples beyond 1.6 M of H<sub>2</sub>SO<sub>4</sub> concentration may be due to (a) oxidative chain cleavage of the jute backbone by excess of reactive vanadium species and (b) hydrolytic chain cleavage of the jute backbone by excess of acid. Further studies were therefore done below 1.5 M of H<sub>2</sub>SO<sub>4</sub> concentration. The ideal sample had 32.5% of grafting at [AA] = 1.45 M, [H<sup>+</sup>] = 1.0 M, [V<sup>+5</sup>] =  $15 \times 10^{-3}$  M, Jute = 0.2 gms at 50°C for a reaction time of 6 h.

#### Effects of Monomer/Jute Ratios

The effects of the monomer/Jute ratio on the grafting of acrylic acid onto jute fibers were studied at a series of monomer concentration between 0.54 (M) to 1.633 (M) at fixed initiator concentration of  $15 \times 10^{-3}$  (M) at a fixed weight of jute fibers (0.2 g) at a fixed time of 6 h and at five different temperatures of 35°C–60°C. The percent grafting was found to increase steadily with increase monomer concentration and temperature simultaneously (Figure 1). This enhancement of percent grafting here may be interpreted in terms of AA concentration and its reactivity. Increase of Monomer/jute ratio increases monomer (AA) concentration at close proximity of the fiber backbone where some of the AA molecules form a donor-acceptor complex, through interaction of their carboxyl functions with the OH-groups on jute backbone. Out of the uncomplexed monomers, those which are at the immediate vicinity of reaction sites become acceptor of the jute radicals resulting in chain initiation and thereafter themselves become free-radical donors predominantly for the complexed monomers converted to strong acceptors and neighbours to them than the remaining uncomplexed one's little far away. These factors result in an increase in the reactivity of the monomers thereby enhancing percent grafting Gaylord<sup>9</sup> and Hebeish<sup>10</sup> have also put forth similar explanation for enhancement of grafting.

#### Effects of Initiator Concentration

Graft copolymerization was studied at a number of initiators concentrations ( $2.5 \times 10^{-3}$  M— $15 \times 10^{-3}$  M) Jute = 0.2 g for fixed concentration of AA = 1.45

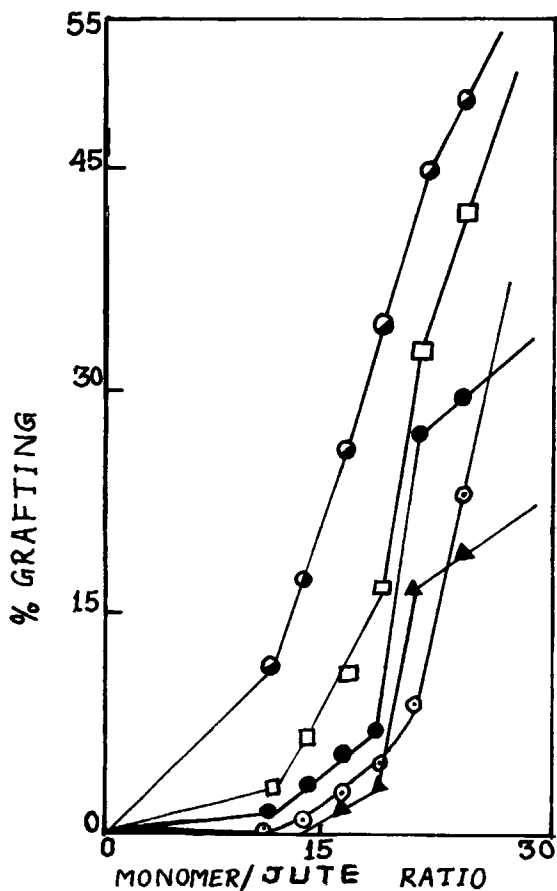


Fig. 1. Variation of graft percent at fixed time: effect of monomer/jute ratio at various temperatures; Jute = 0.2 gm;  $H^+ = 1$  M,  $[V^{+5}] = 15 \times 10^{-3}$  M, Time = 6 h. Plots: (○) 35°C, (▲) 40°C, (●) 45°C, (□) 50°C; (◐) 60°C.

M,  $[H^+] = 1$  M, Time = 6 h at different temperatures (35°C–60°C) (Figure 2). It has been observed that the percent grafting increases more or less linearly on increasing the initiator concentration. The increase of percent grafting with increasing initiator concentration may be ascribed to the increase of active sites on the backbone of jute fibers arising from the attack of different  $V^{+5}$  on polymer matrix.

### Effect of Temperature

Graft copolymerization of acrylic acid onto jute fibers has been studied at temperatures ranging from 35°C to 60°C as shown in Fig. 2. The enhancement of percent graft with rise in temperature may be attributed to (a) activation of the jute backbone and V(V) where a facile oxidation of the former by the latter generates a large number of grafting sites to which monomer addition takes place, (b) increase of temperature increases the rate of diffusion of AA into the fiber matrix, where grafting is also initiated at the interior region of the jute backbone. Samal and coworkers<sup>11-13</sup> has similar observations in the grafting of AM onto cellulose Nylon-6 and Silk fibers.

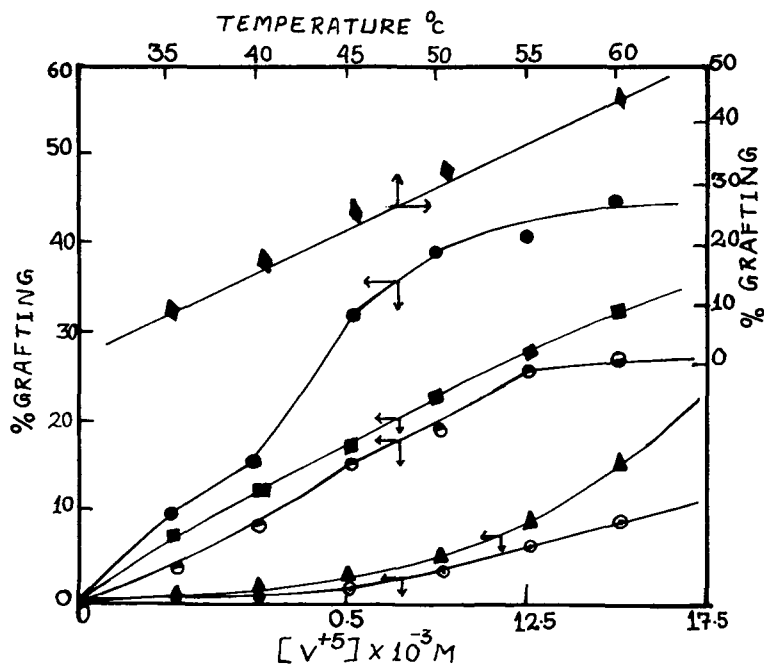


Fig. 2. (a) Variation of graft percent at fixed time: effect of initiator  $[V^{+5}]$  concentration at various temperatures; Jute = 0.2 gm;  $[AA] = 1.453 M$ ;  $[H^+] = 1 M$ ; Time = 6 h. Plots: (○)  $T = 35^\circ C$ ; (△)  $T = 40^\circ C$ ; (◻)  $T = 45^\circ C$ ; (◊)  $T = 50^\circ C$ ; (●)  $T = 60^\circ C$ . (b) Variation of graft percent with temperature. Plot: (◆)

### Effect of Solvent Composition

The effects of organic solvents on the extent of grafting has been studied at various solvent compositions of 5 : 95–50 : 50 (V/V) at  $50^\circ C$  for fixed concentrations of AA (1.453 M),  $V^{+5}$  ( $15 \times 10^{-3} M$ ),  $H^+$  (1 M), jute (0.2 g) for a reaction time of 6 h. The results of such studies with solvents like methanol, Acetone, Formic acid, and Acetic acid are shown in Figure 3 where it is seen that there is a progressive decrease in the graft percentage with increase in solvent composition for methanol, acetone, acetic acid, and Formic acid. This decrease of percent grafting may be ascribed to (a) the oxidation of the solvent molecules by the initiator to various products like glycolic acid and Formaldehyde, thereby seriously impeding jute radical formation, (b) premature termination of the growing grafted chains by solvent radicals, and (c) predominancy of homopolymerization by excess of these solvent radicals. All these factors adversely contribute to retardation of grafting.

### Properties of the Grafts

Acrylic acid grafted jute fibers have four properties:

- (a) *Absorption of water and water vapours: (Water retention).* The extent of absorption of water of both the virgin and grafted jute fibers was

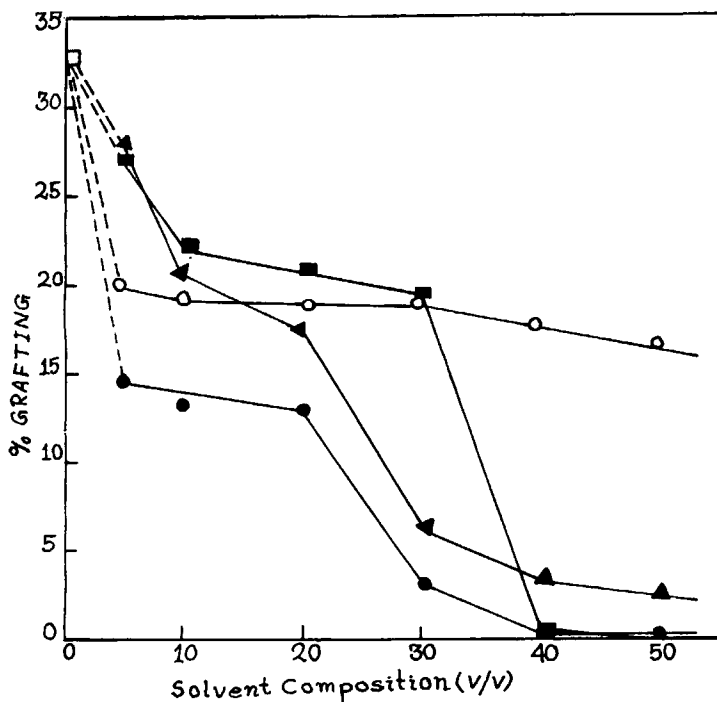


Fig. 3. Variation of graft percent with fixed time: effect of solvent composition. Jute = 0.2 gm; [AA] = 1.453 M;  $[V^{+5}] = 15 \times 10^{-3}$  M;  $[H^+] = 1$  M; Time = 6 h, Temp. = 50°C. Control value = 32.5% Plots: (●) Methanol; (▲) Acetone; (○) Acetic Acid; (■) Formic acid; (□) Control.

determined through measurement of water retention of the samples following the method of Ranby and coworkers<sup>14</sup> with slight modification. The water retention increased on increasing the graft percentage (Table II). One gram of both virgin and the grafted fibers were separately immersed in 100 mL of distilled water for 12 h. The contents were then filtered in sintered glass filter and sucked at 700 mm Hg pressure. The volume of the filtrate was measured and the water retention which is equal to the amount of water absorbed was calculated as grams of water per gram of dry material. The measurement was repeated by drying the samples in an hot air oven at 60°C.

TABLE II  
Water Retention Values of Jute-g-PAA Fibers with Various Percentage Grafting

Percent grafting	Water retention in g/g
0	1.2
6.5	4.8
10.9	8.9
16.8	12.6
32.5	18.7

TABLE III  
Alkali and Acid Solubility of Jute and Jute-g-PAA for 30 Minutes

% Grafting	Alkali solubility %	Acid solubility %
Parent fiber	10.1	28.2
10.9	8.5	19.3
16.8	5.2	14.9
32.5	3.0	9.7

- (b) *Alkali and acid solubility.* The behaviour of the grafts and the virgin jute fibers towards alkali was tested by determining the percentage of alkali solubility with time. For this the samples were immersed separately in aqueous solution of 0.1 (M) NaOH solution for various time intervals for 1 h at 65°C using Jute-liquor ratio 1 : 100. The method adopted was similar to that of Leavean and coworkers.<sup>15</sup> The treatment showed that the grafted samples showed decreased alkali solubility on increasing the percent grafting (Table III). A similar procedure was adopted with 0.1 (M) HCl using a jute-liquor ratio 1 : 100. The results of acid treatment showed decreased acid solubility on increasing the percent grafting (Table III).
- (c) *Tensile properties:* The stiffness or tensile modulus at break of the grafted jute fibers was determined from the values of tenacity and Elongation at break using the relationship<sup>16</sup>;

$$\text{Stiffness at break} = \frac{\text{Tenacity at break}}{\text{Elongation at break}} \times 100$$

The tenacity was expressed as grams/denier. After conditioning the jute samples, they were combed and fiber aggregates of uniform length was taken and weighed and length determined. The tensile properties were determined by a "Dutrons" tensile tester, brand-20 Kgf capacity.

The tensile modulus of the grafted and virgin fibers are presented in Table IV. The results shows that the tensile modulus increases on increasing the percent grafting.

TABLE IV  
Effect of Graft Percent on Tensile Modulus of Acrylic Acid Grafted Jute Fibers

Grafted sample	Grafting	Elongation at break B.L. %	Tenacity g/denier	Tensile modulus (stiffness g/denier)
Parent jute	0	0.92	1.0	110.9
Jute-g-PAA	6.5	1.0	1.2	112.0
Jute-g-PAA	10.9	1.26	1.5	119.04
Jute-g-PAA	16.8	1.3	1.6	123.07
Jute-g-PAA	32.5	1.48	2.1	141.9

TABLE V  
Effect of Graft Percent on Dye Uptake Ability of Parent Jute  
and Acrylic Acid Grafted Jute Fibers

Sample no.	Grafting %	Absorbance O.D.	Concentration of the dye after dyeing	Dye uptake in gm of dye/kg of fiber
1. Parent jute	—	0.115	$3.53 \times 10^{-4}$	$9.7 \times 10^{-2}$
2. Jute + AA	20.045%	0.015	$0.46 \times 10^{-4}$	$12.77 \times 10^{-2}$
3. Jute + AA + Na <sup>+</sup>	20.045%	0.006	$0.184 \times 10^{-4}$	$13.05 \times 10^{-2}$

Initial concentration of the dye solution =  $13.23 \times 10^{-4}$  M.

(d) *Dye uptake*: Sandocryl Golden yellow B-GRL 300% dye was used for dyeing of the fibers. The dye solution was prepared by adding 1 g of dyestuff to 100 cm<sup>3</sup> of hot water with constant stirring to obtain a clear solution. One percent shade was dyed on material. Required amount (100 cm<sup>3</sup>) of dye solution was taken in a beaker and to that 4 cm<sup>3</sup> of 1% ammonium sulphate solution was added. The material to liquor ratio was adjusted to 1 : 40 by adding required amount of water. Then the pH of the dye solution was maintained between 5–5.5 by adding dilute acetic acid dropwise. The concentration of the dye in this solution was measured by Spectrophotometer at 750 nm. The sample was pre-wetted and dipped into the dye solution. The beaker was then kept over a hot plate and temperature was raised to 80°C by 5°C/min., then from 80°C–100°C the temperature was raised slowly by 1°C/min. The dyeing was carried out at 100°C for 45 min till all the colour is exhausted into the fiber. After dyeing the material was rinsed in cold water and air dried. The initial concentration of the dye solution and that remaining after dyeing were determined by using the following formula.

$$C = \frac{O.D.}{ax\lambda}$$

where,

*O.D.* = Optical density

*a* = constant (0.4343 K)

= 750 nms.

The resulting dye uptake ability of the fibers were determined by measuring the difference of the initial and remaining concentration of the dye solution are presented in Table V. The result showed that grafting of acrylic acid increased the dye uptake ability of the jute fibers.

The authors are highly thankful to Professor Y. Ikada, Research Centre for Medical Polymers and Biomaterials, Kyoto University, Japan for fruitful suggestions and continuous inspiration. The financial support by U.G.C., India, New Delhi is gratefully acknowledged.



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Received August 16, 1989

Accepted November 6, 1989