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Radiation (^{60}Co)-Induced Graft Copolymerization of Acrylamide on Jute Fiber

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ABSTRACT

The radiation induced graft copolymerization of acrylamide onto jute fibers was studied following preirradiation of jute in air using a ^{60}Co source of γ-radiation and subsequent polymerization of acrylamide in a limited aqueous system under nitrogen at 60°C. An increase of the time of preirradiation (at a fixed dose rate) increased the percent grafting measurably and the grafting efficiency marginally. Grafting effects showed further improvement on addition of Fe^{2+} or Co^{2+} ions to the system prior to the polymerization step. Increasing the concentration of Fe^{2+} or Co^{2+} ion led to an increase in the grafting parameters with a leveling off effect in the higher concentration range, however. An increase in the polymer (jute) content for a fixed monomer content produced a significant increase in the efficiency of grafting, while % grafting followed a slowly decreasing trend.

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INTRODUCTION

Radiation-induced graft copolymerization of vinyl and related monomers on cellulosic substrates, both by mutual irradiation and by preirradiation techniques, have been reviewed [1-3]. Similar studies using jute fibers are, however scanty [4-9]. This prompted us to undertake further studies of radiation-induced graft copolymerization of acrylamide onto jute fibers, using the preirradiation technique because it leads to a smaller amount of homopolymer formation [10].

EXPERIMENTAL

Jute fibers obtained from the local market were kept suspended in a benzene-alcohol mixture for 72 h, dried, and finally bleached with sodium hypochlorite solution (10%) until they became colorless (~1 h).

Acrylamide monomer obtained from Koch-Light Laboratories Ltd., England, was used without further purification. Ferrous sulfate and cobaltous chloride were obtained from BDH, and hydrogen peroxide (30%) was obtained from Sarabhai M. Chemicals, India.

GRAFT COPOLYMERIZATION

The bleached jute samples were first placed in stoppered glass (borosilicate glass) ampules and exposed to irradiation by γ-rays from a ^{60}Co source in the presence of air (dose rate, 1.8×10^5 rd/h) for a specific time period.

Known quantities of acrylamide monomer and other additives, if any, such as Fe^{2+}, CO^{2+}, and H_2O_2, all in aqueous solution, were then added to the irradiated jute fibers in the respective ampules under nitrogen flushed conditions. Postpolymerization was allowed to take place at 60°C under nitrogen atmosphere for a specified time period. The total volume of water in all the experiments was kept fixed at 5 mL.

After the polymerization, the contents (gross polymer) were poured into a large excess of methanol to precipitate the polymer. The free homopolymer polyacrylamide was separated from the jute-polyacrylamide graft copolymer by repeated extraction with hot water.

RESULTS

Results of graft copolymerization of acrylamide on preirradiated jute fibers under different conditions at 60°C are shown in Table 1 and Figs. 1-6. Results relating to % grafting and grafting efficiency

(%), given in the last two columns of Table 1, are better appreciated from Figs. 1 and 2. The grafting parameters bear the same meaning as described elsewhere [17].

Effect of Variation of Time of Pre-Irradiation on Grafting

Table 1 and Figs. 1 and 2 illustrate that increasing the time of irradiation (8-25 h) results in an initial increase in the % conversion (48-55%) and % grafting (7.9-9.3%) with a leveling-off effect in the later stages while the grafting efficiency (%) follows a small or negligible increasing trend (6.55-7.0%), Fig. 2.

Effect of Fe^{2+} and Co^{2+} Ion

Related results are also shown in Table 1 and Figs. 1 and 2. The presence of Fe^{2+} ion ($FeSO_4.7H_2O = 5 \times 10^{-2}$ mol/L) resulted in a significant increase in the grafting parameters but a decrease in the overall % conversion relative to that obtained in the absence of an additive. Co^{2+} ion ($CoCl_2 = 5 \times 10^{-2}$ mol/L) also produced some enhancement in % grafting and grafting efficiency, but the net improvements were much less pronounced. Addition of H_2O_2 to the Co^{2+} system resulted in further marginal improvement in % grafting. However, the grafting efficiency was lower than that observed in the presence of Co^{2+} alone, but reasonably higher than what was obtained in the absence of any additive. For the Co^{2+}-H_2O_2 additive system, % conversion was significantly higher (51-52%).

Effect of Variation of Concentrations of Fe^{2+} and Co^{2+} Ions

Increase of Fe^{2+} and Co^{2+} ion concentrations resulted in a corresponding improvement in the grafting parameters but a decrease in the % conversion as illustrated by Figs. 3-5.

Effect of Variation of Polymer (Jute) to Monomer Ratio

Related results are shown in Fig. 6. Increase in the weight of jute (0.2-0.6 g) for a given amount of acrylamide (0.5 g) resulted in a significant improvement in the grafting efficiency while the % grafting followed a slowly decreasing trend.

TABLE 1. Graft Copolymerization of Acrylamide on Jute Fiber by the Preirradiation Technique (^{60}Co). Effect of Variation of Time of Preirradiation and Some Additives[a]

Time of preirradiation (h)	Additive, concentration (mol/L)	Percent conversion	Percent grafting	Grafting efficiency with respect to monomer (%)
8	None	48.20	7.92	6.55
16	"	49.40	8.65	7.00
20	"	52.68	9.10	6.90
23	"	54.66	9.15	6.70
25	"	55.34	9.25	6.69
	$FeSO_4.7H_2O$			
8	5×10^{-2}	32.68	13.50	16.52
16	"	34.62	14.30	16.50
20	"	34.80	14.20	16.32
23	"	35.04	14.55	16.60
25	"	35.00	14.50	16.57

	$CoCl_2$			
8	5×10^{-2}	33.24	9.20	11.07
16	"	35.18	9.75	11.08
20	"	35.64	10.20	11.44
23	"	35.66	10.35	11.60
25	"	35.74	10.45	11.69
	$CoCl_2$-H_2O_2			
8	5×10^{-2} (each)	51.40	9.60	8.47
16	" "	51.70	10.30	9.03
20	" "	52.02	10.70	9.34
23	" "	52.02	10.85	9.48
25	" "	52.11	10.80	9.42

[a]In each experiment, jute = 0.2 g, acrylamide = 0.5 g, water = 5 mL, time of polymerization at 60°C = 5 h.

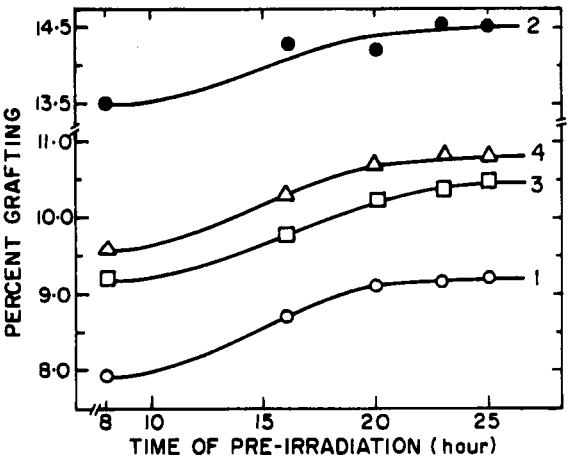

FIG. 1. Effect of variation of time of preirradiation on percent grafting. Dose rate: 1.8×10^5 rd/h, fixed. Additive used: (1) none, (2) $FeSO_4.7H_2O$ (5×10^{-2} mol/L), (3) $CoCl_2$ (5×10^{-2} (mol/L), (4) $CoCl_2$ and H_2O_2 (5×10^{-2} mol/L each).

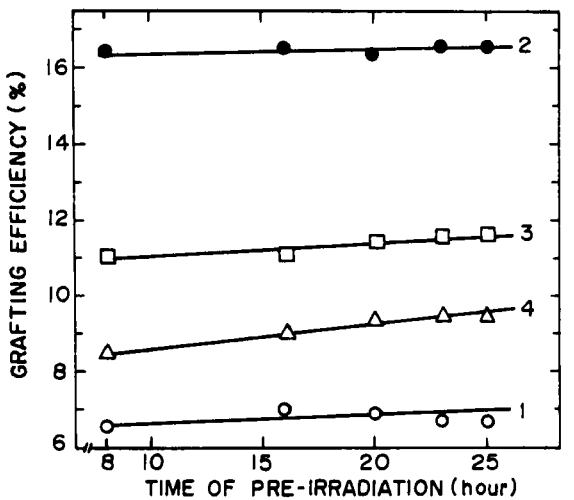

FIG. 2. Effect of variation of time of preirradiation on grafting efficiency (%). Dose rate: 1.8×10^5 rd/h, fixed. Additive used: (1) none, (2) $FeSO_4.7H_2O$, (5×10^{-2} mol/L), (3) $CoCl_2$ (5×10^{-2} mol/L), (5) $CoCl_2$ and H_2O_2 (5×10^{-2} mol/L each).

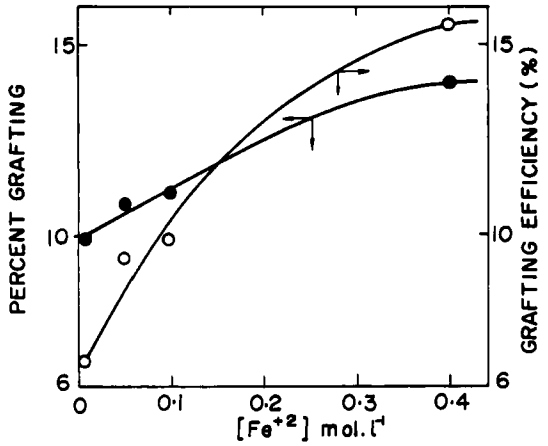

FIG. 3. Effect of variation of $[Fe^{2+}]$ on percent grafting and grafting efficiency (%). Jute = 0.2 g, time of preirradiation = 24 h, dose rate = 1.8×10^5 rd/h, acrylamide = 0.5 g, total volume of aqueous solution = 5 mL, time of polymerization = 5 h, temperature of polymerization = 60°C.

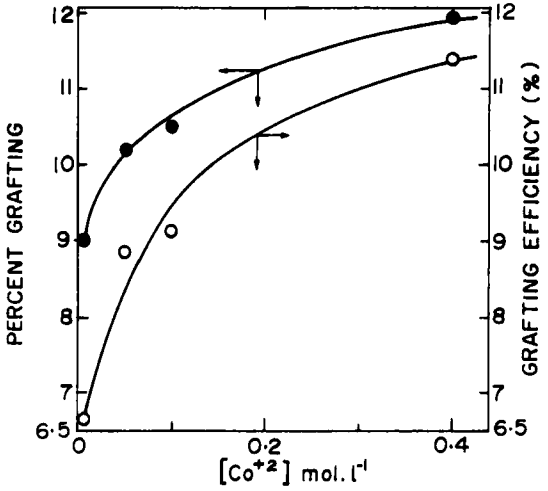

FIG. 4. Effect of variation of $[Co^{2+}]$ on percent grafting and grafting efficiency (%). Jute = 0.2 g, time of preirradiation = 24 h, dose rate = 1.8×10^5 rd/h, acrylamide = 0.5 g, total volume of aqueous solution = 5 mL, time of polymerization = 5 h, temperature of polymerization = 60°C.

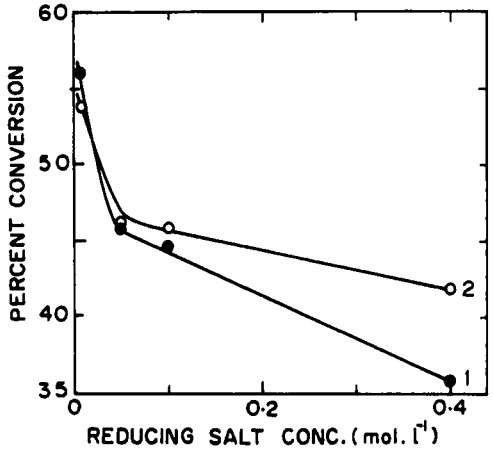

FIG. 5. Effect of variation of $[Fe^{2+}]$ (1) and $[Co^{2+}]$ (2) on percent conversion. Jute = 0.2 g, time of preirradiation = 24 h, dose rate = 1.8×10^5 rd/h, acrylamide = 0.5 g, total volume of aqueous solution = 5 mL, time of preirradiation = 5 h, time of polymerization = 60°C.

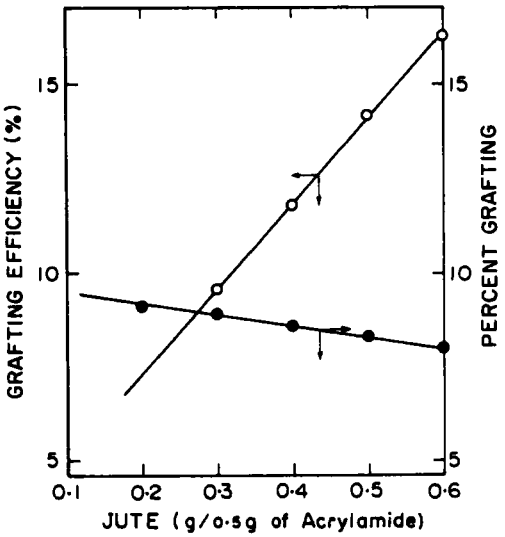

FIG. 6. Effect of variation of polymer (jute) to monomer ratio on grafting efficiency (%) and percent grafting. Time of preirradiation = 23 h, dose rate = 1.8×10^5 rd/h, acrylamide = 0.5 g, total volume of aqueous solution = 5 mL, time of polymerization = 5 h, temperature of polymerization = 60°C.

DISCUSSION

It has been widely reported [10-12] that when a polymer is irradiated in the presence of air, peroxides and hydroperoxides are formed, which can be subsequently decomposed thermally or otherwise, resulting in the formation of graft copolymer and free homopolymer in the presence of an added monomer:

$$\text{ROOR}' \text{ (or ROOH)} \longrightarrow \text{RO}^{\bullet} + \text{R}'\text{O}^{\bullet} \text{ (or HO}^{\bullet}\text{)} \quad (1)$$

As the time of preirradiation increases, the total number of peroxide and hydroperoxide linkages formed for a given weight of the substrate (jute) increases. Consequently, during the subsequent thermal polymerization of acrylamide in its presence, the number of $\text{RO}^{\bullet}$ (and $\text{R}'\text{O}^{\bullet}$) radicals (which lead to the formation of graft copolymer) and $\text{HO}^{\bullet}$ radicals (which lead to the formation of free homopolymer) formed increases, with a consequent increase in both the % grafting and % conversion.

The improvement in the grafting parameters, at a given time of preirradiation, due to the presence of reducing metal ions such as Fe^{2+} or Co^{2+} in the postpolymerization system can be attributed to the ready reactions of these ions (M^{2+}) with the peroxide or hydroperoxide groups by a redox mechanism:

$$M^{2+} + \text{ROOR}' \text{ (or ROOH)} \longrightarrow M^{3+} + \text{RO}^{\bullet} + \text{R}'\text{O}^{-} \text{ (or HO}^{-}\text{)} \quad (2)$$

Redox reactions of the above kind result in the generation of macroradicals ($\text{RO}^{\bullet}$) as before, but reduce the formation of $\text{HO}^{\bullet}$ radicals, with a consequent improvement in the grafting parameters.

The results obtained with Co^{2+}-H_2O_2 system may be explained by consideration of Eqs. (3) and (4) in addition to Eq. (2):

$$M^{2+} + \text{HOOH} \longrightarrow M^{3\bullet} + \text{HO}^{\bullet} + \text{HO}^{-} \quad (3)$$

$$\text{HOOH} \longrightarrow 2\text{HO}^{\bullet} \quad (4)$$

The higher concentration of $\text{HO}^{\bullet}$ radicals results in a higher rate of homopolymerization with a consequent increase in the overall % conversion and a measurable decrease in the grafting efficiency. Furthermore, a higher concentration of growing polyacrylamide radicals is likely to effect a higher extent of chain transfer reaction between them and the polymeric substrate (jute), resulting in an increase in the % grafting.

The results illustrated in Figs. 3-5 are in agreement with the above considerations. An increase in the concentration of Fe^{2+} or Co^{2+} pro-

duces a corresponding improvement in the grafting parameters. The decrease in the overall % conversion with an increase in the reducing metal ion concentration may be attributed to the increasing concentration of Fe^{3+} or Co^{3+} generated during the course of the redox reaction (2), which probably act as effective chain terminators [13].

The greater the amount of jute for a given amount of monomer (Fig. 6), the greater is the amount of peroxide and hydroperoxide groups formed during the course of irradiation, and consequently, the higher is the number of active sites generated on the polymeric substrate during the subsequent decomposition of the peroxy linkages. Thus the grafting efficiency increases. However, as the monomer to jute ratio decreases, the % grafting decreases quite expectedly.

Extensive reports are available on radiation-induced graft copolymerization of different vinyl monomers on cellulose or related polymers, but those involving acrylamide monomer via mutual irradiation or preirradiation (in vacuo or N_2) techniques are scanty [14-16]. Grafting efficiencies in the range of 30-90% were reported for systems employing the preirradiation technique.

Grafting efficiencies obtained in the present studies with jute (cellulose) by the preirradiation technique in air are lower than those reported for the grafting of polyacrylamide on cellulose from cotton or other nonjute sources employing the preirradiation technique in vacuum or N_2. This trend of difference in grafting efficiency (preirradiation in vacuum vs that in air) conforms with that reported for vinyl grafting on polyethylene [10].

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