

Redox-Initiated Graft Copolymerization onto Modified Jute Fibers

INTRODUCTION

A number of reports¹⁻⁹ have appeared in polymer literature so far on modification of jute fiber by graft copolymerization of vinyl monomers. But graft copolymerizations onto modified jute are very few. In most of the reports it has been mentioned that the low percentage of grafting of jute fiber is due to the higher content of lignin. Comparison of percentage of graft yield in the case of defatted and bleached jute fibers have also been reported.^{4,5} From our laboratory graft copolymerizations of vinyl monomers onto chemically modified jute fibers have been reported.⁷⁻⁹ In this communication we wish to report a comparative account of graft copolymerization of methyl methacrylate onto different modified jute fibers by using V^{5+} -cyclohexanol redox initiating system in aqueous solution.

EXPERIMENTAL

Purification of natural jute fiber, methyl methacrylate and grafting reactions, and separation of homopolymer from the grafted fiber were carried out according to the procedure reported earlier.⁷ The chemicals used were all of (BDH) AR grade and purified where necessary. The different modified jutes were prepared in the following manner.

Defatted Jute

Fresh jute fiber samples were divided into three parts: top, middle, and bottom. The middle portions (50 cm) were lightly combed for a long period in order to make the fibers free from impurities. The combed fibers were extracted with alcohol-benzene (1:2 v/v) for 14 h with a refluxing rate of 7-8 cycles/h. After refluxing, the fibers were washed with alcohol and air-dried.

Delignified Jute

The combed middle portion of jute fibers were first subjected to soxhlet extraction with acetone for about 24 h, followed by washing with cold distilled water and air drying. The fibers were then extracted in a 1:2 mixture of alcohol and benzene for 14 h to dewax the sample, and then washed and dried. The dried samples were treated with 17.5% NaOH for 30-45 min and thoroughly washed with distilled water and air-dried.

Chemically Modified Jute

Jute fibers, after the treatment with acetone, alcohol-benzene mixture, and 17.5% NaOH as mentioned above, were then subjected to ethylene diamine treatment for about 30 min, and then washed thoroughly and air-dried. The dried samples were then soaked with 60% $ZnCl_2$ solution at about 20°C for about 4 h. Then the fibers were thoroughly washed with distilled water and air-dried. Effective swelling of the fibers could be possible by employing ethylene diamine and $ZnCl_2$ treatments. Thus chemically modified jute fibers were prepared.

Acetylated Defatted Jute

About 2 g of defatted jute fiber was soaked in glacial acetic acid for 1 h at 20-25°C, decanted, and then soaked in 50 mL of acetic anhydride containing 1 drop of concentrated sulfuric acid for 5 min. The fibers were then filtered over a Buchner funnel, thoroughly washed with water, till the fibers became free from acid, and then air dried. About 11% weight gain was possible due to partial acetylation of defatted jute.

TABLE I
Results of Graft Copolymerization of Methyl Methacrylate
onto Modified Jute Fibers^a

Sample particulars	Percentage of graft yield			
	1 h	2 h	4 h	6 h
Defatted jute	12.9	34.5	31.2	28.4
Delignified jute	47.4	81.6	70.7	64.5
Chemically modified jute	98.2	179.8	168.4	154.2
Acetylated chemically modified jute	139.1	202.4	191.7	183.9
Acetylated defatted jute	29.8	61.7	57.3	49.9

^aTotal volume = 20 cm³, temperature = 60°C, jute = 0.1 g, [MMA] = 0.467 mol/L, [cyclohexanol] = 0.2356 mol/L, [V⁵⁺] = 0.005 mol/L, [H₂SO₄] = 0.15 mol/L.

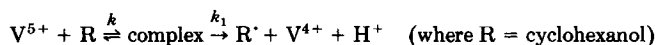
Acetylated Chemically Modified Jute

The chemically modified jute fibers were subjected to acetylation by the same procedure as mentioned in case of acetylation of defatted jute. About 10% weight gain was possible due to partial acetylation of chemically modified jute.

The graft percentage is calculated as the percentage increase in weight over the original weight of the sample.

RESULTS AND DISCUSSION

The mechanism of this redox system is likely that V⁵⁺ first forms a complex with the organic substrate, i.e., cyclohexanol, which decomposes, giving rise to a free radical that initiates the polymer backbone grafting:



Then the jute macroradical which is formed by the abstraction of hydrogen from reactive jute molecule combines with methyl methacrylate in order to propagate the chain. On subsequent termination grafted polymer is obtained.

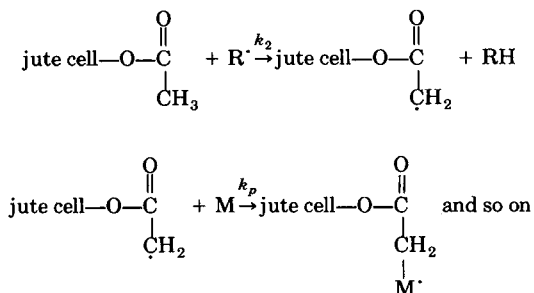
The results of percentage of graft yield in case of different modified jute fibers are represented in Table I. The order of the percentage of graft yield is as follows: acetylated chemically modified jute > chemically modified jute > delignified jute > acetylated defatted jute > defatted jute.

The percentage of graft yield was found to be minimum in case of defatted jute which may be attributed to the higher lignin content of the defatted jute. The delignified jute showed more tendency to grafting than the defatted jute. During alkali treatment, the alkali-sensitive linkage in jute are supposed to be ruptured, by which some of the functional groups of cellulose and/or hemicelluloses of jute are made free, thus creating more free sites for grafting in case of delignified jute.

In the case of chemically modified jute, the percentage of graft yield was found to be much more than the corresponding delignified jute. The softening of the fiber due to treatment of ethylene diamine and ZnCl₂ solution in addition to the removal of certain impurities and lignin might be responsible for producing more grafting sites.

In case of acetylated chemically modified jute, the percentage of graft yield was found to be maximum. The formation of certain carbon centers due to acetylation might be responsible for forming more reactive grafting sites than the corresponding —OH groups which are also a probable site for grafting. In this case the acetylated jute macroradical is formed by the

abstraction of hydrogen through the free radical and in presence of monomer methyl methacrylate (M) the chain propagates:



By subsequent termination it gives rise to grafted polymer.

In the case of acetylated defatted jute the percentage of graft yield was found to be more than that of defatted jute but less than that of corresponding delignified jute. The more grafting percentage may be attributed to the formation of more carbon centers in the case of acetylated defatted jute. However, the lower grafting percentage of acetylated defatted jute than the corresponding delignified jute may be due to the presence of a certain lignin which hinders in forming more grafting sites.

It is observed in all experiments that the percentage of graft yield increases up to 2 h, but, after 2 h, graft yield decreases to some extent. This might be attributed to the partial dissolution of grafted fiber on prolonged exposure to high temperature of 60°C. Similar types of observations have also been found earlier.⁷⁻⁹

CONCLUSION

It was concluded from the above experimental results that the higher lignin content of natural jute is responsible for the lower grafting yield. However, the softening of jute fiber after removal of certain impurities and lignin content enhances the graft yield considerably.

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