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Grafting of Methacrylonitrile and Ethyl Methacrylate onto Jute Fibre: Physico-chemical Characteristics of Grafted Jute

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Abstract: Modification of bleached jute fibre was done by graft co-polymerization with vinyl monomers e.g. methacrylonitrile and ethyl methacrylate, in aqueous medium using H_2O_2-$Na_2S_2O_3$ as redox initiators. To make the process efficient, the optimized polymerization condition was established. The maximum percent grafting and grafting efficiency obtained at optimum grafting condition were 11.3 and 20.4% for MAN, respectively and that of 17.6 and 27.5% for EMA. Modification of bleached jute fibre with MAN and EMA reduced the loss in breaking strength and the yellowing on exposure to sunlight in air.

Key words: Jute fibre, grafting, monomer, breaking strength, colour fastness

INTRODUCTION

In the earlier days, jute as a large volume of agricultural fibrous crops served a crucial role to mitigate the every day needs in a wide range of usages. But in recent years, the rival synthetic products are dominating over the usages of jute products. Due to the low cost, high service and expected qualities of the synthetic products, the defects of jute have become more prominent. For the proper utilization of this large volume of the agricultural products of the world, scientists are now trying to find out the ways of remedy of the inherent defects of jute. Despite of some drawbacks of jute, it has major advantage, i.e. it is biodegradable whereas the synthetics are not biodegradable thus causing serious pollution (air, water, soil, etc.) problems and the partition of the land resulting the low yield of crops.

Due to the presence of lignin and its complex structure, jute products show the poor colour fastness and higher loss in tensile strength on exposure to sunlight, air and other external influences. To make the proper use of jute, it is crying need to eradicate these defects and this can be possibly done by chemical modification of jute fibres through grafting. This is indeed a very fascinating field of research which enhances the desired properties of the graft product.

The graft co-polymerization reaction of vinyl monomers onto jute fibres was activated by various methods, such as radiation[1-4] and chemical[5-8] or photo-induced initiation[9]. The use of chemical redox systems in aqueous media has played a major role for both scientific and technological purposes. Thus, the physico-chemical properties of grafted jute fibre largely depend on the chemical characteristics of both the fibre and vinyl monomers as well as on the extent of grafting.

In the present investigation, efforts have been exerted to optimize the grafting process of jute fibre with methacrylonitrile and ethyl methacrylate monomers in aqueous media and to see the effect on inherent mechanical and physical properties of jute due to grafting.

MATERIALS AND METHODS

Tossa variety of jute fibre was collected from local market, Rajshahi, Bangladesh. Methacrylonitrile (MAN) was used freshly after distillation under reduced pressure. Ethylmethacrylate (EMA) was freed from stabilizer by washing with 5% sodium hydroxide solution and water. It was then dried with anhydrous sodium sulphate and distilled under reduced pressure in nitrogen before used[10]. All other chemicals, e.g. $Na_2S_2O_3$, H_2O_2, etc. used were of CP grade.

About 60 cm from the bottom of jute fibre was discarded and then 30 cm was taken for investigation. The dirty materials were removed by treating the fibre with 6.5 g of detergent and 3.5 g of soda per litre at 75°C for 30 min[11]. The washed fibre was then bleached by treating with $NaClO_2$ of strength 5 g L^{-1} at pH 4 and at 85-90°C for 90 min[11,12]. The bleached fibre was treated with 0.2% sodium metabisulphite ($Na_2S_2O_5$) solution for 15 min to neutralise chlorine action.

The graft copolymerization of bleached jute fibre was carried out in a 100 mL stoppered Erlenmeyer flask. Polymerisation was done with 30-90% monomer and

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0.25-1.50% $Na_2S_2O_3$-H_2O_2 redox initiator based on the weight of the fibre at 50-100°C for 30-180 min in the fibre-liquor ratio of 1:50. At the end of the reaction period, the grafted jute fibre was thoroughly washed with hot water followed by warm methanol to remove the loosely adhered polymer[5,8].

Percent grafting and grafting efficiency were calculated by taking the weight of the dried fibre before and after grafting with the monomer. A correction was made for the eventual weight loss occurred during the treatment in the reaction system by using a blank sample treated without monomer. Following formulas were adopted to calculate the percent grafting and grafting efficiency[8].

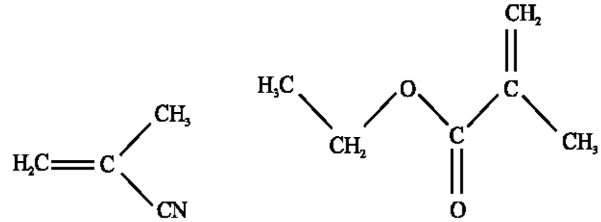
$$\textbf{Grafting (\%)} = \frac{B\text{-}A}{A} \times 100$$

$$\textbf{Grafting efficiencey (\%)} = \frac{B\text{-}A}{A} \times 100$$

Where, A, the weight of bleached fibre before grafting; B, The weight of the grafted jute fibre; C, the weight of total monomer used.

Yellowing of bleached and bleached modified fibres was measured with Grey scale. In this investigation the specimens were exposed in the open air under the sunlight in the months of April to August for 250 h and after every 50 h, the fastness was assessed by comparing the change in colour of the specimen with that of the standard[13].

Torsee's Schopper type-05-100 tensile tester was used for measuring the tensile strength of jute fibre. Tensile strength of each specimen was measured according to International Standard[14] (Strip method) described in previous research[11].



Methacrylonitrile **Ethylmethacrylate**

Chemical structure of MAN and EMA

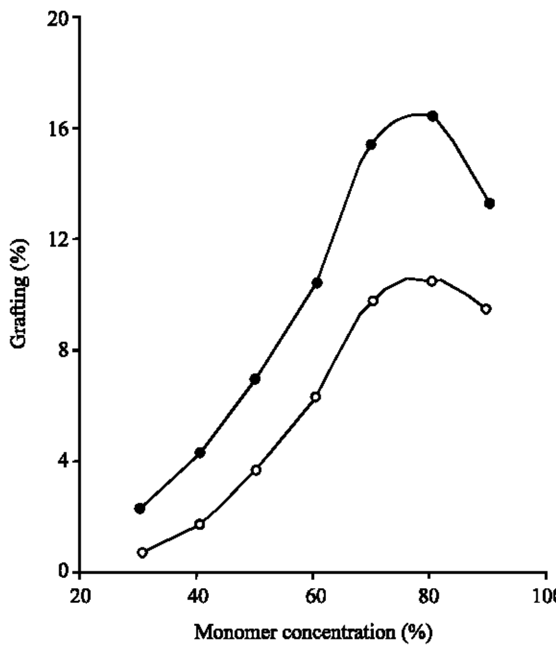


Fig. 1: Effect of monomer concentration on percent grafting of MAN and EMA monomers onto bleached jute fibre ($Na_2S_2O_3$-H_2O_2, 1.00%; time, 90 min; temp., 80°C; liquor ratio, 1:50). ○, MAN; ●, EMA

RESULTS AND DISCUSSION

Bleached jute fibre was chemically modified by MAN and EMA monomers to see their effect on the inherent properties of jute fibre. In the modification process it was seen that the grafting was depended on the monomer concentration, initiator concentration, reaction time and reaction temperature.

In Fig. 1 it is seen that the percent grafting and grafting efficiency increases with the increase of monomer concentration upto 80% for both MAN and EMA monomers, respectively and the corresponding percent grafting and grafting efficiency are 10.6 and 16.7% for MAN, respectively and that of 16.4 and 22.5% for EMA. Beyond these concentrations percent grafting and grafting efficiency started to decrease. The decrease in percent grafting is due to the increasing homo-polymerization rate over grafting at the higher monomer concentration[15].

From Fig. 1 it is also seen that, percent grafting and grafting efficiency of EMA is higher than that of MAN. It is due to the different chemical features of the poly-functionality of them. From the chemical structure, it is seen that EMA has two double bonds at opposite side and MAN has only one double bond. Another reason is that the presence of other substituents as methyl group (-CH_3) might also react with fibres. EMA contains two methyl groups and MAN contains only one methyl group. Thus, the presence of more in number of reactive site in the EMA, it gives greater grafting.

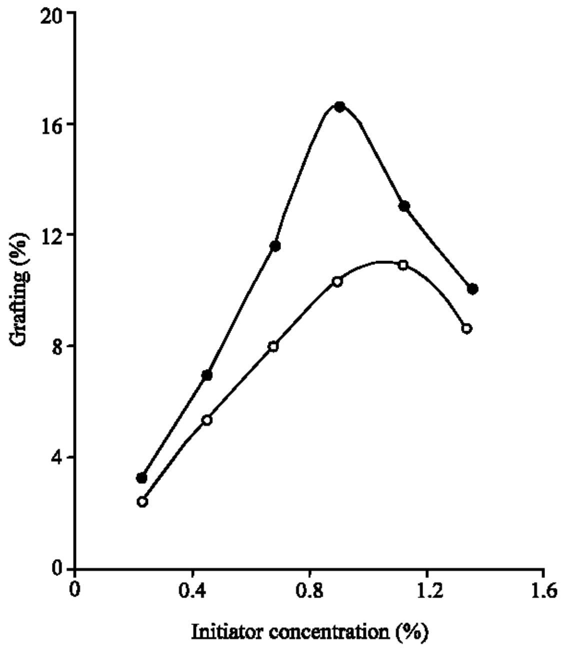


Fig. 2: Effect of initiator ($Na_2S_2O_3$-H_2O_2) concentration on percent grafting of MAN and EMA monomers onto bleached jute fibre (monomer, 70%; time, 90 min; temp., 80°C; liquor ratio, 1:50). ○, MAN; ●, EMA

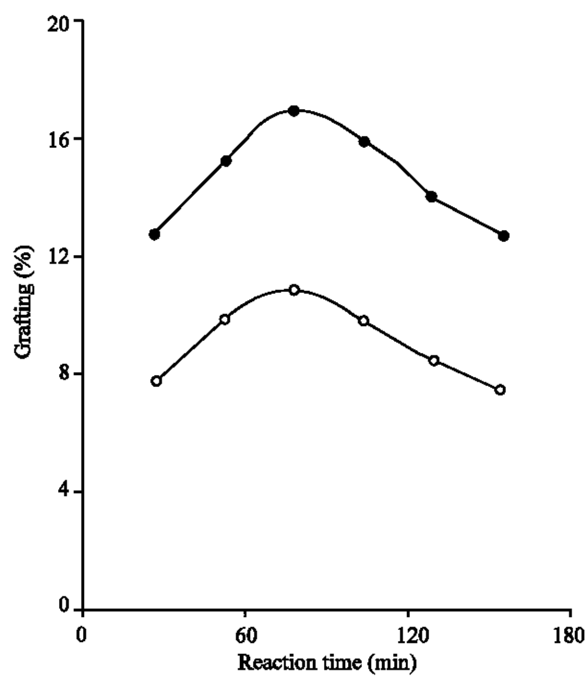


Fig. 3: Effect of reaction time on percent grafting of MAN and EMA monomers onto bleached jute fibre (monomer, 70%; $Na_2S_2O_3$-H_2O_2, 1.00%; temp., 80°C; liquor ratio, 1:50). ○, MAN; ●, EMA

As the redox initiator ($Na_2S_2O_3$-H_2O_2) generates macro-radicals on the fibre backbone as well as activates monomers in the reaction system, the increasing concentration of the initiator gave the higher percent grafting (Fig. 2). But at maximum concentration of initiator, the activated monomer concentration increases to high which brought out homopolymerization and faster rate of termination of the growing chain resulting decreased grafting yield[10,16,17]. The maximum percent grafting was 11.1 and 16.8% obtained at 1.25% initiator for MAN and 1.0% initiator for EMA, respectively.

Figure 3 shows percent grafting increased with the increase of the reaction time up to 1.5 h. In this span of time the activated monomer combines with active sites on the fibre matrix. After 1.5 h monomers find no more reactive sites on fibre backbone and so, become homopolymerized. Hence, at longer reaction time, the percent grafting decreased due to partial dissolution of grafted fibre[18,19].

Grafting onto jute fibre become hardly possible below 50°C due to its rigid cellulosic structure compared with other fibres[18,20]. Figure 4 shows the percent grafting increases initially with the rise of temperature from 50 to 90°C for EMA and from 50 to 80°C for MAN and then falls with further increase of temperature. At 80 and 90°C, the percent grafting of MAN and EMA on bleached jute fibres was 11.3 and 17.6%, respectively. The increasing trend of grafting was due to the increase in the rate of production of active free radicals which increased the

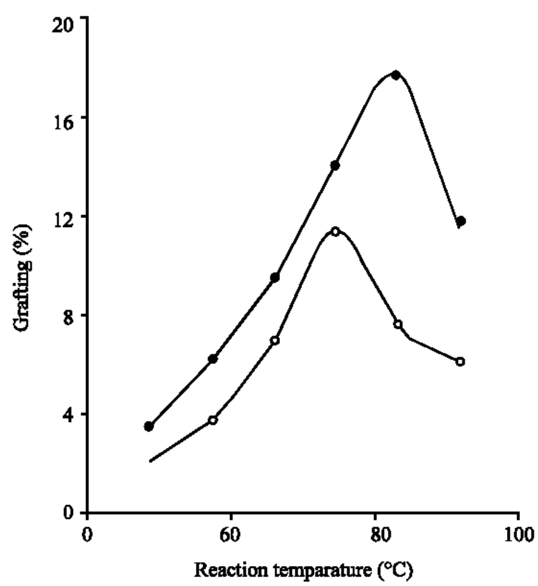


Fig. 4: Effect of reaction temperature on percent grafting of MAN and EMA monomers onto bleached jute fibre (monomer, 70%; $Na_2S_2O_3$-H_2O_2, 1.00%; time, 90 min; liquor ratio, 1:50). ○, MAN; ●, EMA

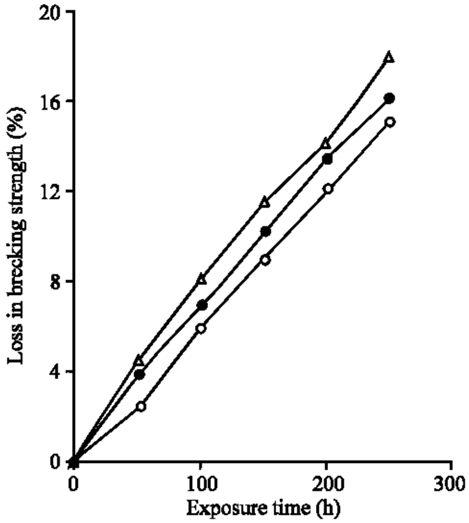


Fig. 5: Effect of sunlight on loss in breaking strength of bleached, MAN-and EMA-modified jute fibres. Δ, bleached jute fibre; ○, MAN; ●, EMA

Table 1: Colour fastness of bleached, MAN- and EMA-modified jute fibres on exposure to sunlight in air

Exposure period (h)	Fastness grade and colour		
	Bleached fibre	EMA modified fibre	MAN modified fibre
0	5 (Cream white)	5 (Cream white)	5 (Cream white)
50	4 (Slightly yellowish)	4-5 (Whiteness decreased)	4-5 (Whiteness decreased)
100	4 (Slightly yellowish)	4 (Slightly yellowish)	4-5 (Whiteness decreased)
150	3-4 (Slightly yellowish)	4 (Slightly yellowish)	4 (Slightly yellowish)
200	3 (Slightly yellowish)	3-4 (Slightly yellowish)	4 (Slightly yellowish)
250	3 (Slightly yellowish)	3-4 (Slightly yellowish)	3-4 (Slightly yellowish)

number of grafting sites at a higher rate. The increase in temperature increased the rate of diffusion of monomer into the jute matrix also contributed for higher grafting[15]. Beyond the optimum temperature the increase in activation energy increased the rate of homopolymerization and premature termination of growing grafted chains.

Physico-chemical characteristics

Effect of sunlight (UV) on the strength of jute fibre: From Fig. 5, it is seen that the loss in breaking strength of bleached, MAN and EMA modified jute fibres are 18.0, 15.2 and 16.1%, respectively on exposure to sunlight in air at 250 h. Loss in breaking strength of EMA grafted jute after 250 h is slightly lower than that of MAN grafted fibres. The loss in breaking strength of bleached (ungrafted) jute fibre is also higher than that of modified jute fibres. The loss in strength of jute took place due to the oxidative changes in presence of moisture and sunlight (UV)[18]. Lower affinity of the grafted jute fibre towards moisture showed less susceptibility to the degrading action of light[3]. Roy[21] showed from his X-ray work that the fibre became more rigid on grafting resisting the penetration of moisture into the active core area of the fibre which ultimately reduced the action of UV towards atmospheric oxidation. As a result, the loss in breaking strength decreased with the increase of polymer loaded onto the jute fibre.

Effect of sunlight (UV) on the yellowing of jute fibre: The yellowing of the bleached and modified fibres are more or less similar. Yellowing of jute fibre was due to the photo-chemical and photo-oxidative changes of lignin into the quinonoid type compound in presence of moisture and light[22]. As the grafted jute fibre shows less affinity towards moisture can somehow protect the yellowing trend of the fibre. Polymer loaded in case of EMA modified fibre was more, so good result was found as compared to that modified with MAN (Table 1).

CONCLUSIONS

Jute, the reactive fibre, can be protected from the adverse environment by blocking its reactive sites with suitable vinyl monomers i.e. MAN and EMA. This modification can bring out some physico-chemical changes in fibre structure that sustains its textile properties for comparatively longer period of time.

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