

Novel Jute Yarns Grafted with Methyl Methacrylate

M. Montazer, A. Salehi

Textile Engineering Department, Amirkabir University of Technology, Tehran, I.R. Iran

Received 15 July 2006; accepted 25 August 2007

DOI 10.1002/app.27342

Published online 30 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This research work involves graft copolymerization of jute fibers with methyl methacrylate (MMA), initiated by ceric ions, and optimization of the grafting parameters as a function of different polymerization conditions. It was considered to produce a hydrophobic jute fiber with enhanced properties. To achieve this, the effects of monomer concentration and grafting percentage on FTIR spectra, mechanical properties, moisture regain, oil-adsorption capacity, and surface morphology were investigated, and optimum percentage of MMA with reasonable properties was suggested. The results indicated that ceric ions initiated graft copolymerization of MMA onto jute with 30% of

weight of monomers at optimum conditions of acid concentration and temperature. The FTIR studies proposed grafting of MMA onto jute at hydroxyl groups. The results showed that mechanical properties and moisture regain (%) of samples decrease with increasing of graft percentage. The most remarkable features of this investigation include reducing oil-adsorption capacity with increasing of lipophilic monomer percentages after one limitation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2067–2073, 2008

Key words: jute; methyl methacrylate; grafting; oil adsorption; moisture regain

INTRODUCTION

In the recent years, chemical modification of jute fibers through grafting has received considerable interest due to the wide variety of monomers available.^{1–3} Currently, grafting has become a potentially powerful method for producing substantial modification of the properties of natural fibers with the retention of its desirable properties.³ Chemically, jute is a lignocellulosic fiber. Unlike cotton fiber, jute is not uniform in chemical composition, which is evidenced by the multicellular structure of the fiber.² Jute fiber is facing tough competition from the synthetic fibers as the latter often offer certain advantages in terms of many physical properties, durability, and production economics.⁴ The survival of jute in competition with the synthetic fibers lies in the retention of jute as a preferred material in the eyes of the consumer, but it must be constantly developed and improved to retain that status. Therefore, grafting onto jute has been receiving considerable attention in recent years to incorporate the desired properties.^{2,4}

Vinyl monomer can be grafted onto the jute fiber with different initiator systems, such as ceric salts. Ceric salts in aqueous acidic solution either by themselves⁵ or in combination with reducing

agents^{6–8} graft the vinyl monomer onto natural and synthetic fibers. A number of studies have been conducted in the past to deal with the mechanism and the kinetics of graft copolymerization involving different monomers and natural fibers. The reducing agents could be alcohols,^{8–10} aldehydes, ketones,¹¹ and carboxylic acids.¹²

The effect of using $\text{FeCl}_3\text{-H}_2\text{O}_2$,¹³ $\text{K}_2\text{S}_2\text{O}_8$, KMnO_4 initiator systems for rafting on tensile properties of jute fiber was studied.^{14,15}

However, to develop jute applications such as jute composites with better mechanical properties and environmental performance, it is necessary to impart hydrophobicity to jute fibers. A decrease in moisture regain has been observed for several naturally occurring lignocellulosic fibers by grafting with vinyl monomers such as methyl methacrylate (MMA), ethyl acrylate, styrene, vinyl acetate, acrylonitrile, etc.¹⁶

This research work deals with the production of hydrophobic jute for using in mist and wet places with low moisture regain and low tendency for oil adsorption. For this propose, the jute yarns were firstly bleached by sodium chlorite to reduce the lignin content of the yarns and then grafted with MMA using Ce^{4+} in the presence of sulfuric acid. Different properties of the various grafted yarns were examined. The results of graft copolymerization of MMA onto bleached jute yarn were reported. The most interesting results were formation of grafted jute yarns with lower moisture regain and, at the same time, lower oil retention.

Correspondence to: M. Montazer (tex5mm@aut.ac.ir).

MATERIALS

The jute yarns were gifted by Ecbaton Carpet of Iran, MMA purchased from Merck (Tehran, Iran), and other reagents were of analytical grade.

EXPERIMENTAL

Raw jute yarn was first washed in 5% (w/v) sodium hydroxide solution at 80°C for 30 min and then bleached with sodium chlorite (5 g/L) solution in acidic condition using formic acid at 100°C for 25–30 min and L : G of 30 : 1. This was done to reduce the lignin content of the jute yarns. The bleaching method used was the optimum bleaching conditions to reduce the lignin content with lowest possible damages to the mechanical properties of the yarns. The prepared bleached jute yarns were finally dried and prepared for graft copolymerization.

Bleached jute yarns were treated with solution containing ceric ammonium sulfate [30%, o.w.f. (on weight of fiber)] and sulfuric acid (0.5M) at room temperature for 10 min. MMA monomer was then added to the solution to initiate the polymerization at 50°C.

The concentration of MMA monomer was varied from 100 to 300% of the weight of jute yarns and the time of reaction was varied from 1 to 4 h.

MMA homopolymer and oligomers adhering to the jute yarns and present within the jute yarns were removed by treating with hot dimethyl formamide (DMF) at 70°C for 30 min. The grafted jute yarns were then washed with hot water and dried at room temperature.

The weight gain was calculated by increase in the weight of controlled jute yarn after MMA graft copolymerization as follows:

$$\text{Weight gain \%} = \left[\frac{(\text{dry weight of grafted jute} - \text{dry weight of original jute})}{\text{dry weight of original jute}} \right] \times 100$$

FTIR spectrum

Infrared adsorption was measured by KBr disk method using Nicolet NEXUS 670 spectrometer.

Mechanical properties

The mechanical properties of the samples were measured on Instron from Textechno. In all samples, the elongation rate was selected 5 mm/min and the length of each sample was 10 cm.

Scanning electron microscopy

The morphological structure of grafted jute yarns was examined after gold coating (3AL-TEC systems)

with PHILIPS XL30 scanning electron microscopy (SEM) at an acceleration voltage of 15 keV. The magnification used was 1000× and 2000×.

RESULTS AND DISCUSSION

Effect of reaction time

The jute fiber samples were pretreated with ceric ammonium sulphate and sulfuric acid for 10 min at 30°C with L : G of 30 : 1. This was done to prepare the jute fibers for grafting, otherwise the efficiency of grafting would be very low. After passing the nitrogen through the reaction vessel and increasing the temperature to 50°C, the MMA with concentration of 100% (o.w.f.) was added and the grafting carried out over 4 h. Finally, the sample was treated with DMF for 30 min and then washed with cold water for 10 min to remove all of the oligomers, homopolymers, and untreated monomers from the sample. The samples were then dried and weighed. The graft copolymerization was carried out for different times ranging from 1 to 4 h. The results are showed in Figure 1.

The mechanism of graft copolymerization of vinyl monomers onto cellulosic materials has been proposed by Chauhan et al.¹⁷ According to their proposal, ceric ions form complexes with glycolic hydroxyl groups of glucopyranoside at C2 and C3 carbons and these complexes disproportionate to produce cellulosic radicals. The monomers also formed similar complexes and then grafting was initiated on the monomer and the cellulosic chains.

The weight gain after 1 h was about 7%. With increasing time to 2 h, weight gain increased to 16%, and finally, after 4 h the weight gain was about 35%. It can be proposed that increasing the reaction time may increase the rate of chain transfer reaction and the homopolymer chains can link to the cellulosic chains on CHOH radicals. It can also be explained by the availability of the monomer in the swollen phase which increases with time. This is in agreement with the work of Mohanty and Singh, which reported similar results on grafting of MMA onto jute by cerium-DMSO initiator system.¹³

It can be concluded that with increasing of reaction time to 4 h, the weight gain increases.

Effect of acid concentration

Sulfuric acid is necessary for graft copolymerization of MMA onto jute by ceric ions. The main purposes of using sulfuric acid are salvation of ceric ammonium sulphate and activation of initiator on the cellulosic chains to produce free radicals. Various concentrations of acid were used and the results are demonstrated in Figure 2.

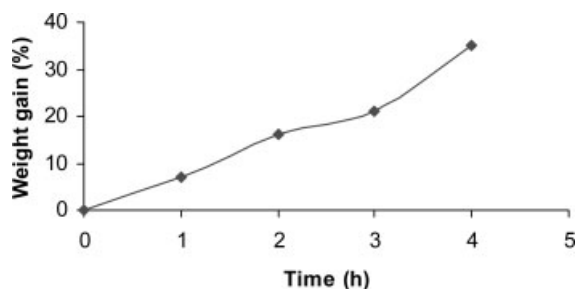


Figure 1 Effect of reaction time on weight gain.

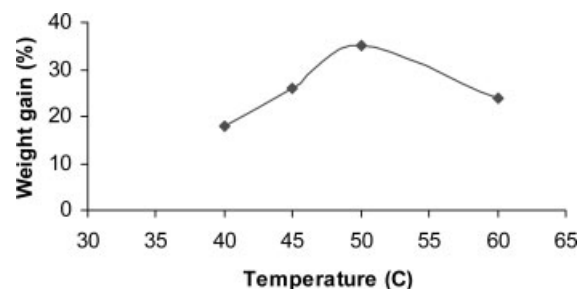


Figure 3 Effect of temperature on weight gain.

It can be seen from Figure 2 that the existence of acid is necessary for the initiation of the copolymerization as no weight gain occurs without acid. This means that probably no free radicals are produced without acid. Increase of acid concentration up to 0.05 mol increases the weight gain and further increase has an opposite influence on the weight gain. It can be suggested that at lower concentration of acid, the initiator was activated, polymerization was initiated, and branches of MMA polymers formed on the cellulosic chains. However, increasing of acid concentration may increase the degradation of cellulosic chains and cause reduction of weight gain.

Effect of temperature

The results of influence of temperature on weight gain are illustrated in Figure 3. As temperature is an effective parameter in polymerization, the optimum temperature should be considered. Increasing temperature up to 50°C leads to increasing of weight gain due to activation of monomer and initiator. However, further increase of temperature reduces the weight gain, which is the result of increasing of kinetic energy that causes more collision of monomers and forms the homopolymer easily.

Effect of monomer concentration

The effect of MMA monomer concentration on jute grafting at 50°C is indicated in Figure 4.

The results in Figure 4 show very low grafting of MMA with concentration of less than 100% (o.w.f),

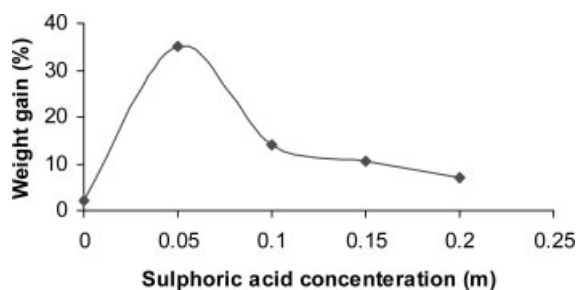


Figure 2 Effect of sulfuric acid concentration on weight gain.

but increasing of monomer concentration increases the grafting percentage. However, 300% of MMA causes the weight gain raise to 123%. With 50% MMA, the polymerization conditions lead to the formation of MMA homopolymers. The amount of monomer grafted onto jute is less than 50% which can be an evidence of homopolymers formation. Increasing of monomer concentration leads to increase of the tendency of monomer toward the fiber, and hence copolymerization occurs easily and grafting rate increases.

These results show that jute yarns have a low reactivity to MMA monomer, or cerium ammonium sulfate is not a very effective initiator system for grafting of MMA onto jute yarns.

Effect of initiator concentration

Initiator concentration versus weight gain is illustrated in Figure 5. Increasing of the initiator concentration increases the weight gain. This means that higher amount of initiator can be effective for producing higher weight gain. However, this initiator is expensive and the rate of increase becomes lower with increasing of concentration. This recommends the usage of optimum concentration of initiator of 30% (o.w.f).

FTIR studies

FTIR spectra of raw and bleached jute yarns are shown in Figure 6. It can be observed that both spec-

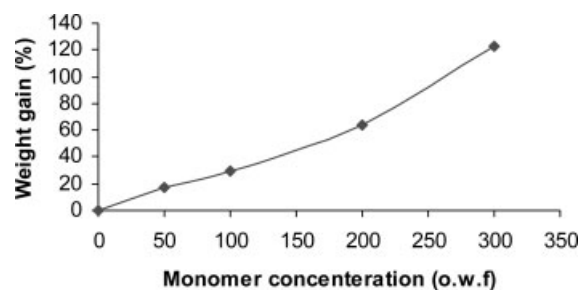


Figure 4 Effect of monomer concentration on weight gain.

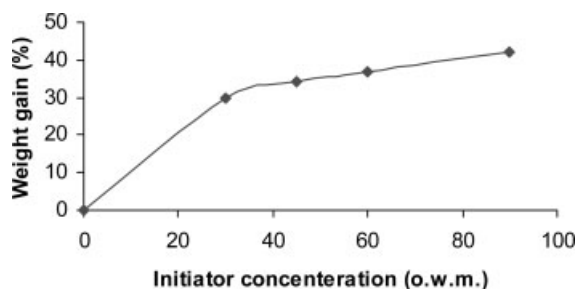


Figure 5 Effect of initiator concentration on weight gain.

tra indicate a characteristic broad absorption band of the hydroxyl group around 3400 cm^{-1} of cellulosic chain. However, both spectra seem to be similar. This suggested that the chemical structure of the jute yarns has not been changed by the bleaching with sodium chlorite.

The FTIR spectra of the chemically modified jute with MMA at 25 and 130% (weight gain) and the bleached jute yarn are shown in Figure 7. It can be seen that the spectrum of bleached jute yarns shows the characteristic broad absorption peak at about 3400 cm^{-1} , whereas the spectrum of MMA-grafted jute shows an additional peak at 1731 cm^{-1} that relates to ester group. One would have expected that the intensity of $-\text{OH}$ peak reduced as a result of grafting, since it is the probable site for grafting.

The ratio of intensity of hydroxyl groups (3438 cm^{-1}) to ester groups (1731 cm^{-1}) decreases with increasing of weight gain. This means that higher amount of grafting occurred on the yarns with higher weight gain. These results may show that the jute yarn grafted with MMA.

Mechanical properties

The effect of grafting on the mechanical properties of jute yarns is showed in Table I.

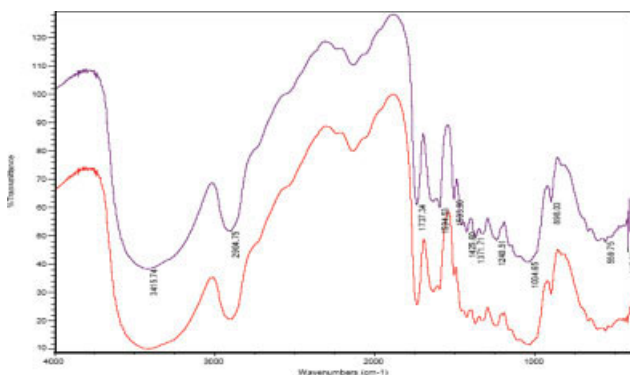


Figure 6 FTIR spectra of (a) raw jute yarn and (b) bleached jute yarn [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

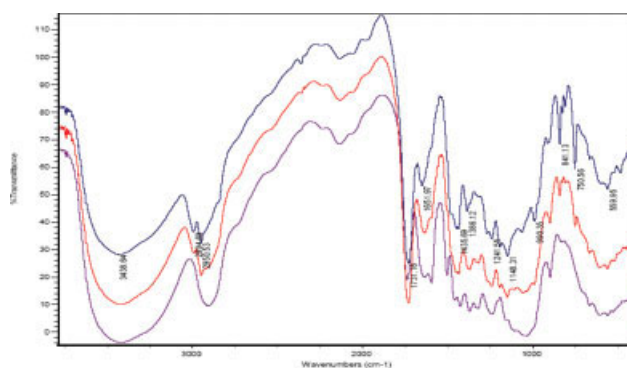


Figure 7 FTIR spectra of a (a) bleached jute yarn, (b) 25% MMA-grafted jute yarn and (c) 130% MMA-grafted jute yarn. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The initial jute yarn and washed jute yarn indicated a similar tenacity, load, and elongation. This means that washing has no influence on the mechanical properties of the jute yarn (Table I). The results of breaking load, tenacity, and elongation in Table I show that the tensile properties of the bleached jute yarns decrease. This can be due to the acidic media used for bleaching, which has negative effects on the mechanical properties of jute yarns and damages the jute yarns. Grafting of jute yarns in acidic media with MMA also has negative influences on the mechanical properties of jute yarns. As the grafting percentages on the jute yarns increase, the more acidic conditions apply and result in a higher reduction in tenacity, load, and elongation of the treated yarns.

The reasons for decreasing of breaking load and tenacity could be as follows:

1. Breaking of interchain bonds and decreasing of the polymerization degree of cellulose during bleaching and polymerization process as a result of using chlorite, ferric salt, and sulfuric acid.
2. Disorientation of the cellulosic chain of jute due to growing of MMA chains.
3. Increasing of weight at constant length of jute yarns.

Oil retention

For investigation of oil retention, the controlled jute yarn and grafted jute yarn with different weight gains were soaked in 100 mL of crude oil at room temperature for 30 min.

The samples were then pressed with 450 gram force (grf) for 20 min to remove additional oil. The percentage of retention oil is calculated as follows:

$$\% \text{ retention oil} = (W_2 - W_1)W_1 \times 100$$

TABLE I
Effect of MMA Concentration on Mechanical Properties of Modified Jute Yarn

Sample	Tenacity (cN/tex)	Elongation at break (mm)	Load (N)
Initial jute	11.02	28.24	47.81
Washed jute	11.01	28.24	47.80
Bleached jute	7.17	20.68	39.18
25% grafted jute with MMA	3.32	16.38	23.19
40% grafted jute with MMA	3.05	15.94	13.24
105% grafted jute with MMA	0.87	15.81	8.56
130% grafted jute with MMA	0.63	13.11	4.78

where W_1 is the weight of the yarn before oil treatment and W_2 is the weight of jute yarn after oil treatment. Table II shows the results of oil treatments.

The initial jute yarn has 225% oil retention. This is related to the open structure of the jute yarn, and the oil can wick through the open capillary of the jute fiber inside the fibers. When the jute yarns were bleached with sodium chlorite, some of the impurities were removed from the fibers and the fibers were left with more open structure that allows the oil to easily wick through the jute yarn and produces more spaces for retention of oil inside the bleached jute yarns. The results can be divided into three categories for the grafted yarns. The oil retention of control jute yarn was 225%, and with increasing of weight gain to 25% the oil retention decreased to 132%. In the second category, with increasing of weight gain to 41% the oil retention increased marginally, and in the third category, with increasing of weight gain the oil retention decreased again.

Poly MMA is a hydrophobic polymer and grafting of MMA onto jute was considered in the pith channel of jute fibers structure. Therefore, grafting caused the decreasing of capillary force in the pith channel, leading to the decrease of oil retention. However, the rate of decrease is high for the first 25% of grafting and is low for the higher percentages of grafting.

Moisture regain

For determination of moisture regain (%), all of the sample were pretreated at 50% relative humidity at

25°C for 24 h and then dried in oven at 60°C for 30 min.

Moisture regain of controlled jute yarn was 12.8% and the reduction of regain % calculated as follows:

$$\text{Reducing percentage} = \left(\frac{\text{regain of control jute} - \text{regain of grafted jute}}{\text{regain of control jute}} \right)$$

The effect of graft yield on the moisture regain is shown in Table III.

Poly MMA is a hydrophobic polymer, and grafting of this polymer onto jute yarn and filling of pith channel caused reduction of moisture regain. It can be seen from Table III that with increasing of grafting percentages, the moisture regain reduces. This means that increasing of MMA on the jute fiber may fill up the capillary spaces present on the surface and inside the fibers and cover up the fiber surfaces with the nonwater-absorbable materials. This reduces the moisture regain and makes the yarn more hydrophobic. This can protect the yarn from the water and microbial attack.

The interesting feature of these later results is the decreasing of both oil retention and moisture regain in the MMA-grafted jute yarns. The reduction of the moisture regain is a predicted result as some hydrophilic groups of hydroxyl reacted with MMA and more hydrophobic chains are introduced to the yarns. It was also proposed that the oil retention increases for the MMA-grafted jute yarns. However, the actual results were opposite and the reason was due to filling up the pith channel of the jute yarns by the MMA.

TABLE II
Oil Retention of Jute Yarns

Sample	Oil retention (%)
Initial jute yarn	225
Bleached jute yarn	276
25% grafted jute with MMA	132
41% grafted jute with MMA	137
105% grafted jute with MMA	113
130% grafted jute with MMA	97

TABLE III
Percentages of Reduced Moisture Regain Capacity

Sample	Moisture regain reduced to initial jute yarn (%)
25% (GY) with MMA	23.5
41% (GY) with MMA	26.23
105% (GY) with MMA	40.32
130% (GY) with MMA	49.25

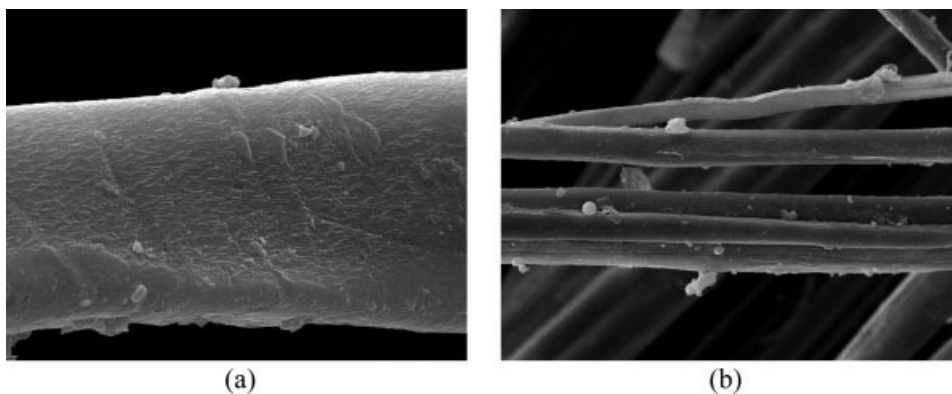


Figure 8 SEM of original jute yarn: (a) $\times 2000$, (b) $\times 1000$.

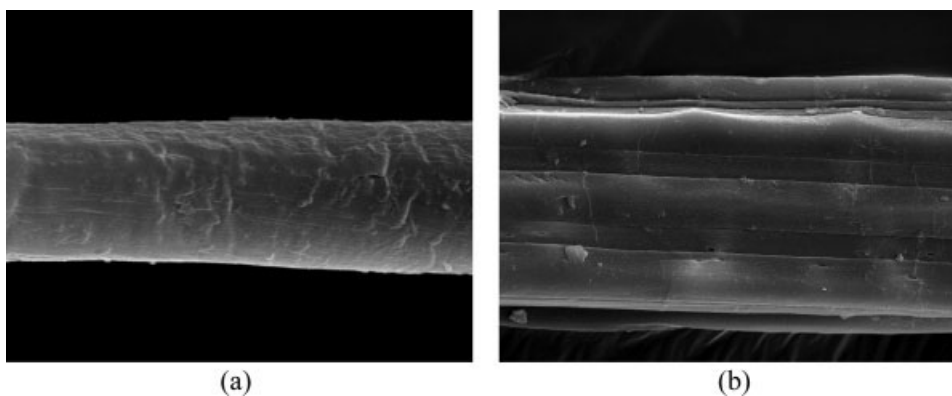


Figure 9 SEM pictures of bleached jute yarn: (a) $\times 2000$, (b) $\times 1000$.

Morphological structure

The morphological structure of MMA-grafted jute yarns was examined by SEM.

Surface structure is an effective parameter in handle; if surface of yarn fabric was smooth then handle of this fabric will be soft.

Figures 8 and 9 show that the surface of raw jute fiber in comparison with bleached jute fiber has not

been obviously changed. Both samples have a smooth surface. However, the original jute yarn contains some impurities that can be seen on the fiber surface (Fig. 8). These impurities have been removed in the bleached sample (Fig. 9).

Figures 10 and 11 show the MMA-grafted jute fiber with 25 and 130% of weight gain. These figures indicate that with increasing of weight gain, the smoothness of jute fibers will be reduced and more

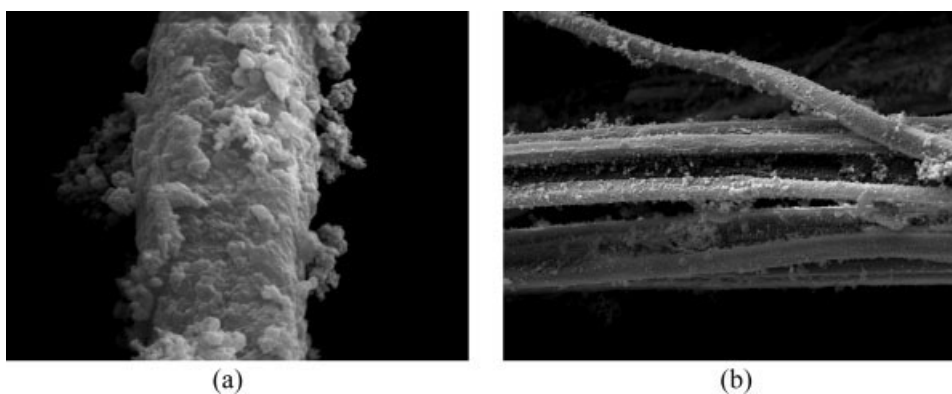


Figure 10 SEM pictures of 25% grafted jute yarn with methyl methacrylate: (a) $\times 2000$, (b) $\times 1000$.

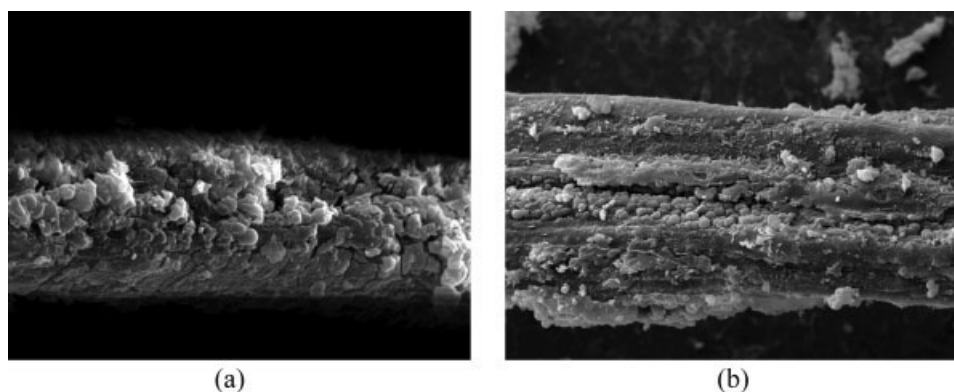


Figure 11 SEM pictures of 130% grafted jute yarn with methyl methacrylate: (a) $\times 2000$, (b) $\times 1000$.

MMA grafted on the fiber surfaces. It can be seen from Figure 11 that the fiber surface is completely covered by the MMA polymers.

When the weight gain is high, the grafting occurred on the surface of fibers and then fibers adhere together and increase the roughness of jute yarns.

CONCLUSIONS

This work was carried on grafting of jute with MMA to obtain jute with novel properties for using in moist and wet areas. The ceric ions initiated the graft polymerization of MMA onto jute with 30% of weight of monomers at optimum conditions. The usage of acid should be optimized and control of temperature is crucial in copolymerization. FTIR spectra confirm that the grafting of MMA onto jute occurs at hydroxyl groups. The moisture regain of the jute yarns reduced significantly by grafting treatment with MMA. However, the oil retention also decreases by grafting of jute yarns with MMA. The tenacity and elongation at break decreases for grafted jute yarns with increasing of grafting. This work shows that more hydrophobic and rigid jute

fibers with lower capacity for oil retention can be made by grafting with MMA.

References

1. Sikdar, B.; Basak, R.; Mitra, B. *J Appl Polym Sci* 1995, 55, 1673.
2. Misra, M. *J Appl Polym Sci* 1987, 33, 2809.
3. Mohanty, E.; Singh, B. *J Appl Polym Sci* 1998, 69, 2569.
4. Mohanty, A.; Patnaik, S. *J Appl Polym Sci* 1989, 37, 1171.
5. Nayak, N. C.; Das, H. K.; Sing, B. C. *J Appl Polym Sci* 1991, 42, 1391.
6. Rout, A.; Rout, S. P.; Singh, B. C. *Makromol Chem* 1977, 178, 639.
7. Rout, A.; Rout, S. P. *Eur Polym J* 1977, 13, 467.
8. Katai, A.; Kulshrestha, V. K. *J Polym Sci Part C: Polym Symp* 1963, 2, 403.
9. Mino, G.; Kaizerman, S. *J Polym Sci* 1959, 38, 393.
10. Narita, H.; Okamoto, S. *Makromol Chem* 1969, 125, 15.
11. Anthanarayanan, V. S.; Santappa, M. *Proc Indian Acad Sci* 1965, 62, 150.
12. Subramanian, S. N.; Santappa, M. *J Polym Sci Part A: Polym Chem* 1972, 10, 797.
13. Mohanty, E.; Singh, B. C. *J Appl Polym Sci* 1998, 69, 2568.
14. Mukhopadhyay, A. K.; Sakar, B. K. *J Appl Polym Sci* 1982, 27, 4525.
15. Tripathy, S. S.; Jena, S. *J Appl Polym Sci* 1985, 30, 1399.
16. Varma, D.; Murali, S. *Indian J Fibre Text Res* 1989, 14, 9.
17. Chauhan, G. S.; Misra, B. N.; Kaur, I.; Singha, A. S.; Kaith, B. S. *Indian J Fibre Text Res* 1999, 24, 269.