

Original Article

# Dyeing and Thermal Behavior of Ethyl Acrylate and 2-Hydroxyethyl Methacrylate-Modified Jute Fibres

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**Abstract** - This paper deals with the effect of dyeing and thermal behavior of ethyl acrylate and 2-hydroxy ethyl methacrylate-modified bleached jute fibre in a  $K_2S_2O_8/FeSO_4$  redox system. The graft yield increased with the increase of monomer, initiator, and reaction time up to certain values, and then it decreased. Under optimum conditions, the highest graft yield for EA-modified and 2-HEMA-modified bleached jute fibre was 22.5% and 24.79%, respectively. Fourier Transform Infrared Spectroscopy was used to confirm the presence of monomers on the treated jute fibre. Thermogravimetric analysis was used to study the thermal behavior of the modified fibre. It is observed that jute fibre dyed with Reactive Orange 14 and Direct Blue 1 exhibited better colour fastness on exposure to sunlight in the air than dyed with Reactive Brown 10 and Direct Orange 1. Modified jute fibre showed improved thermal and mechanical stability as well as dyeability the fibre.

**Keywords** - Jute fibre, Grafting, Ethyl Acrylate, 2-Hydroxy Ethyl-Methacrylate.

## 1. Introduction

Jute, a lignocellulosic polymer is the most abundant renewable agricultural raw material that plays an important role in the economic development of Bangladesh. Only two of the species, *Corchorus Capsularis* and *Corchorus olitorious*, are cultivated for their fibre. About 95% of the world's production, jute is produced in Bangladesh and India as the worm and humid climate and land, which is constantly enriched by alluvial deposits (mud), are suitable for growing. Jute is used mainly for producing traditional products like hessian, sacking, carpet backing, twine, mats, rope, etc. In recent years, it has been threatened by cheap synthetic fibres that are becoming more popular. Researchers have thought about many eco-friendly alternative fibres and chemical changes because of problems with the environment. So, it is important to improve the quality of jute fibre so that it can be used in business, meet the total fabric needs of the countries that import it, and reduce the amount of competing synthetic fibres that are imported.

Due to a slowdown in the traditional main market for jute, as a packing materials, is being used more and more to make decorative home textiles like curtains, upholstery, floor coverings, soft luggage/fancy shopping bags, wall coverings, wall hangings, and so on [1]. Although jute fibres are widely used to produce multifarious products.

However, it has some inherent drawbacks, e.g. its coarseness, rigidity, photo yellowing, poor colour fastness, etc., which seriously limit its general use, especially for textile purposes. The main technical problem with dyed/printed jute products used for different things is that they don't have the level of colour fastness needed for end-use. Jute is a coarser type of fibre, so its weight per unit area is much higher than that of cotton, wool, or silk. This means that it needs more chemicals and dyes to get the same shade or finish, which means that chemical processing costs more. Chemists who work with textiles find it hard to solve these technical problems that come up when jute is processed chemically. Therefore, to minimize the undesirableness for intensified textile uses, graft copolymerization of some vinyl monomers onto jute fibre has been attempted during recent years using various chemicals, as well as photochemical and radiation-induced methods of initiation.

The graft copolymerization onto jute fibre is a challenging field of research with enormous prospects. It is expected that the properties of the fiber on modification by the grafting process can improve it in such wonderful ways that the modified fibre can be utilized in the manufacture of decent, fine, and good-grade tensile products. Therefore, to minimize the undesirableness for intensified textile uses, graft copolymerization of vinyl



monomers onto jute fibre has been attempted in recent years. Methacrylate monomers can also be used on the jute fibre with a potassium persulfate initiator, which is catalyzed by Fe(II) for the modification of jute. In the present investigation, ethyl acrylate (EA) and 2-hydroxyethyl methacrylate (2-HEMA) were graft copolymerized onto jute fibre using  $K_2S_2O_8$  as an initiator in the presence of  $FeSO_4$  as a catalyst and dyed with reactive and direct dyes. The assessment of colour fastness and breaking strength of the fibre has also been investigated. Then, grafted jute fibers are segmented copolymers with a linear backbone of one composite and randomly distributed branches of other composites.

## 2. Experimental

### 2.1. Materials

Jute fibre was collected from Rajshahi Jute Mills and required chemicals like sodium chlorite, sodium hydroxide, ethyl acrylate (EA), 2-hydroxy ethyl-methacrylate (2-HEMA), potassium persulphate, methyl acrylate, dyestuffs, and other essential analytical grade chemicals were purchased from BDH, Merck, Sigma-Aldrich, etc.

### 2.2. Methods

#### 2.2.1. Bleaching of Jute Fibre

By the term “bleaching”, we mean to impart whiteness to fibres and fabrics by treating them with some agents known as bleaching agents. These agents fall into two categories:

1. Oxidizing bleaching agents (such as sodium chlorite ( $NaClO_2$ ), Sodium hypochlorite ( $NaOCl$ ), Calcium hypochlorite [ $Ca(OCl)_2$ ], hydrogen peroxide ( $H_2O_2$ ), bleaching powder [ $Ca(OCl)Cl$ ], etc.), and,
2. Reducing bleaching agent. (such as sulfur dioxide [ $SO_2$ ], sulfurous acid [ $H_2SO_3$ ] and etc.)

For each gram of jute fibre, 50 ml of 0.5% sodium chlorite was taken and, bleaching was conducted at pH 4, and the temperature was maintained within 85-90 °C for 90 minutes. After the bleaching, fibre was washed well with distilled water, immersed in 0.2% sodium disulfite ( $Na_2S_2O_5$ ), and dried in open air.

#### 2.2.2. Modification Process of Jute Fibre

The graft copolymerization of jute fibre was done in an Erlenmeyer flask with a 100 mL stopper. Based on the weight of the fibre, polymerization was done with 240–330% monomers (Ethyl Acrylate and 2-Hydroxyethyl Methacrylate), 18–25%  $K_2S_2O_8$  as an initiator, and 1–6%  $FeSO_4$  as a catalyst. At 60–110°C and a 1:50 ratio of fibre to liquid. The initiation reaction of polymerization is carried out by initiators. Initiators are thermally unstable compounds and decompose into products called free radicals. These free radicals can attack monomers and initiate the polymerization reaction. The polymerization reaction took 30–150 minutes. When the time was up, the jute fibre was washed three times

with warm distilled water and then dried Graft yield using the following formula [2]:

$$\text{Graft yield, \%} = \frac{W_1 - W_0}{W_0} \times 100$$

Where  $W_1$  is the weight of the grafted jute fibre after modification,  $W_0$  is the weight of the un-grafted jute fibre before modification.

#### 2.2.3. Dyeing of Jute Fibre

Dyeing of textile materials is a process of applying a dye so that the materials not only change their colour but also quickly retain the dye [3]. Direct dyestuffs (direct orange 31 and direct blue 1) were dissolved by first pasting with cold water, and then hot water was added. The fibre liquor ratio was maintained at 1:30. Dyeing was carried out at 90 °C for 60 minutes. Besides, reactive dyes, reactive orange 14, and reactive brown 10 were taken for this experiment. Dyeing was carried out at 60°C for 60 minutes in a water bath with stirring.

### 2.3. Instrumental Analysis and Characterization

#### 2.3.1. FTIR Analysis

The FTIR spectra of alkali-activated bleached and grafted (with EA and 2-HEMA) jute fibres were recorded by the FTIR spectrophotometer (FTIR-8900, Shimadzu, Japan). About 2% of the powder sample was mixed with KBr, and IR spectra of the sample were measured within the range 4000-400  $cm^{-1}$ .

#### 2.3.2. Thermal Analysis

The TGA of alkali-activated and modified jute fibre (4-6 mg) was measured with a TGA analyzer (SEIKO-EXTAR TG/DTA-6300, SEIKO, Instrumental Company, Japan). The tests were carried out between 30° to 700° C. The heating rate and the airflow rate were 20°C/min and 200 ml/min.

#### 2.3.3. Tensile Strength Test

The breaking strength of the jute was measured by using the tensile strength tester (Torsee's Scopper Type-OS-100). Jute fibres were cut into equal pieces of the length of 30 cm (weight 0.5gm) and the length of each specimen between the jaws was maintained at 10 cm. Then, the breaking strength was measured, and the average of 10 readings was taken.

#### 2.3.4. Colour Fastness Test

A colour fastness test was carried out on modified jute fibres. Specimens of the fibres were attached separately on a board by a glass rod and placed under the sun in the open air for six hours each day and continued for 250 hours. After every 50 hours, the change in colour of the specimens was assessed by the Greyscale [4]. To test the colour fastness to washing, a bath was prepared with 5 gm of wheel soap per liter of distilled water. The fibre liquor ratio was 1:50. One gram of dyed jute fibre of length 10 cm was entered into the bath, and the bath temperature was maintained at 50±2°C for 30 minutes. The changing colour and the staining of the fibre were assessed with the Greyscale [5].

### 3. Results and Discussion

#### 3.1. Optimization of Graft Copolymerization

The following parameters were considered: monomer concentration, initiator concentration, catalyst concentrations, modification temperature, and modification time to select the optimum conditions of modified jute fibre with EA and 2-HEMA [6]. In the experiment, it was seen that the percentage of graft yield of EA and 2-HEMA increased with increasing monomer percentage, as shown in Figure 1(a). The effective monomer concentrations were 80% for EA, and 70% for 2-HEMA, and the corresponding graft yield and efficiency were 22.5 and 24.79% and 26.13 and 35.24%, respectively.

The graft yield increased as the concentrations of both monomers increased. After a certain value, it declined as the monomer concentration increased further. This is a result of the increasing homopolymerization rate rather than grafting at the increased monomer concentration. The effective concentrations of potassium peroxodisulphate as an initiator were 4.5 % for EA and 4% for 2-HEMA, corresponding to 23.81% and 26.12% graft yield, respectively.

From Figure 1(b), the emergence of graft yield may be due to the creation of a large number of grafting sites on the cellulose backbone of jute fibre. At the high concentration of the initiator, an excess of activated monomers becomes available. These resulted in the synthesis of homopolymers, leading to a monomer deficiency close to the cellulose macroradicals [7].

Consequently, the graft yield begins to decline. The stunting effects of graft yield at increasing concentrations of  $K_2S_2O_8$  may be a result of homopolymerization predominating over grafting. The termination of an expanding grafted chain is mostly caused by free radicals, which occur from the breakdown of an excess initiator.

The concentrations of catalyst,  $FeSO_4$ , were 5 % for EA and 4.5% for 2-HEMA, corresponding to 23.8% and 26.12% graft yield and 29.76% and 37.31% grafting efficiency, respectively and is shown in Figure 1(b). Then, the graft yield % decreased. As the concentration of the catalyst increases, more  $Fe(II)$  ions are generated. Additionally, more reactive sites appear on the surface of the jute.

From Figure 1(c), it was observed that the graft yield grafting efficiency and homo-polymer of EA increased by increasing the ferrous sulfate concentration up to 5% for EA and up to 4.5% for 2-HEMA. Then, it decreased gradually as the catalyst concentration increased.

Grafting efficiency and graft yield increases up to a certain concentration of catalyst, but above this concentration, they decrease. The decrease in graft yield and grafting efficiency beyond 5% for EA and 4.5% for 2-HEMA

may be attributed to a detrimental factor arising from excess  $Fe(III)$  ions produced on oxidation of  $Fe(II)$ , leading the retardation of rate through premature termination of the growing grafted chains [8, 9]. It was also observed from Figure 1(c) that the catalytic sensitivity of 2-HEMA was more than that of EA. This is caused by the fact that 2-HEMA is sensitive to both  $Fe(II)$  and  $Fe(III)$ , which is oxidized from  $Fe(II)$ . However, EA is less sensitive to  $Fe(II)$ . It is assumed that the formation of  $Fe(III)$  retard the rate of grafting. The effective concentrations of ferrous sulfate as a catalyst are 5% for EA and 4.5% for 2-HEMA, corresponding to 23.82% and 24.98% graft yield and 29.77% and 35.68% grafting efficiency, respectively.

Figure 1(d) demonstrates that graft yield increased as the reaction time increased, up to 150 minutes for EA and 90 minutes for 2-HEMA modified jute fibre. During this period, the activated monomer interacted with the active sites of the fibre matrix. After the optimum time, the monomers explored more reactive sites on the cellulose fibre backbone and became homopolymerized. Again, longer reaction times reduced graft yield. This could be the result of the partial breakdown of the grafted bleached jute fibre.

Figure 1(e) depicts the influence of polymerization temperature on EA and 2-HEMA grafting onto bleached jute fibre. The increased graft yield up to 60°C may be recognized [10].

- i) Increase in the rate of production of active free radicals, which increases the number of grafting sites at a higher rate.
- ii) An increase in temperature increases the rate of diffusion of monomers (EA and 2-HEMA) into the fibre matrix.

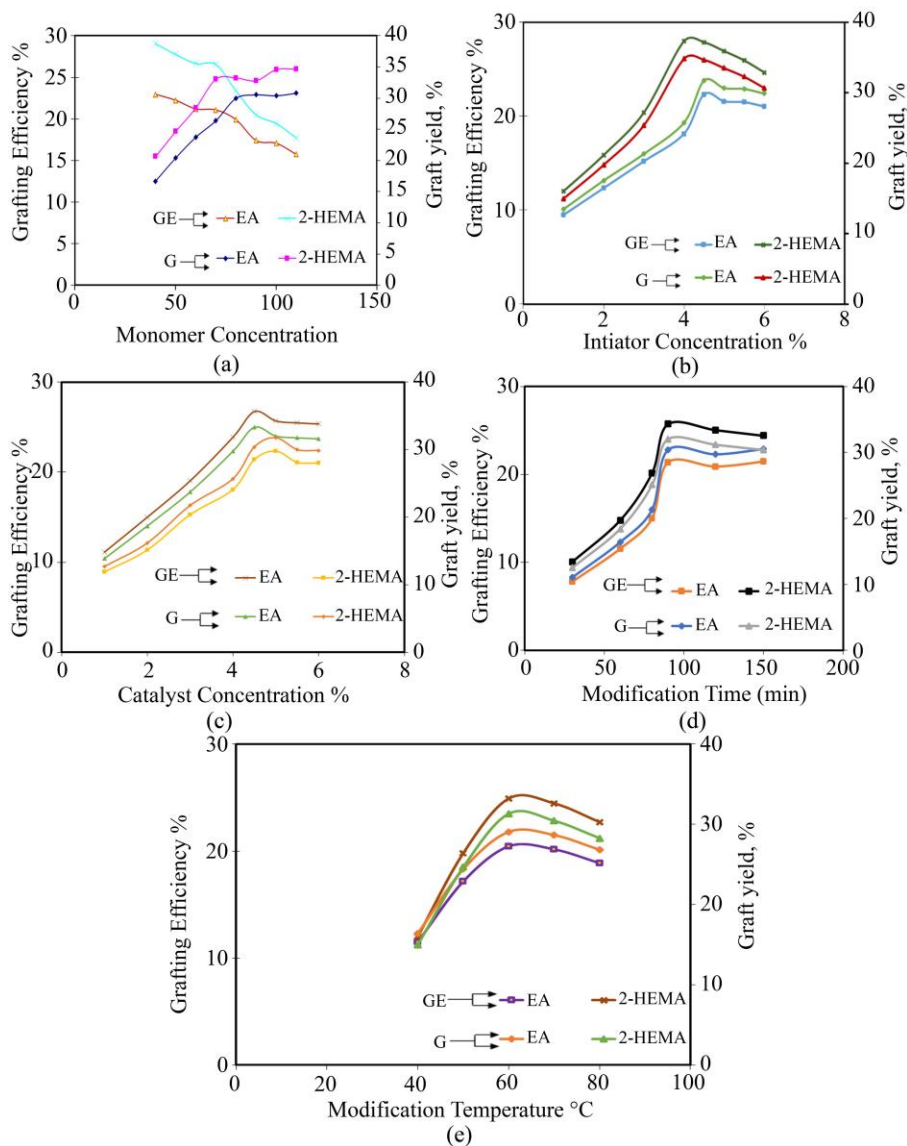
The decrease in graft yield beyond 60°C, both for EA and 2-HEMA, may be attributed [11].

- i) The increase in activation energy for graft copolymerization
- ii) Premature termination of growing grafted chains by excess  $Fe(III)$  ions produced on oxidation of  $Fe(II)$  ions.

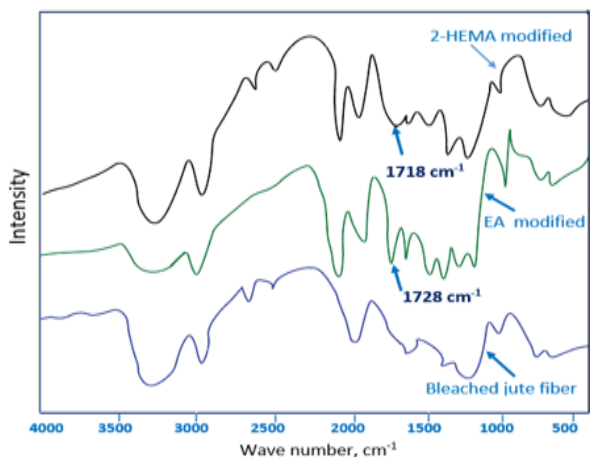
The effective modification temperature for both EA and 2-HEMA was determined to be 60°C. At the optimal temperature, the graft yield and grafting efficiency of EA and 2-HEMA are 21.8% and 27.25%, respectively, and those of 2-HEMA are 23.26% and 33.22% respectively.

#### 3.2. FTIR Analysis

The FTIR spectra of bleached jute fibre and grafted jute fibres were mostly similar except for the new additional peak in the grafted jute fibre. The absorption band appeared at around 1728  $cm^{-1}$  for EA and around 1718  $cm^{-1}$  for 2-HEMA as a result of (ester group) stretching in the grafted fibres [12-14], as shown in Figure 2, which ensured the successful grafting of jute fibre with monomers.



**Fig. 1** Graft yield and Grafting efficiency of EA and 2-HEMA by analyzing the parameters (a) Monomer concentration, (b) Initiator concentration, (c) Modification Temperature, (d) Catalyst Concentration and (e) Modification time



**Fig. 2** FTIR spectra of bleached, EA-modified, and 2-HEMA-modified jute fibre

### 3.3. TGA Analysis

It is observed from Figure 3 that the loss in weight up to 294°C for alkali-activated bleached fibre was around 6.6% and that for EA and 2-HEMA modified fibres were 4.2% and 11.3% up to 315°C and 318°C respectively. The actual pyrolysis region of alkali-activated bleached fibre was 294 °C to 412 °C and that for the EA and 2-HEMA modified fibres were 315°C to 422°C and 318 °C to 422°C respectively. So, as analyzing TGA, the thermal stability of EA and 2-HEMA modified fibres was increased than unmodified fibre, which might have happened due to the incorporation of acrylate monomers into the fibre.

### 3.4. DTG Analysis

From Figure 4, it can be seen that the maximum rate of pyrolysis of alkali-activated bleached fibre is 1.197 mg/min,

occurring at 327.4°C. However the rate of pyrolysis of EA and 2-HEMA modified fibres is 0.817 mg/min and 1.195mg/min. at 339.9°C and 353.8°C respectively. This indicates that modified fibre degrades more slowly, even at high temperatures, than unmodified fibre.

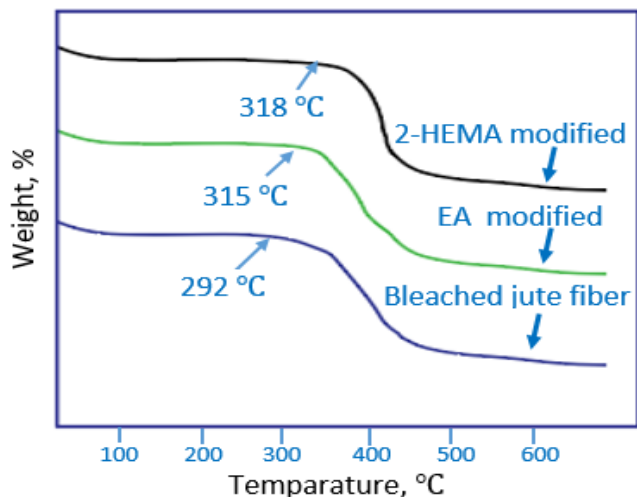


Fig. 3 TGA curves of bleached, EA-modified, and 2-HEMA-modified jute fibre

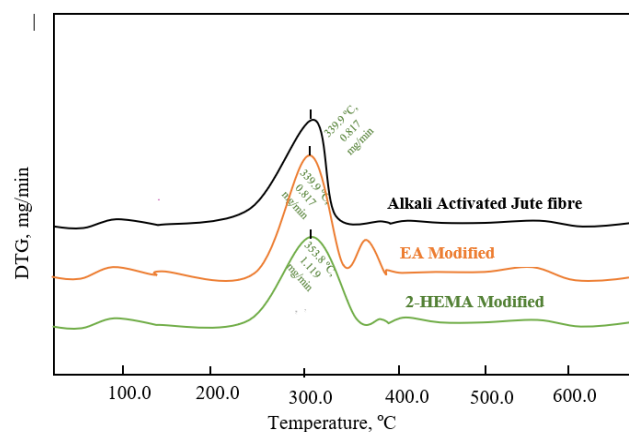


Fig. 4 DTG curves of bleached, EA modified and 2-HEMA-modified jute fibre

### 3.5. Tensile Strength Test

Table 1 shows that the breaking load of modified fibre was higher than that of unmodified fibre. It is also seen that the breaking load of 2-HEMA-modified jute fibre was higher than that of EA-modified fibre. The difference may be due to the fact that 2- HEMA is a rigid polymer, and EA is a soft polymer.

Table 1. Breaking strength of alkali-activated bleached and modified fibres

Breaking Load (Kg/Yarn)		
Bleached jute fibre	Modified fibre with	
	EA	2-HEMA
27.5	28.91	29.52

### 3.6. Dyeing Characteristics

The process which is used to transfer the colour to the substance being dyed is generally known as dyeing [15]. Dyeing, in the proper sense of the word, has a deeper meaning than merely imparting colour to the fibres; the colour must be uniformly distributed throughout the substance of the fibre [16].

Colour fastness was measured by Grey Scale, Fastness grade 5 is the control. In the colour fastness test, it was seen that the direct dyes (Direct Orange 31 and Direct Blue 1) withstood their colour on bleached and modified jute fibre to a great extent on washing with a soap solution. From the structural feature of the dyes, it was seen that the number and strength of covalent bonds were in the order of Direct Blue 1 > Direct Orange 31.

It was also observed that reactive range 14 exhibited slightly better colour fastness on washing with soap solution than Reactive Brown 10. The variation of covalent bonds might be the cause of showing better colour fastness of Reactive Orange 14.

It was observed that jute fibre dyed with Reactive Orange 14 in the presence of electrolyte  $[Al_2(SO_4)_3]$  exhibited better colour fastness on exposure to sunlight in the air than the fibre dyed with Reactive Brown 10.

From the structure of dyes, it was observed that Reactive Orange 14 contains one di-chloro-tri-azinyl group, whereas Reactive Brown 10 contains one mono-chloro-tri-azinyl group. Thus, the number of covalent bonds between Reactive Orange 14 and the jute cellulose would be more and stronger than that of Reactive Brown 10. So, Reactive Orange 14 exhibited better colour fastness on exposure to sunlight. Similarly, it was observed that jute fibre dyed with Direct Blue 1 exhibited considerably better Colour fastness on exposure to sunlight in the air than Direct Orange 31.

## 4. Conclusion

In the present work, graft copolymerization of two monomers, EA and 2-HEMA, onto bleached jute fibre was revealed. The influence of the graft yield of the monomers on the jute fibre is dependent on both the parameter variables (monomer concentration, initiator concentration, catalyst concentrations, modification temperature, and modification time) and the jute fibre.

FTIR was used to investigate the chemical bond between the monomer and the hydroxyl group of bleached jute fibres. The grafted fibre demonstrated enhanced physicochemical features, such as tensile strength and thermal stability. By means of graft polymerization, a novel form of jute fibre was produced. Such a procedure can render jute fibre more suited for use in the production of clothes, home textiles, etc.

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