A NEW APPROACH FOR GRAFT COPOLYMERIZATION OF JUTE

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Abstract

The graft copolymerization of glycidyl methacrylate (GMA) on jute fibers at ambient conditions is the desired goal. Graft copolymerization of (GMA) on jute fibers was carried out using Ammonium Persulphate Acetone Sodium Bisulphite (APS/ASBS) initiating redox system. The grafting reaction was studied with respect to graft yield (GY), grafting efficiency (GE) and total conversion (TC). Factors such as pH value, liquor ratio (L: R), redox initiator concentration, addition sequence, reaction time, temperature and GMA concentration [M], were investigated. The results obtained showed that the optimal grafting yield is obtained at the following conditions: initiator concentration of 20/40 mmole/l for APS/ASBS respectively, liquor ratio(I:20), pH value 3, time 120 min., temperature 20°C, and monomer concentration [M] 150% based on weight of substrate (OWS). Grafted and scoured jute fibers were characterized via thermal gravimetric analysis (TGA) and infra red spectroscopic analysis (IR).

Key words: Ammonium Persulphate, Acetone Sodium Bisulphite, glycidyl Methacrylate, graft copolymerization, jute fibers

Introduction

Graft copolymerization of GMA has received a significant attention due to the pendant epoxy groups which enter in many chemical reactions[1-6], thus offering the opportunity for chemical modification of different substrates for various uses[7-8]. Glycidyl Methacrylate has been used to graft copolymerize many substrates such as, leather and different textiles[9-15] to improve their chemical and physical properties.

Jute is produced in greater amounts than any other fiber with the exception of cotton. Jute is a natural multicellular vegetable fiber that degraded in soil, beside on its combustion no toxic fumes or residues are emitted.[16]

Also, it shows a good resistance to microorganisms [17]. Jute is widely used as a fiber through the world, especially in fabrics of low cost, and was promoted as a fashion fabric for use in wearing apparel. On the other hand, Jute fabric is widely used for bagging, backing fabric for carpeting, home furnishings such as draperies and a variety of craft activities[18].

The aim of the present work is to modify jute fibers at ambient conditions through grafting with GMA in presence of APS/ ASBS as initiator.

Experimental

Materials

Raw jute fiber (Corchorus capsularis) (kindly supplied by El-Nassr Company for Jute industry, Egypt), was scoured by boiling in 7g/1 of NaOH solution and 2g/1 nonionic detergent (Cibapon® R_Ciba) at 85°C for 60 min. using a liquor ratio of 1:50 then rinsed with hot, cold water successively then neutralized by 1 % acetic acid solution and dried.

Chemicals

Glycidyl Methacrylate (GMA) (Fluka), ammonium persulphate (APS), acetone, and sodium bisulphite were of analytical grade chemicals. The acetone sodium bisulphite (ASBS) adduct was prepared according to a predescribed method. [19]

Grafting Method

A known weight of jute fiber was introduced in a stoppard conical flask containing the desired calculated amounts of monomer emulsified in distilled water using (Cibapon®R) as an emulsifier. The flask was then stirred for 5 min. at ambient conditions; varying amounts of the redox initiator (APS/ ASBS) were added drop wise during 10 min. intervals. The polymerization reaction was allowed to proceed under continuous stirring at the desired pH value, L: R, initiator concentration, time, temperature and [M]. At the end of the reaction the grafted sample was washed using acetone in soxhlet apparatus to get ride of the homopolymer formed.

Testing and Analysis

Stability of epoxy Content

The epoxy content was determined according to a reported method.[20] and the stability of epoxy group was determined according to the following equation,

$$\text{Stability of Epoxy group \%} = \frac{\text{Determined epoxy content}}{\text{Calculated epoxy content}} \times 100$$

Infra - Red Spectra

Measurements were performed using Nexus 670-FTIR spectrometer Nicolet USA at the range of 4000-400 Cm-1 and a resolution of 4 Cm-1.
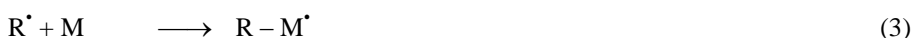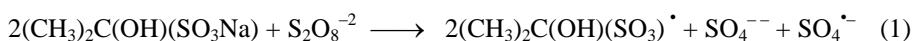
Thermal Gravimetric Analysis (TGA)

The TGA for the jute and GMA-g-jute was carried out at a temperature 0–600°C Under Nitrogen atmosphere with a heating rate of 10°C / min. using Shimadzo TGA-50, Japan.
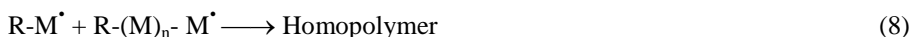
Results and discussion

The reaction mechanism

   Initiation

$$2(CH_3)_2C(OH)(SO_3Na) + S_2O_8^{-2} \longrightarrow 2(CH_3)_2C(OH)(SO_3)^{\bullet} + SO_4^{--} + SO_4^{\bullet-} \quad (1)$$

$$R^{\bullet} + J\text{-}OH \longrightarrow RH + J\text{-} O^{\bullet} \quad (2)$$

$$R^{\bullet} + M \longrightarrow R - M^{\bullet} \quad (3)$$

   Propagation

$$J\text{-} O^{\bullet} + M \longrightarrow J\text{-}O\text{-}M^{\bullet} \quad (4)$$

$$J\text{-}O\text{-}M^{\bullet} + n\,M \longrightarrow J\text{-}O\text{-}(M)_n\text{-}M^{\bullet} \quad (5)$$

$$R\text{-}M^{\bullet} + nM \longrightarrow R\text{-}(M)n\text{-}M^{\bullet} \quad (6)$$

   Termination

$$J\text{-} O^{\bullet} + R\text{-}(M)n\text{-} M^{\bullet} \longrightarrow Graft \quad (7)$$

$$R\text{-}M^{\bullet} + R\text{-}(M)_n\text{-} M^{\bullet} \longrightarrow Homopolymer \quad (8)$$

Where R is a free radical species as produced in equation (1), J-OH is an abbreviation for jute and M is GMA.

1- Effect of pH value

Fig (1) clarifies the dependence of GY, GE and TC on the pH value. It is clear that all the aforementioned parameters increase by increasing the pH value up to pH 3 after that begin to decrease ,which can be attributed to the formation of more stable cellulose radicals at pH 3, while by increasing or decreasing the pH the opportunity for homopolymer formation increases[21].

2- Effect of liquor ratio (L: R)

The data plotted in Fig (2) show the effect of liquor ratio on GY, GE and TC. It is evident that all the studied parameters (GY, GE and TC) show their dependence on the L: R used. It is clear that by increasing the L: R the values of GE, GY and GE decrease. This can be attributed to the decrease of the amount of reactant ingredients in both reaction medium due to the dilution, Thereby minimizing the extent of graft

copolymerization [21].

3- Effect of the initiator concentration and addition sequence

Fig (3) shows the effect of the initiation redox system (APS /ASBS) on the GY, GE and GE, and using the following addition sequence.

A) APS was added 5 min. before adding ASBS to the emulsified monomer.

B) ASBS was added at first followed by addition of APS after 5 min. to the emulsified monomer

C) The two components of the redox initiator system were added together at the same   time.

It is evident from data fig (3-5) that the graft yield increases by increasing the initiator concentration up to (20/40) mmole/l of (APS/ ASBS) and began to decrease thereafter, regardless of their addition to the reaction medium. This means that, the initiator concentration increases the number of free radical species on the jute backbone as well as in the polymerization medium increases, thereby enhancing the graft yield. The decrement beyond the optimum redox initiator concentration is a manifestation of faster rate of termination as a result of excessive radical concentration in the polymerization medium[22]. Also fig (5) shows that the increase in GY, GE and TC, as a function of sequence of addition, follows the order.

Addition of both of initiators components> addition of ASBS before APS > Addition of APS before ASBS.

4- Effect of grafting conditions, i.e. Temperature and time

Grafting of jute carried out at different temperatures (20 , 40 , 50 and 60°C), for different times (15 - 180 minutes) , while keeping the other parameters constant, It is shown in fig(6-9) that ,the GY, GE and TC increase by increasing the reaction time from 15 - 120 minutes and then decreases. This is observed for all the studied temperatures under investigation. This could be ascribed to the decrement in the concentration of both initiators and monomer in the reaction medium, beside the shortage in active sites on the jute backbone as the reaction proceed.

On the other hand, the data in Fig (6-9) show that GY, GE, and TC values decrease gradually by increasing the reaction temperature [23] and it can be observed that the best GY, GE and TC obtained at 20 QC. This can be explained as follows: the presence of bisulphite accelerates the decomposition of persulphate at lower temperature to generate free radicals [20].

5- *Effect of Monomer concentration*

To investigate this parameter, jute fibers were grafted by using different monomer concentrations. The epoxy groups on the PGMA-g-jute were calculated analytically and by elementary analysis. The stability of epoxy was estimated according to the equation mentioned in the experimental part. Results in table (1) and Fig (10) clarifies that the graft yield % and epoxy content (mole epoxy/100 gm) increase noticeably by increasing the monomer concentration up to (150% ows). Increasing the monomer concentration up to (200% ows) leads to a slight decrease or nearly level off. The enhancement of grafting by increasing GMA concentration up to (100% ows) could be associated with the greater availability of monomer molecules in the vicinity of jute backbone in particular, and in the reaction medium in general [24].

6- *I.R. Spectral analysis*

Fig (11) shows the I.R. spectra of scoured jute (A), poly [GMA] (B) and poly [GMA]-g-Jute copolymer (C) respectively. The spectral bands of copolymer at 1731 Cm-I and at 906 Cm^{-1} are confnming the presence of carboxylic ester carbonyl which is not found in the scoured jute spectrum [25]. Also, the graft copolymer shows a band around 3000 Cm^{-1} characteristic of the Assym. Stretching of the methane group, there is also, -C-O-C- Symm. Stretching of the epoxide at 1272 Cm^{-1}, which are not present in the scoured jute[26].

The variation of the intensity of -OH group which is lower in poly [GMA]-g-Jute than scoured jute represents a good proof for the occurrence of grafting process.

7- Thermo Gravimetric Analysis and Differential Gravimetric Analysis (TGA &DGA)

Thermo gravimetric Analysis TGA is a simple and an accurate method for studying the decomposition pattern and the thermal stability of the polymers. Fig(12-13) show the primary thermograms for both scoured and grafted polyglycidyl methacrylate jute (gute-g-GMA) respectively. It is clear that the thermal decomposition took place in two main degradation steps for the ungrafted jute and three main degradation steps for the grafted one. The thermal degradation steps are known as, dehydration, main decomposition and carbonization [27].

As an evident the first step degradation for scoured jute has an initial weight loss of 3.1% around 67°C while, the (Jute-g-GMA) has a weight loss of 2.5 5 around

50°C which is mainly due to the evaporation of absorbed moisture [28]. It is also interesting to note that (Jute-g-GMA) starts the decomposition reaction at temperature lower than that of scoured jute which can be explained as follow: The graft copolymerization reaction generally reduces the crystalline regions of jute and increases the amorphous regions [29]. The crystalline structures are thermally degraded at higher temperatures compared to the amorphous structures [30].

The main decomposition step is due to formation and evaporation of some volatile compounds. The weight loss value obtained in this stage was 59.5% around temperature of 349°C and 293°C for scoured and grafted jute respectively. It is clear that the remainder weight from (Jute-g-GMA) is greater than the scoured jute which indicates that the graft polymerization reaction increases the stability of Jute, due to lower decomposition temperature of grafted sample lead to decrement in the volatile compounds keeping greater undecomposed amount.

Conclusion

Glycidyl methacrylate was grafted onto jute fibers in presence of Ammonium Persulphate. Acetone Sodium Bisulphite as initiator. It is concluded from the results obtained that the optimum conditions for grafting are initiator concentration of 20/40 mmole/l for APS/ASBS respectively, liquor ratio (1 : 20), pH value 3, time 120 min., temperature 20°C, and monomer concentration [M] 150% based on weight of substrate (OWS).

Table (1) Effect of monomer concentration on GY% and stability of epoxy groups

Stability of epoxy	Actual epoxy	Ca1c. Epoxy conten	GY%	Monomer [M] (ows)
97	0.109	0.112	19	0.5
88.9	0.242	0.272	63	0.75
85.3	0.309	0.362	105	1.0
82.6	0.329	0.398	130	1.5
83.4	0.316	0.383	125	2.0

Reaction conditions: Temp. = 20°C, pH=3, L: R=1:20, time =120 min. and [APS/ASBS] =20/40 mmole/l.
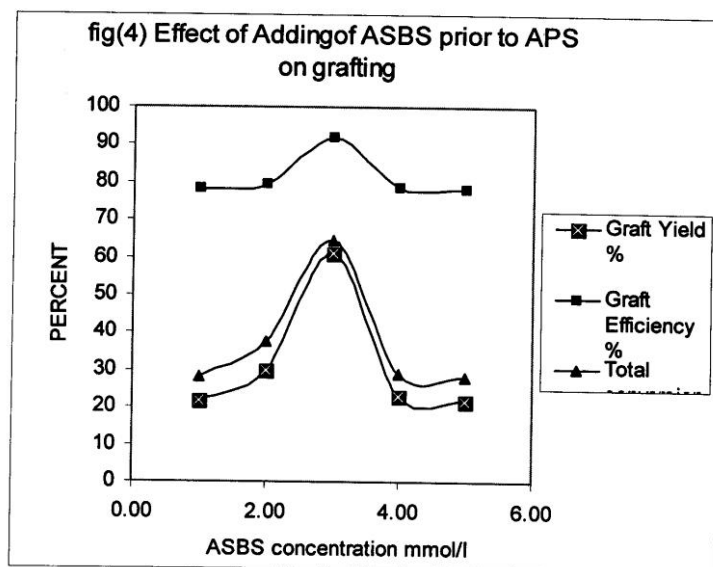
fig(1) Effect of pH on grafting
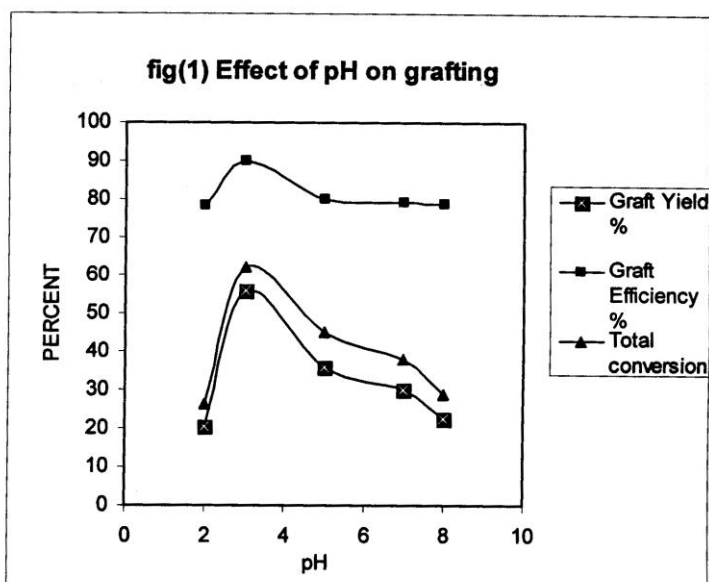
Reaction condition : Time= 2 Hours,[M]=100% OWS,Temp.=40°C,L:R=1:20, [APS]=20mmol/l and [ASBS]=40mmol/l

fig(2) effect of L:R on grafting
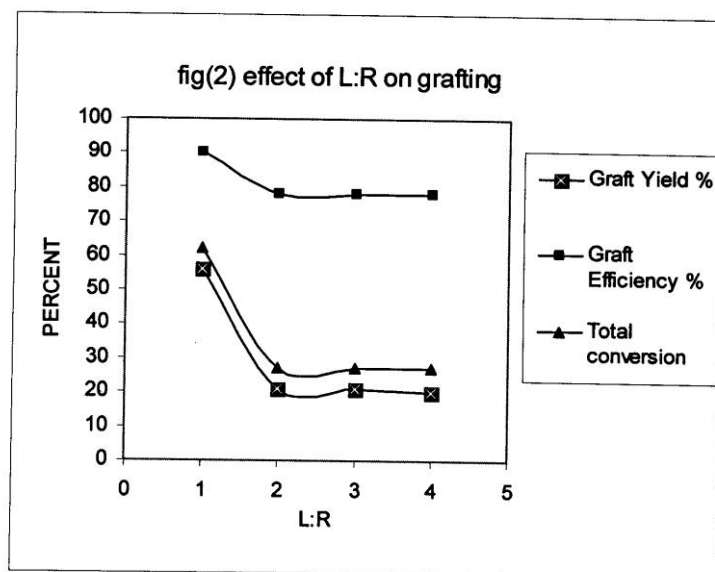
Reaction condition : Time= 2 Hours,[M]=100% OWS,Temp.=40°C,pH=3, [APS]=20mmol/l and [ASBS]=40mmol/l

fig(3) Effect of Adding APS prior to ASBS on grafting
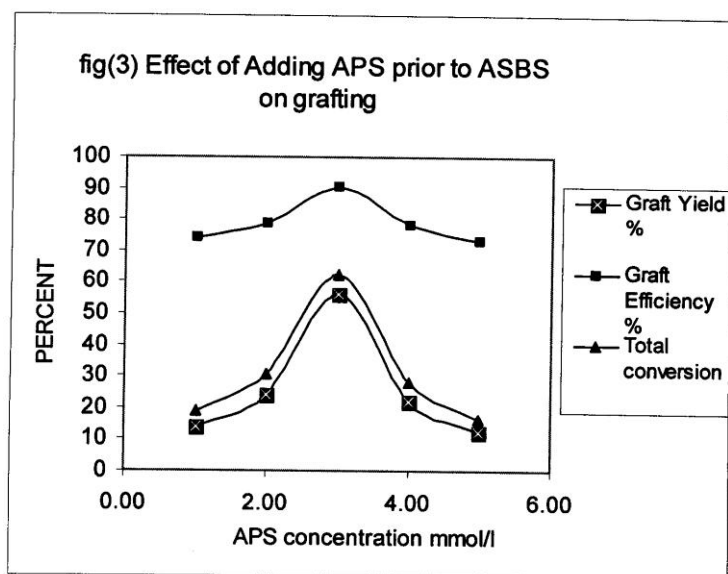
Reaction condition : Time= 2 Hours,[M]=100% OWS,Temp.=40°C,pH=3, L:R=1:20 and [ASBS]=40mmol/l

fig(4) Effect of Addingof ASBS prior to APS on grafting

Reaction condition : Time= 2 Hours,[M]=100% OWS,Temp.=40°C,pH=3, L:R=1:20 and [APS]=20mmol/l

fig(5) Effect of Adding both initiator together on grafting
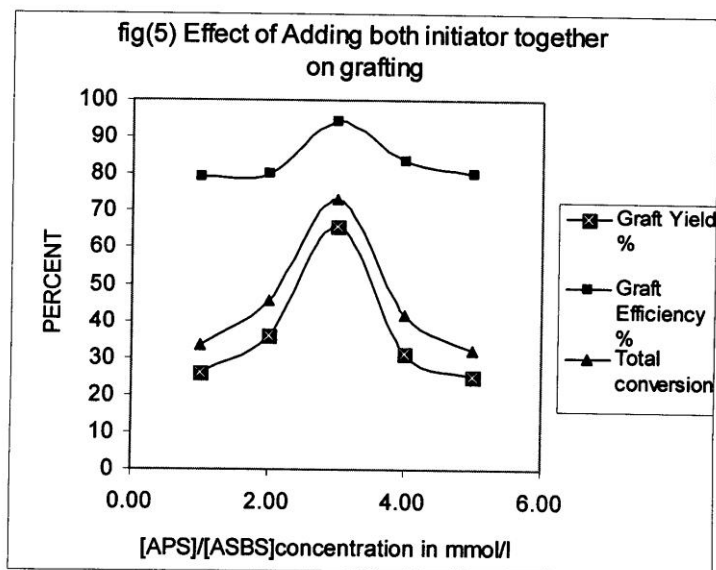
Reaction condition : Time= 2 Hours,[M]=100% OWS,Temp.=40°C,pH=3 and L:R=1:20

fig(6) Effect of Time at 60°C on grafting
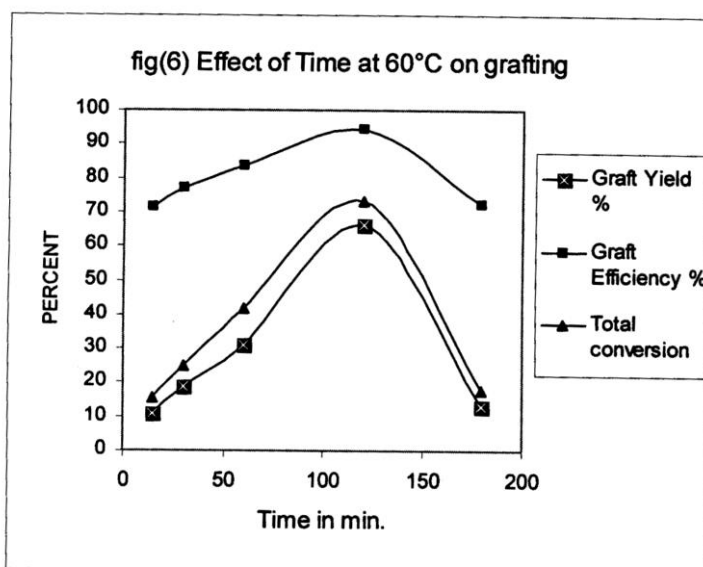
Reaction condition :[M]=100% OWS,Temp.=60°C,pH=3,L:R=1:20 and [APS/ASBS]=20/40 mmol/l

fig(7) effect of time at 50°C on grafting
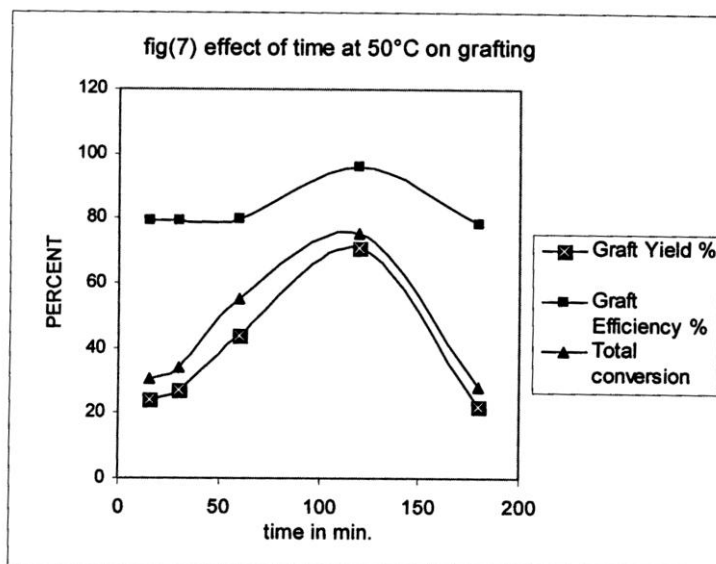
Reaction condition :[M]=100% OWS,Temp.=50°C,pH=3,L:R=1:20 and [APS/ASBS]=20/40 mmol/l
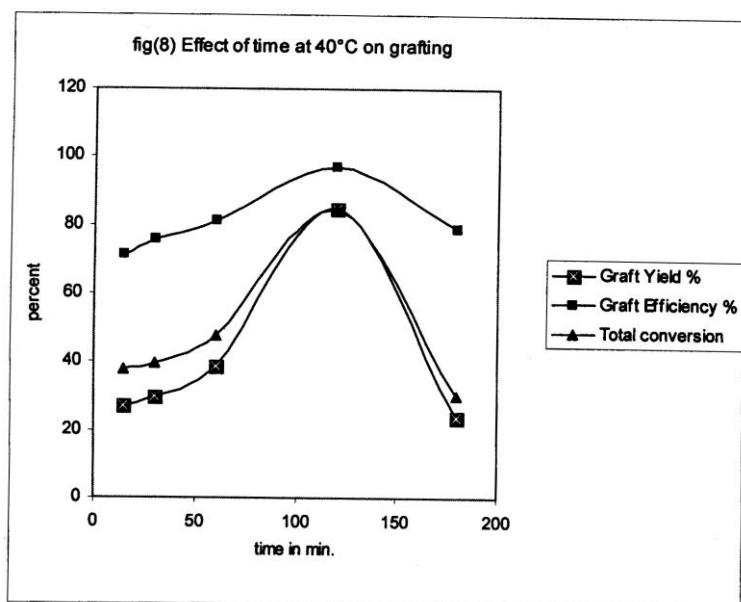
fig(8) Effect of time at 40°C on grafting

Reaction condition :[M]=100% OWS,Temp.=40°C,pH=3,L:R=1:20 and[APS/ASBS]=20/40 mmol/l

fig(9) Effect of time at 20°C on grafting
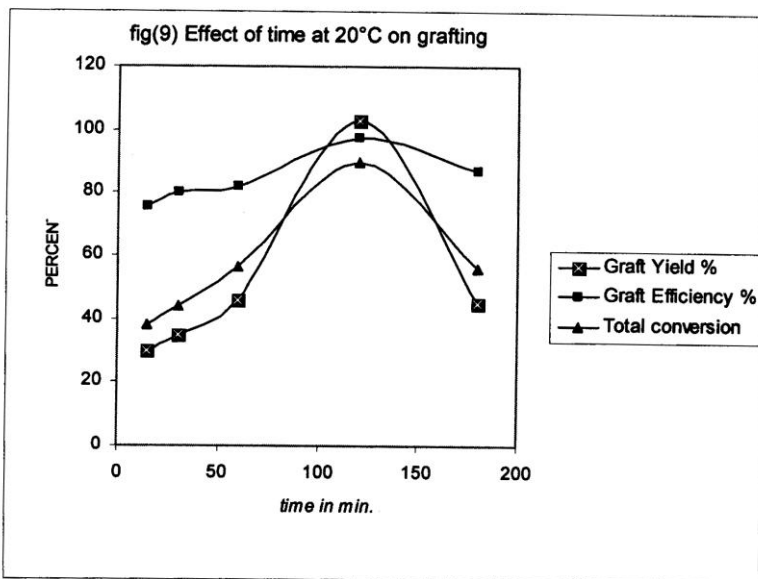
Reaction conditions: [M]=100% OWS,Temp.=20°C,pH=3,L:R=1:20 and [APS/ASBS]=20/40 mmol/l

fig(10) Effect of Monomer concentration on grafting
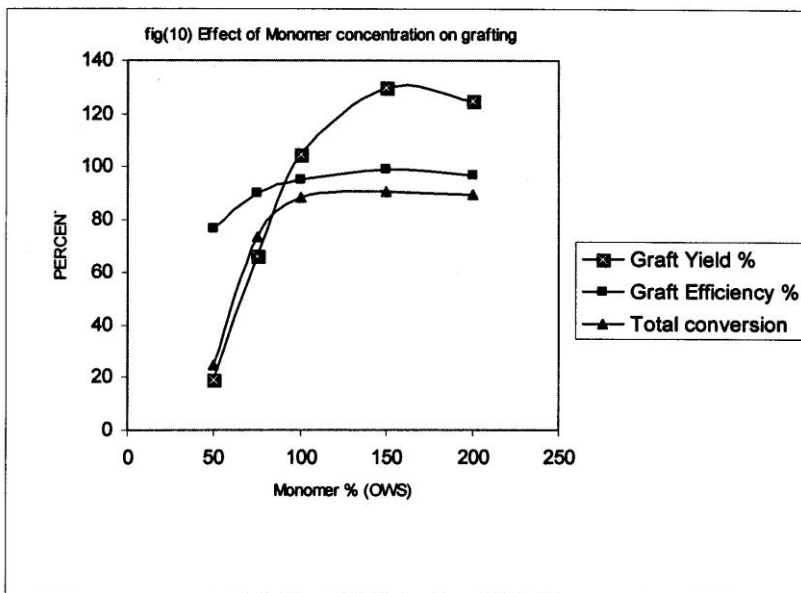
Reaction conditions: Temp. =20°C, pH=3, L: R=1:20 and [APS/ASBS] =20/40 mmol/l
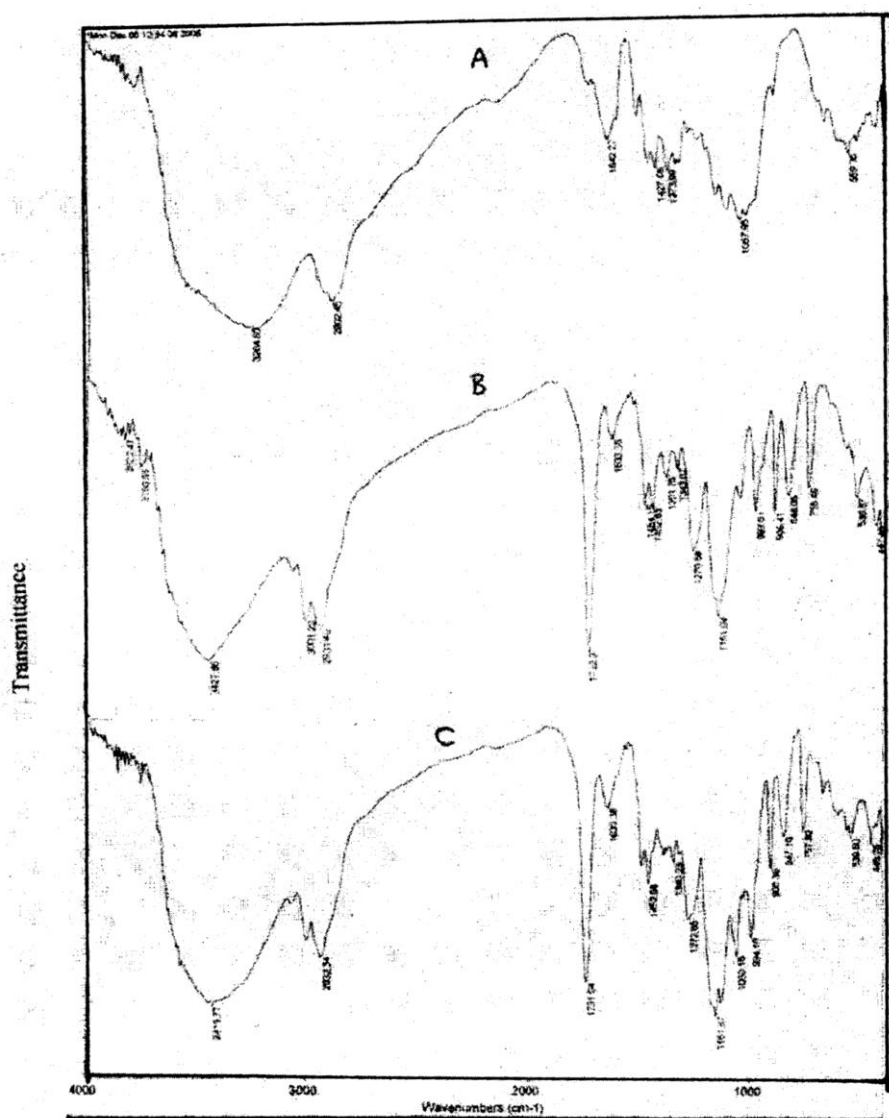
Fig. (11) Infrared transmittance spectra of (A) Scoured jute, (B) poly (GMA) and (C) poly (GMA)-g-jute
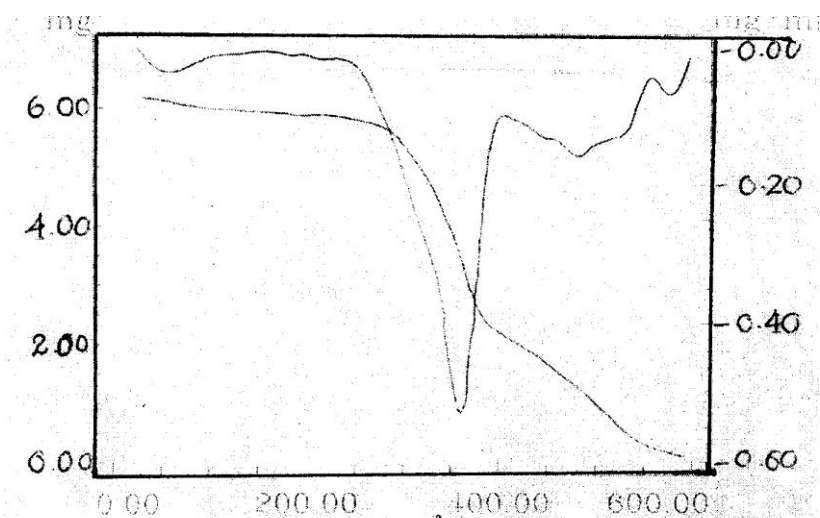
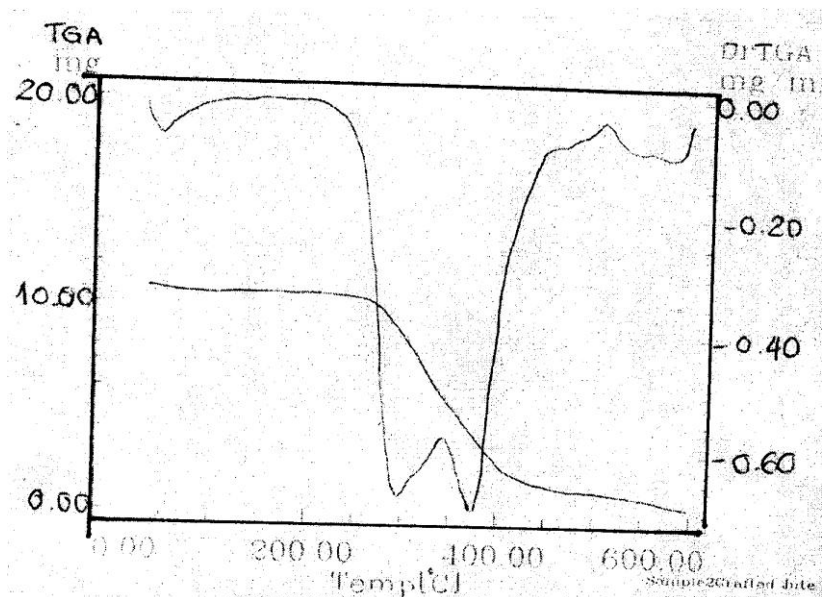**Fig. (12) Grafted Jute Sample.**

Fig. (13) Grafted Jute Sample.

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