

# Studies on Jute Fiber Composites with Polyesteramide Polyols as Interfacial Agent

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## Synopsis

Polyesteramide polyols have been synthesized by melt condensation using a mixture of alkanolamines, polyethylene glycols, and dicarboxylic acids/anhydrides, and the behavior of resin samples as interfacial agents in unidirectional as well as random composites of jute/epoxy and jute/polyester has been evaluated. Mechanical properties of these composites with or without interfacial agents have been determined along with the effect of water uptake on such properties. The incorporation of polyesteramide polyol (PEAP) resins as interfacial agents has been found to significantly improve the mechanical properties of jute fiber composites. It has also been found that increasing the hydroxyl value of PEAP results in a better bonding of the composites up to a certain optimum limit of hydroxyl value beyond which the molecular weight of the interfacial agent as well as its bonding strength decreases. Use of PEAP resin of optimum hydroxyl value and molecular weight also significantly improves the water resistance capacities of jute/epoxy composites.

## INTRODUCTION

Fiber-reinforced composite materials using synthetic resins have attained significant development in the last few decades because of their desirable properties such as light weight, high strength-to-weight ratio, and comparatively easy processability. Most commercially important composites are based on glass fibers as reinforcing material. Other fibers which have been successfully utilized for composite preparation include carbon fiber, boron fiber, asbestos fiber, etc., though their applications are not as widespread as glass-fiber-reinforced composites.

Attempts have also been made to prepare composites based on natural fibers, though their use till today is very limited and mainly confined to those areas where mechanical strength requirement is not very high. One such natural fiber, which has been tried by some workers earlier, is jute. Thus, as early as 1926, attempts were made to develop jute fiber composites by Bhatnagar.<sup>1</sup> Subsequently, various workers<sup>2-5</sup> tried to modify jute fiber composites by using various resins and also by applying a gel coat or a thin glass fiber/resin layer to improve resistance to environmental degradation. Probable application areas included hi-fi enclosures, cafeteria trays, and irrigation ditch liners. Winfield and Winfield<sup>6,7</sup> described the construction of low cost housing units from jute-reinforced polyester resins. Wells et al.<sup>8</sup> prepared jute-epoxy composites using different varieties of jute with a view to studying whether any particular variety of jute plant would give rise to fiber with superior properties.

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In spite of these efforts, however, there has not been any extensive commercial utilization of jute fiber composites. One of the several reasons for this failure lies in the poor adhesion between resin matrix and jute fiber leading to debonding of the composite on aging. There has been hardly any detailed study on the vital aspect of interfacial bonding in such natural fiber composites, though recently the usefulness of such interfacial bonding agents in case of palm fiber composites has been indicated.<sup>9</sup>

Since fiber-matrix interface plays an important role in determining the mechanical properties of composites, the present work has been undertaken to develop jute fiber composites using suitable interfacial agents, which will act as a bridge between the resin matrix and the fibers imparting better mechanical properties in dry as well as wet conditions. Keeping in view the cellulosic structure of jute fiber, a multifunctional resin like polyesteramide polyol may be expected to act as a suitable interfacial agent having compatibility with both the fibers and the resin matrix. Synthesis of such functional polymers and their applications is of current interest, mainly due to their potential industrial applications for obtaining polymers of desired properties by subsequent reactions. Several workers have synthesized and characterized regularly alternating, block and random polyesteramides by melt, solution, and interfacial polycondensation methods.<sup>10-19</sup> Many workers have synthesized unsaturated polyesteramide by modifying unsaturated polyester backbone with mono- or polyfunctional alkanolamine or aliphatic-aromatic amines and diamines.<sup>19</sup> These unsaturated polyesteramides are mostly used as binders for inorganic components such as glass, sand, etc.<sup>19,20</sup> Amide-modified saturated polyester polyols have been studied by many workers,<sup>21-28</sup> but their uses are mostly restricted to polyurethane formulations.

In the present study multicomponent polycondensation reactions between alkanolamines, poly(ethylene glycol) ether, and diacids/anhydrides have been carried out and the behavior of polyesteramide polyol product samples as interfacial agents in unidirectional as well as random composites of jute/epoxy and jute/polyester has been evaluated. Some mechanical properties of these composites with or without interfacial agents have been determined along with the effect of water uptake on such properties. Physicochemical properties of the polyesteramide resin samples obtained at various stages of conversion have been studied to have some understanding of the mechanism of such multicomponent polycondensation reactions.

## EXPERIMENTAL

### Materials

**Chemicals.** Adipic Acid (Pfizer): recrystallized from concentrated nitric acid and used; phthalic anhydride (BDH) used as such; maleic anhydride: recrystallized from chloroform; reagent grade diethanolamine (BDH) and monoethanolamine (BDH) were distilled twice under reduced pressure before use; poly(ethylene glycol)-200, poly(ethylene glycol)-600 (NOCIL, India) used as such, acetone (A.R. grade).

**Fibers:** Raw unidirectional jute fibers (*Corchorus capsularis* spp. or white

jute) and jute felts were obtained from Indian Jute Industries Research Association (IJIRA), Calcutta. Raw jute fibers were dried at 110°C before use. All jute felts were washed with a mild detergent solution, rinsed, and dried prior to using them as reinforcements for composites.

**Epoxy Resin.** Unmodified epoxy resin, Ciba-Geigy of India Limited, Bombay, having initial viscosity 5000–8000 CP, sp. gr. 1.15 to 1.2, gel time with 10% hardener Hy-951 is 40 min at 120°C.

**Polyester Resin.** Hylak polyester resin HSR-8111 was obtained from Bakelite Hylam, India. This is a general purpose polyester resin having a viscosity of 700 cS at 25°C, styrene content 36%, sp. gr. 1.12, gel time – 20–25 min at 25°C with 1.5% catalyst MEKP having active oxygen content 9.2% and 1.5% of accelerator cobalt naphthenate solution (6% Co metal).

### Preparation of Interfacial Agents—Polyesteramide Polyols (PEAP)

The functional polyesteramides were prepared reacting hydroxyl and amine donors in a three-necked flask equipped with a stirrer. Temperature was increased slowly to about 100°C when dicarboxylic acid/anhydride was added. The temperature was then raised to about 170–180°C and the reaction continued under stirring and in a stream of oxygen-free dry nitrogen till water evolution ceased. The progress of the reaction was followed by checking periodically the acid value and amine content of the reaction mixture. The excess glycol and alkanol amine was removed by sparging with nitrogen and used as such as interfacial agents for natural fiber composites. The following analytical methods were used to study the progress of the reaction.

**Determination of Acid Value.** Acid value of the samples prepared was determined following the standard method BS 2782 Method 432 B.

**Determination of Total Amines.** The nonaqueous titration method of Palit<sup>29</sup> was followed.

**Determination of Monoethanolamine and Diethanolamine in Mixture of Amines.** The salicylaldehyde method of Critchfield and Johnson<sup>30</sup> using the bromocresol green indicator has been followed. A minor change in the above method was made, namely, the addition of isopropanol and ethylene glycol in the solvent system during Schiff's reaction. Acid consumption due to secondary amine obtained by this method was subtracted from the total amine values to yield the acid consumption due to primary amine.

**Determination of Hydroxyl Value.** Hydroxyl values have been determined by subtracting the amine value obtained by the above<sup>29</sup> from the total of hydroxyl and amine obtained as per the procedure of Ogg et al.<sup>31</sup>

### Laminate Preparation

Jute fibers were treated with a solution of polyesteramide polyols developed in our laboratory and dried at 60°C for 24 h. Treated fibers were placed in an open mold of 300 mm × 1.8 mm × 12.5 mm and were bonded with epoxy/polyester resins along with appropriate curing agents and were pressed to stops in a closed mold. This was cured under a pressure of 500 psi for 3 h at 120°C. Fiber content up to 70 ± 1 vol % could be achieved.

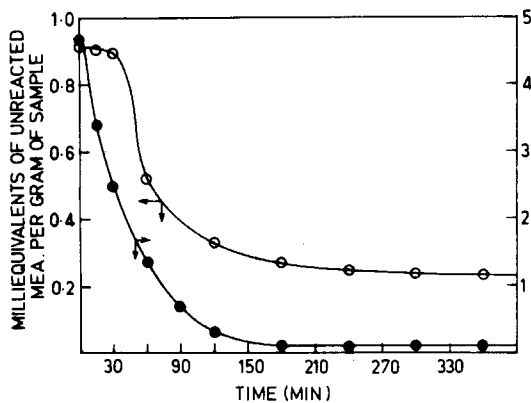


Fig. 1. Plot of meq unreacted MEA/g sample vs. time (min): (●) sample No. 1; (○) sample No. 2.

### Test Methods

Flexural strength ( $\text{MN}\cdot\text{m}^{-2}$ ) and flexural moduli ( $\text{GN}\cdot\text{m}^{-2}$ ) of the laminate test specimens were measured in accordance with ASTM D 790-66. The average scattering of their mean values is  $\pm 10\%$  and  $\pm 6\%$ , respectively. The flexural properties were determined in an Instron Tester Model 1122 at  $25^\circ\text{C}$  and  $50 \pm 2\%$  relative humidity with a sample conditioning of 48 h.

### RESULTS AND DISCUSSION

Table I lists reaction conditions and properties of saturated and unsaturated polyesteramide polyols obtained by polycondensation of the mixture of alkanolamines/poly(ethylene glycol) ether with dicarboxylic acid/anhydrides using

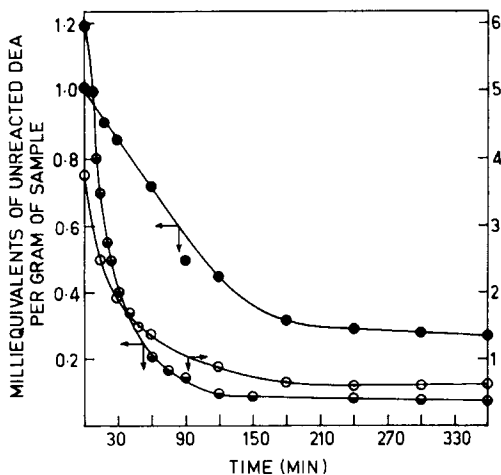


Fig. 2. Plot of meq unreacted DEA/g sample vs. time (min): (●) sample No. 1; (○) sample No. 2; (◐) sample No. 6.

TABLE I<sup>a</sup>

Sample no.	Composition	Mole ratio		Mole ratio MEA/DEA	Mole ratio amines/acid, PEG anhydride	Mole ratio acid, PEG, DEA/ anhydride	Mole ratio alkano/ amines/ acid, PEG, DEA/ anhydride	Mole ratio	Reaction time (h)	Acid value	Hydroxyl value	meq of unreacted		$\eta_1/\eta_2$ (10% soln in DMF)	Appearance/ remarks
		MEA/DEA	DEA/PEG									MEA	DEA		
1	MEA + DEA	4	—	—	1.2	—	—	1:0:0	6.0	7.89	210.3	0.1086	0.280	1.91	Pale yellow waxy solid
2	MEA + DEA	0.25	—	—	1.2	—	—	1:0:0	6.0	17.5	236.42	0.237	0.660	2.86	Pale yellow viscous liquid
3	DEA	100%	—	—	1.2	—	—	1:0:0	6.5	—	—	—	—	—	Gelled after 6.5 h
4	PEG-200 + DEA	—	2	—	—	1.4	—	0:0.4:0.6	8.0	9.2	162.9	—	0.242	2.1	Pale yellow viscous liquid
5	PEG-600 + DEA	—	2	—	—	1.2	—	0.6:0.4:0	7.5	13.2	122.27	—	0.147	2.87	Pale yellow viscous liquid
6	PEG-200 + DEA	—	2	—	—	1.1	—	0.6:0:0.4	6.5	15.1	132.3	—	0.068	3.67	Pale yellow viscous liquid
7	PEG-600 + DEA	—	2	—	—	1.0	—	0:0.4:0.6	7.0	10.6	66.71	—	0.182	3.87	Pale yellow viscous liquid
8	PEG-600 + DEA	—	2	—	—	0.9	—	0:0.4:0.6	6.5	11.2	52.2	—	0.087	4.1	Pale yellow viscous liquid

<sup>a</sup> MEA = monoethanolamine, DEA = diethanolamine, c = adipic acid, d = maleic anhydride, e = phthalic anhydride, PEG = poly(ethylene glycol). Reaction temperature is maintained between 170°C and 180°C in all the cases. Reaction conditions and properties of saturated and unsaturated polyesteramide polyols (PEAP) obtained in polycondensation of PEG/alkanolamines with dicarboxylic acid/anhydrides. High temperature melt condensation method.

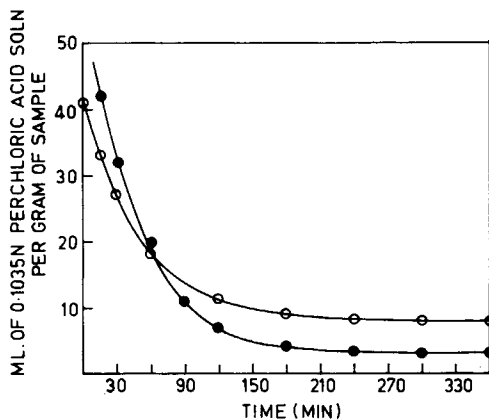


Fig. 3. Plot of mL 0.1035N perchloric acid solution per gram of sample vs. time (min), indicating the consumption pattern of total amines with time: (●) sample No. 1; (○) sample No. 2.

the high temperature melt condensation method. Results indicate that there is a substantial change in the physical properties of the polyesteramide polyols (PEAP) from waxy solid to viscous liquid to gel as the content of DEA is increased. Gelling at 100% DEA level may be due to formation of highly branched structure via hydrogen bonding. The resultant polyesteramide polyol using increasing concentration of DEA has higher acid value, and the content of unreacted alkanolamine is also high. That the residual acid has the catalytic effect on hydrolytic decomposition of the resultant polyesteramide polyol and may also promote crosslinking with unreacted alkanolamines on storage is presently under investigation. It is also found from the table that on substitution of

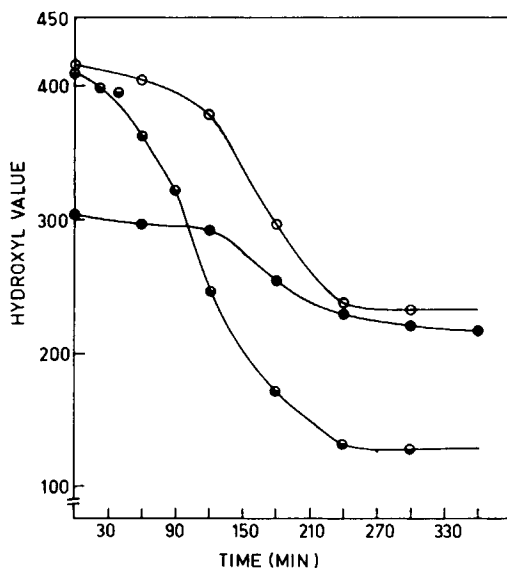


Fig. 4. Plot of hydroxyl value vs. time (min): (●) sample No. 1; (○) sample No. 2; (◐) sample No. 6.

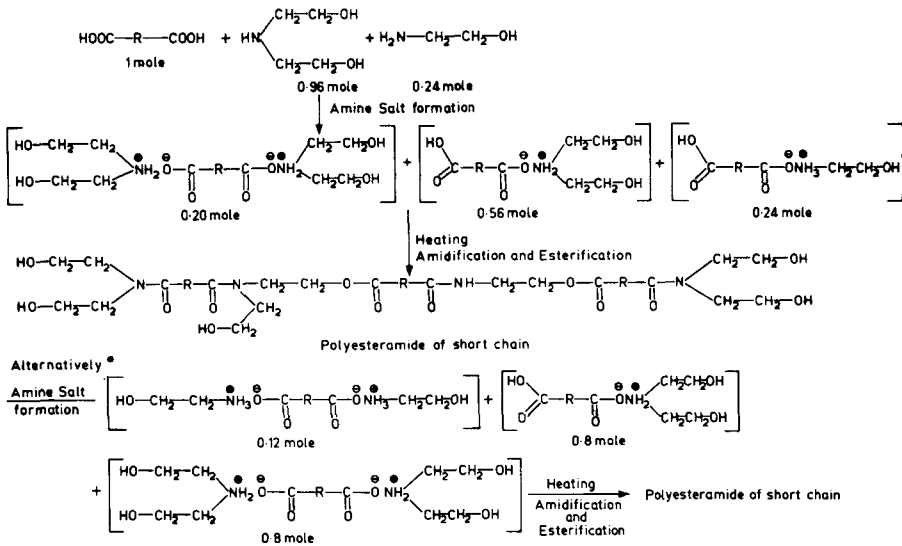


Fig. 5. Reaction between alkanolamines and dicarboxylic acid/anhydride. Alternatively\*, basicity of MEA being greater than DEA, the reaction may also proceed as shown.

monoethanolamine with PEG, there is a marked change in viscosity which increases with decrease in concentration of PEG and DEA in the total reaction mixture. It is presumed that increasing concentration of acids results in the formation of higher molecular weight products as is evidenced from the corresponding hydroxyl and viscosity values of the samples.

### Probable Reaction Scheme

During the multicomponent polycondensation reactions involved, the reactivity of individual functional groups varies widely and this poses some problem

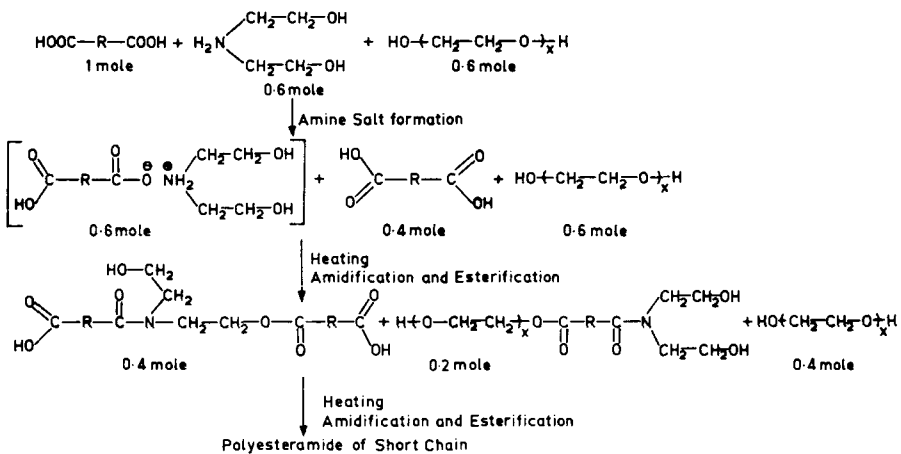


Fig. 6. Reaction between alkanolamine, poly(ethylene glycol) ether, and dicarboxylic acids/anhydrides.

in elucidating the mechanism of the reactions involved. Major reactions forming amide and ester are believed to proceed according to the schemes shown in Figures 5 and 6.

Figures 1–4 indicate the consumption pattern of amines, both primary and secondary, and the value of the hydroxyl functions during the course of the reaction. It is also significant to observe (Fig. 3) that the content of unreacted total amines increased sharply with increasing rates of DEA in the reaction mixture. This is probably due to incomplete conversion of amine salts to amide linkage, which leads to amine salts remaining as such in the chain. The presence of amine salts in the chain is further supported by the fact that there is a reduction in solution viscosity of the samples in pyridine and a further reduction in solution viscosity when a small amount of strong base like dibutyl amine is added.

### IR Spectra

IR spectra showed the characteristic bands expected for the polyesteramide formation and are very similar for all the polymers except for the relative intensities of the absorptions of —COO and —CONH groups:

1730–1700 $\text{cm}^{-1}$	—	C=O	for ester,
1630–1590 $\text{cm}^{-1}$	—	C=O	for amides.

A broad band between 3500 and 3300  $\text{cm}^{-1}$  indicates the presence of unreacted alkanolamines and the hydroxyl functional group in the resultant polyesteramide.

### Evaluation of Composite Properties with PEAP at the Interface

Composite samples were made using both unidirectional and random jute fibers with the prepared polyesteramide polyol at the interface. Mechanical properties of the jute/epoxy and jute/polyester composites are shown in Table II. As was expected, incorporation of the interfacial agent significantly improved the mechanical properties of composites. The water resistance capacities of the composites also improved marginally. The improvement in mechanical properties of jute/polyester composites is lower than jute/epoxy composites. Since the binding force between the fiber matrix and polyesteramide polyol was mainly due to hydrogen bonding between the hydroxyl groups of the cellulose and polyesteramide polyol, it was expected that increasing the hydroxyl value of the PEAP could result in better bonding. Accordingly, several PEAP samples were prepared, differing in their hydroxyl values. Figure 7 indicates the flexural strength and modulus values against hydroxyl number of interfacial agents used. The results in both cases indicate a maxima followed by a downward trend. The results thus indicate that there is an optimum hydroxyl number of the interfacial agent above which the mechanical properties degrade. Since increase in the hydroxyl value of the resins results in lowering of the molecular weight as evidenced by lowering of viscosity, it is presumed that the fall in mechanical properties of the composites with the use of PEAP having higher than the optimum limit of hydroxyl value might be due to lowering of the molecular weight of the interfacial resin samples. In order to study the effect of boiling water on the retention of flexural strength and modulus of the composites using the resin



TABLE II  
Properties of Jute/Epoxy and Jute/Polyester Composites with Polyesteramide Polyols (PEAP) as Interfacial Agent<sup>a</sup>

Composite sample no.	Fiber	Composite flexural strength (MN·m <sup>-2</sup> )	Composite flexural modulus (GN·m <sup>-2</sup> )	% retention of strength after immersion in boiling water		% retention of flexural modulus after immersion in boiling water	
				2 h	4 h	2 h	4 h
Unidirectional jute/epoxy composites							
A	Raw jute	291	37	51.2	46.1	53.2	48.9
B	With PEAP, OH number 162.2	329	37	50.2	46.2	52.2	45.8
C	With PEAP, OH number 122.27	350	38	53.1	47.9	55.0	49.1
D	With PEAP, OH number 66.71	386	41	61.0	56.2	56.1	51.3
E	With PEAP, OH number 52.2	370	45	57.5	51.9	55.8	52.0
Random jute/epoxy composites							
F	Jute felt	132	13				
G	Jute felt with PEAP, OH number 66.71	144	13				
Unidirectional jute/polyester composites							
H	Raw jute	260	—				
I	With PEAP, OH number 122.27	277	—				
J	With PEAP, OH number 66.71	284	—				

<sup>a</sup> PEAP treatment: treated with 10% of PEAP based on weight of jute-composite, density of all samples  $1.2 \times 10^3 \text{ kg·m}^{-3}$ . All samples contained  $70 \pm 1\%$  of fiber by volume in a resin matrix.

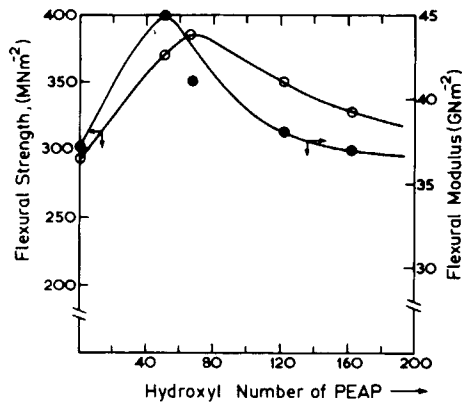


Fig. 7. Plot of flexural strength, flexural modulus vs. hydroxyl number of polyesteramide polyols (PEAP).

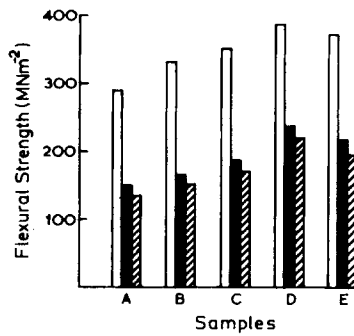


Fig. 8. Effect of immersion in boiling water on flexural strength ( $\text{MN}\cdot\text{m}^{-2}$ ); shaded and hatched areas refer to samples after immersion in boiling water for 2 h and 4 h, respectively.

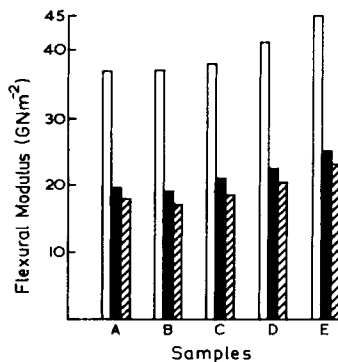


Fig. 9. Effect of immersion in boiling water on flexural modulus ( $\text{GN}\cdot\text{m}^{-2}$ ); shaded and hatched areas refer to samples after immersion in boiling water for 2 h and 4 h, respectively.

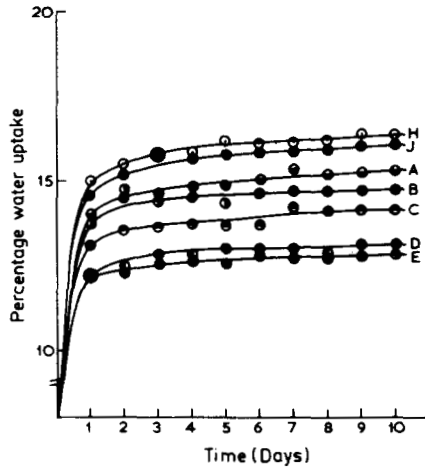


Fig. 10. Plot of percentage water uptake of jute fiber composites vs. immersion time (days) in cold water.

samples of different hydroxyl values at the interface, the composite samples were tested for their flexural strength and modulus after immersion in boiling water for 2 h and 4 h. The results (Figs. 8 and 9) indicate that the retention of strength against the corresponding hydroxyl values of the resin samples follow the same pattern as with the dry samples. Percentage water uptake and percentage increase in thickness of the composites (Figs. 10 and 11) indicate that increase in the hydroxyl value of the resin at the interface results in increased water uptake and swelling of the composite. The overall performance of the composite vis-à-vis their mechanical properties and water resistance capacities thus point out that significantly better results can be achieved using the resin of an optimum hydroxyl value and molecular weight. It is evident from Table II that random

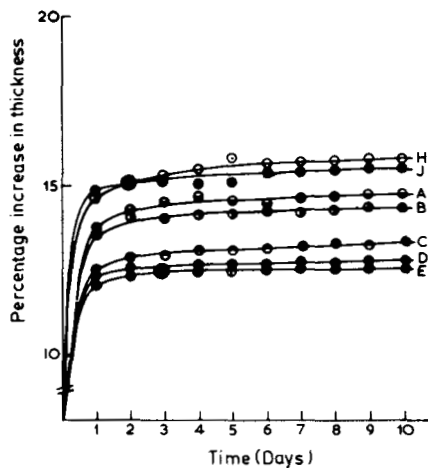


Fig. 11. Plot of percentage increase in thickness of jute fiber composites vs. immersion time (days) in cold water.

jute/epoxy composites using jute felts showed a poor performance with regard to mechanical properties.

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