Studies on Process Variables for Natural Fiber Composites—Effect of Polyesteramide Polyol as Interfacial Agent

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Synopsis

A systematic study of the process variables for polyester composites based on different natural fibers like jute, sisal, ramie, and pineapple has been made with a view to determine the most suitable processing conditions for such composites. Effect of polyesteramide polyol (PEAP) as interfacial agent in such composites has also been discussed. Fracture modes of jute/polyester (JP) composite sample having different fiber volume fractions have been examined by scanning electron microscope (SEM). Fracture surfaces of untreated and PEAP-treated JP composite samples have been examined in SEM, both before and after 72 h immersion in boiling water, to study the nature of interfacial bonding on fiber treatment with PEAP. A qualitative improvement in bonding in case of PEAP-treated JP composites is evident from SEM photomicrographs. This is also supported by physicomechanical properties of the composite samples.

INTRODUCTION

The use of natural fibers as reinforcement in polymer composites to replace wholly or even partly the conventional inorganic fibers like glass is presently receiving increasing attention because of the advantages of cost as well as availability as renewable resource material. Mukherjea et al.[1,2] have reviewed the limitations in the applications of jute fiber composites and indicated the importance of interface in determining the properties of such natural fiber composites (NFC). Use of natural fibers is rather complicated, since the fibers vary greatly in chemical composition and physical properties, depending on their generic characteristics, place of growth, and preparation conditions. It is, however, important for the commercial production of NFC that processing conditions should be such that the product should have uniform characteristics. This would require a systematic study of the different parameters involved in the processing of the NFC with a view to develop optimum processing conditions. The processing parameters involved are duration of cure, temperature of cure and curing pressure, which are again dependent on the composition, i.e., fiber–resin ratio, which is an independent variable.

A systematic study of the processing variables in the production of jute/polyester as well as other natural-fiber-based polyester composites has

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been made with a view to determine the most suitable process conditions for a particular fiber. The use of interfacial agents in such composites has also been discussed. Since each of the variables affects the composite properties in its own way and also the variables are interdependent to a certain extent, the system presents a multivariable problem. Flexural strength of the composite has been taken as the objective function since it reflects the overall physicomechanical properties of a composite.

In this particular system, there is hardly any analytical expression available relating the flexural strength to the individual variables and the parameters are interdependent in an uncertain manner. Hence, following the numerical search technique (Shapiro et al.[3]), one of the parameters has been varied, keeping the others constant at some arbitrary values. The choice of the arbitrary values is guided partly by intuition and to a large extent by the results of the previous workers.[4-7] The variation is studied over a range of values and plotted against the objective function to determine the most suitable value of the parameter, which is then kept constant and a second parameter is varied to an optimum value. In this way, the most suitable process conditions for jute–polyester composites have been determined.

EXPERIMENTAL

Natural Fibers

Raw unidirectional jute fibers (Corchorus Capsularis or white jute) were obtained from IJIRA, Calcutta. Raw jute fibers were dried at 110°C before use. Ramie (Boehmeira Nivea, 20–25% gum content); degummed ramie; sisal (Agave Sisalana); pineapple (Ananos Cosmosus) fibers were obtained from Jute Technological Research Laboratory (JTRL), Calcutta. All these fibers were dried at 110°C before use.

Resin

Hylak polyester resin HSR-8113 was obtained from Bakelite Hylam, India. This is a G.P. grade polyester resin having a viscosity of 700 cS at 25°C, styrene content 40%, sp. gr. 1.12, gel time 20–25 min at 25°C with 1.5% MEKP catalyst (active oxygen content 9.2%) and 1.5% cobalt naphthenate solution accelerator (6% Co metal).

Release Agent

A 10% polyvinyl alcohol solution (cold water soluble grade) was used for formation of films on the mold surfaces.

Interfacial Agent

Polyester amide Polyol (PEAP) was developed in our laboratory[8] and used as interfacial agent. The properties of PEAP have been listed in Table I.

Laminate Preparation

Unidirectional composite laminates in polyester resin matrix were prepared using matched-die molding method. Treated and untreated fibers (jute, ramie,

TABLE I
Reaction Conditions and Properties of Unsaturated Polyesteramide Polyol (PEAP)[a]

Sample no.	Composition PEG[b] + DEA[c]	Mole ratio DEA[c]/PEG[b]	Mole ratio PEG, DEA/ acid, anhydride	Mole ratio *c/e*	Reaction time (h)	Acid value	Hydroxyl value	DEA unreacted (meq)	η_1/η_2 (10% soln in DMF)	Appearance/ remarks
A	PEG + DEA	2	1	0.6 : 0.4	9	16	87.42	0.136	3.93	Pale yellow pasty mass

[a] Reaction temperature is maintained between 190 and 200°C in all the cases. Reaction conditions and properties of unsaturated polyester amide polyols (PEAP) obtained in polycondensation of PEG, diethanolamine with dicarboxylic acid, anhydride. High temperature melt condensation method.

[b] = Poly(ethylene glycol) ether −600.

[c] = Diethanolamine.

[d] = Maleic anhydride.

[e] = terephthalic acid.

sisal, degummed ramie, and pineapple) were dried before use. A measured amount of fiber along with polyester resin and appropriate curing agents was then placed in the mold (300 × 12.5 × 1.8 mm). The mold was enclosed and pressed to stop in a hydraulic press. A number of laminates were prepared under different processing conditions.

Conditioning

The laminate test specimens were conditioned for 48 h before testing for their flexural properties. For wet conditioning, the laminate test specimens were immersed in boiling distilled water for different periods of time, after which they were cooled in distilled water at room temperature for at least 15 min. Then the samples were dried with a clean cloth and tested as soon as possible.

Test Methods

Flexural strength (MPa) and flexural modulus (GPa) of the laminate test specimens were measured in accordance with ASTM D790-66. For each data point, five samples were tested, and strength values were reported as mean of these values. The % C_v was also calculated and mentioned wherever necessary. The flexural properties were determined in an Instron tester (Model 1122) at 25°C and 50 ± 2% relative humidity.

Sample size specification:

Total length	80 mm
Span	50 mm
Width	11.5–13 mm
Thickness	1.8–3 mm

Fracture Studies by Scanning Electron Microscopy (SEM)

A scanning electron microscope (PSEM-500, Philips International, Holland), operating between 6 and 12 kV, was used to study the fracture surfaces. The surfaces were sputter-coated with gold to minimize the charging problem. Specimens were positioned at an angle (33.5°).

RESULTS AND DISCUSSIONS

Fiber Volume

Figure 1 represents the change in flexural strength of the composite with the fiber volume fractions (V_f). The flexural strength of the composites improved almost in a linear manner, with increasing V_f up to about 40% fiber volume. Thereafter, the rate of increase in strength with V_f dropped a little, but continued up to 70% fiber volume. The improvement in strength with increased V_f is assumed to be due to the increasing reinforcing effect of the fibers, whereas the fall in the rate of improvement after 40% of fiber volume may be due either to the increase in void with the increase in V_f or to the nonhomogeneity caused by insufficient matrix media. With more than 70% V_f, the composites showed resin-starved areas. Although the improvement beyond

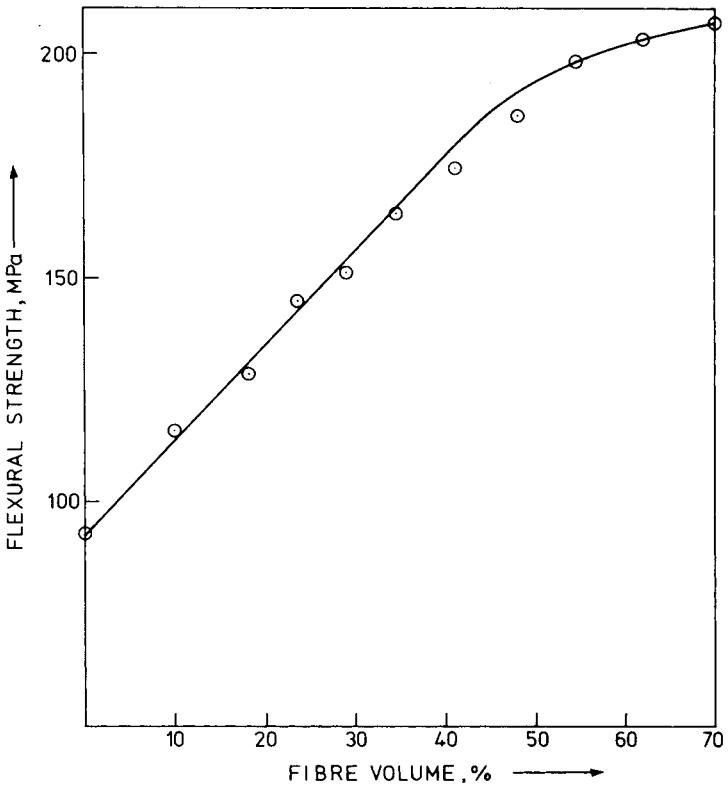

Fig. 1. Effect of fiber volume on flexural strength of jute polyester (JP) laminates.

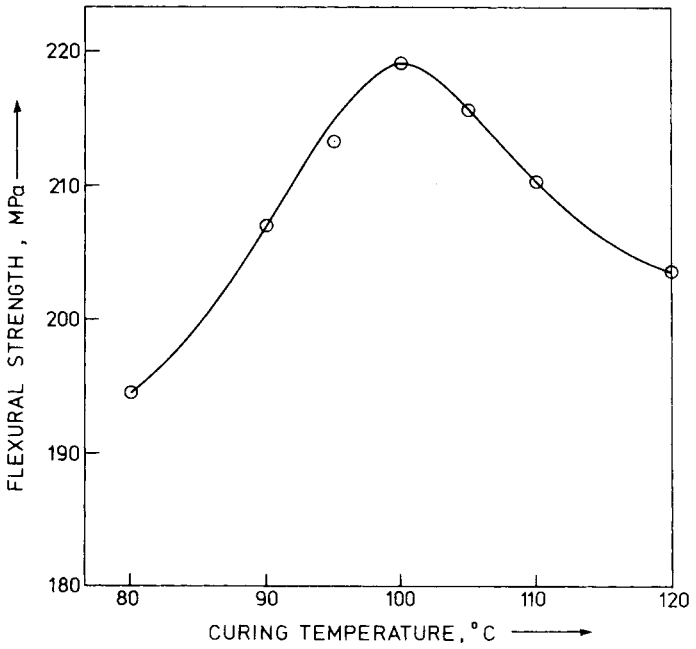

Fig. 2. Effect of curing temperature on flexural strength of JP laminates.

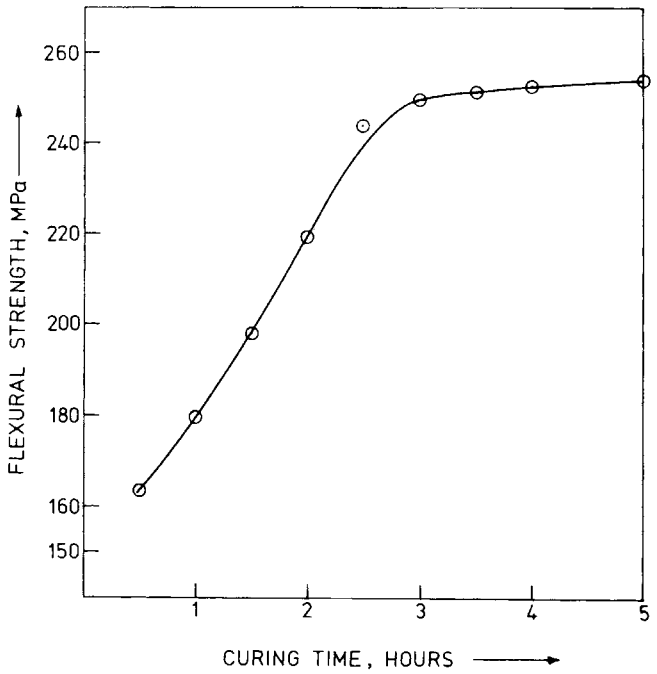

Fig. 3. Effect of curing time on flexural strength of JP laminates.

55% V_f is minor, the optimum fiber volume is taken as 68 ± 2%, as the matrix material is almost 10 times costlier than jute.

Curing Temperature

Effect of curing temperature on the flexural strength of the composite, keeping the curing time constant, is shown in Figure 2. The strength increases up to a curing temperature of about 100°C, but then it continually decreases with further increase in temperature. Lower flexural strength at temperatures below 100°C is due to undercure of the composite, as is manifested from the blisters on the surface. Thermal degradation of either jute or resin or both takes place at temperatures higher than 100°C as is evident from fine cracks developing on the surface of the laminates prepared. As neither unusually long cure cycle nor thermal degradation is desirable, the best cure temperature is set at about 100°C.

Cure Time

The variation of flexural strength with duration of cure at 100°C has been plotted in Figure 3. It is found that the strength improves steadily up to a cure time of about 3 h. After that, the improvement becomes marginal. The initial improvement happens to be a function of the degree of cure attained with the passage of time. Increase in flexural strength of about 5–7% (maximum) may be attained by post cure operation at 100°C for 2 h. Considering the cost of energy involved for this minor improvement, the curing time may be fixed at 3 h.

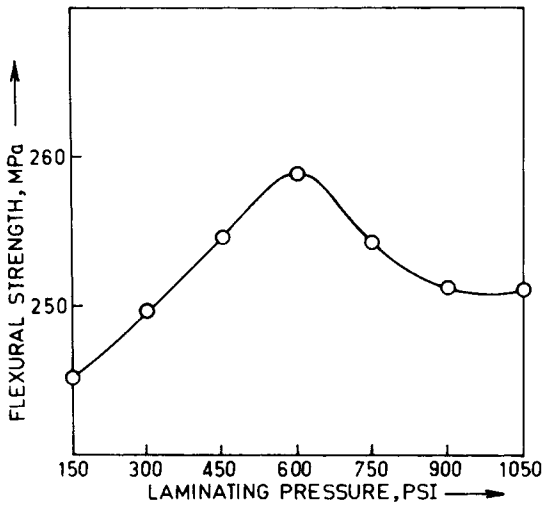

Fig. 4. Effect of laminating pressure on flexural strength of JP laminates.

Laminating Pressure

Variation of flexural strength against laminating pressure keeping other parameters constant has been shown in Figure 4. With the increase in pressure, a small increase in strength was observed initially, but when the pressure exceeded 600 psi, the samples showed a marginal fall in strength. An increase in the pressure initially caused a better flow of the resin and a reduction in the volume of the voids, while much higher pressure may induce a crushing action on jute fibers causing a reduction in the composite strength.

Table II gives the changes in the value of % C_v (coefficient of variation) with the sequential advancement of the optimization study. As the most suitable values of the processing parameters are obtained one by one, the value of C_v (the scattering of the individual values about the mean value) decreases and the lowest value is obtained when all the four parameters have been optimized. Higher scattering is essentially due to the nonuniformity in the composite samples resulting from the arbitrarily chosen values of the processing parameters. Thus this study has led to the preparation of the best possible uniform composite sample. The % C_v could not be reduced further because of the inherent variations present in the natural fibers.

TABLE II
Change of C_v with Progress of Optimization of Processing Variables

Fiber volume (%)	Cure temp (°C)	Cure time (h)	Laminating pressure (psi)	C_v (%)
68 ± 2	90	2	300	11.81
68 ± 2	100	2	300	10.46
68 ± 2	100	3	300	8.50
68 ± 2	100	3	600	7.87

TABLE III
Properties of Unidirectional Composites Based on Different Natural Fibers like Jute, Sisal, Ramie, Degummed Ramie, Pineapple Fibers Using PEAP as Interfacial Agent[a]

Sample	% Fiber by volume	Mean flexural strength (MPa)	Flexural strength (% C_v)	Mean flexural modulus (GPa)	Flexural modulus (% C_v)	% Retention of flexural strength after immersion in boiling distilled water, 72 h	% Water up take after immersion in boiling distilled water, 72 h	Hardness scale, Shore A	Density (g/cc)
JP	68 ± 2	258.8	7.87	39	2.36	38.33	18.79	95.0	1.141
JTP	68 ± 1	280.4	4.42	41	2.19	40.69	17.46	95.0	1.149
RP	62 ± 2	196.8	6.30	43	3.72	42.48	18.20	97.5	1.137
DRP	66 ± 2	197.6	6.59	36	1.92	40.20	18.47	90.0	1.162
DRTP	67 ± 3	223.04	5.98	37	1.69	44.90	15.80	90.0	1.173
SP	65 ± 2	225.3	11.30	49	5.67	31.40	22.40	92.5	1.0775
STP	64 ± 3	250.9	6.89	49	4.92	31.9	21.4	92.0	1.0933
PP	67 ± 2	221.8	4.49	33	1.98	39.58	20.34	90.0	1.124

[a]JP = jute/polyester, JTP = jute-treated polyester, RP = ramie/polyester, DRP = degummed ramie/polyester, DRTP = degummed-ramie-treated/polyester, SP = sisal/polyester, STP = sisal-treated polyester, PP = pineapple/polyester; PEAP treatment = Treated with 8.52% PEAP (sample no. A of Table I) based on weight of fiber. pH of treating solution maintained between 7.1 and 7.2. Operating conditions: cure temperature = 100°C; cure time = 3 h; laminating pressure = 600 psi.

Unidirectional Composites Based on Different Natural Fibers

Unidirectional composites were prepared with natural fibers other than jute maintaining the same processing conditions as determined in the preceding section.

Table III lists the mechanical properties of unidirectional composites based on different natural fibers like jute, sisal, pineapple, ramie, and degummed ramie. Effect of the interfacial agent, polyesteramide polyol (PEAP) developed in our earlier study,[1] on the mechanical properties of these NFC composites has also been indicated.

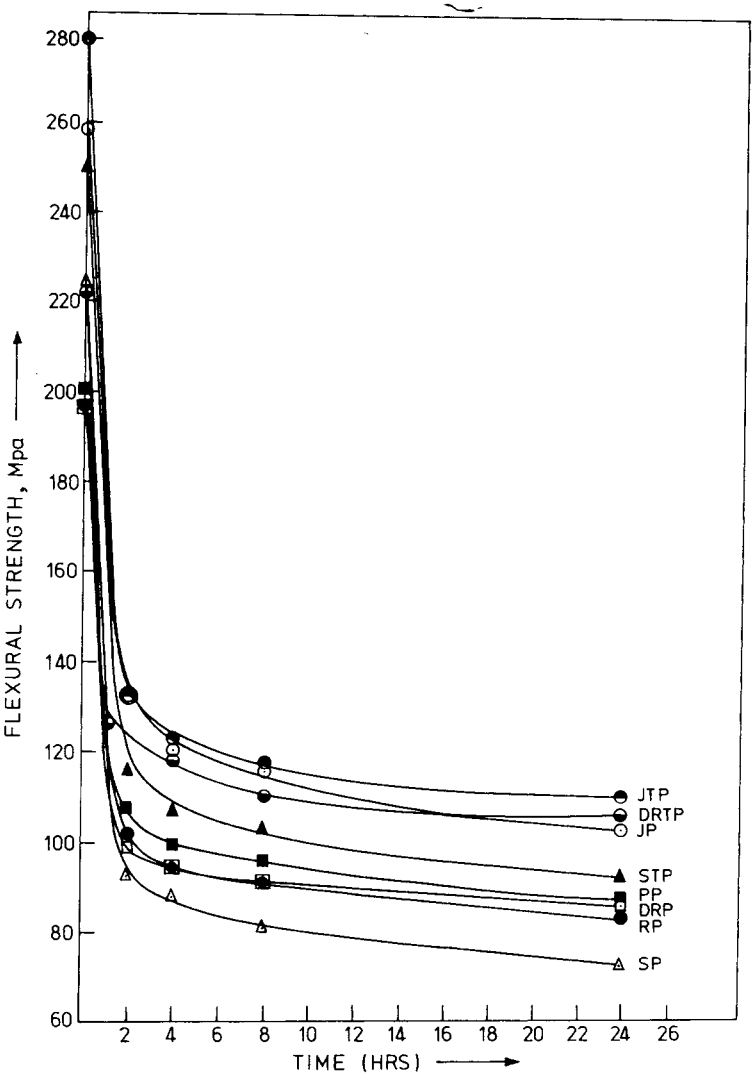

Fig. 5. Flexural strength of different natural fiber composites in boiling distilled water: JP = jute–polyester; JTP = jute-treated polyester; SP = sisal–polyester; STP = sisal-treated polyester; DRP-degummed ramie–polyester; DRTP-degummed-ramie-treated polyester; RP = ramie–polyester; PP = pineapple–polyester.

It is found that, for composites reinforced with fibers other than sisal, % C_v values in case of flexural strength are quite low. This indicates that the processing conditions optimized for jute are also applicable to those for ramie, degummed ramie, and pineapple fibers. Some modifications in the processing parameters appear to be necessary for sisal probably because of its inherent twist, relative hardness, and higher average diameter.

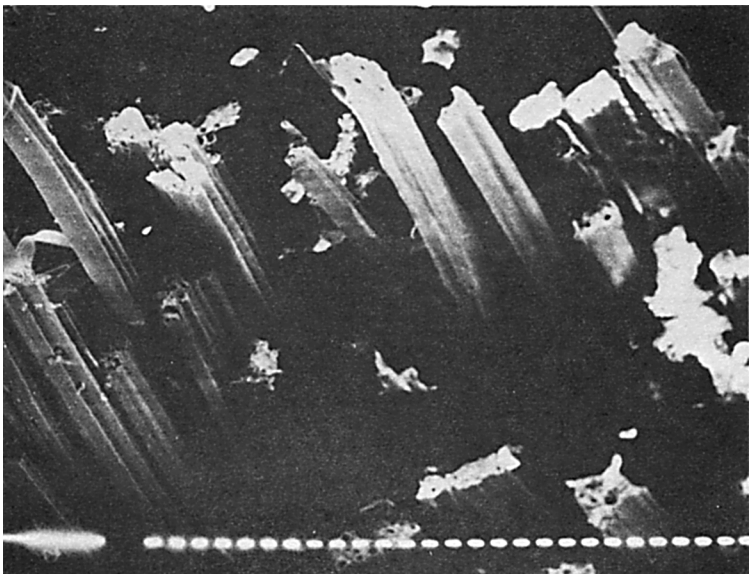

Fig. 6. (200×) SEM of jute polyester (JP) composite specimen (dry, no interfacial agent, 18.3% fiber volume) after flexural strength testing, showing transverse fracture.

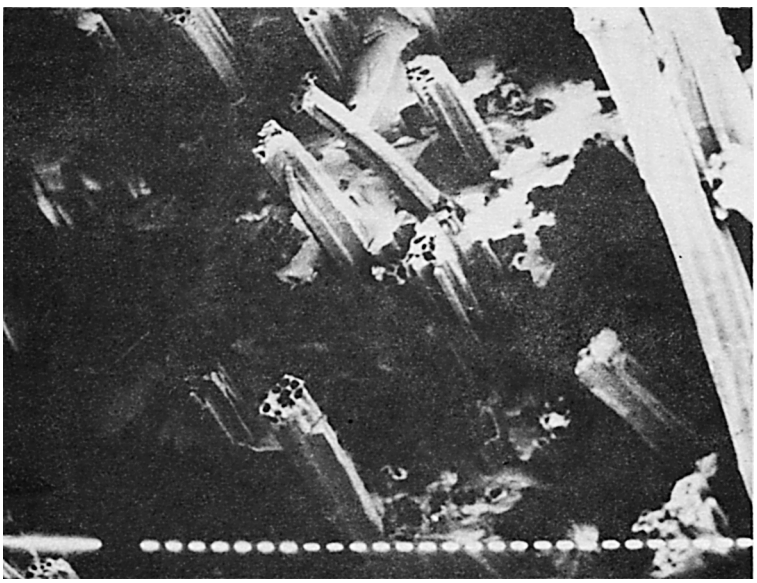

Fig. 7. (200×) SEM of JP composite specimen (dry, no interfacial agent, 40.9% fiber volume) after flexural strength testing, illustrating fiber pullout and damage in addition to transverse fracture.

The results indicate an overall improvement in flexural strength in case of treated fiber composites compared to the untreated fiber composites, the improvement ranging from 8.5% in case of jute polyester composites, 11% in case of sisal polyester composites, and 12% in case of degummed ramie–polyester composites. Marginal increase in density of the prepared natural fiber composites on prior treatment with interfacial agent (PEAP) is probably due to better wetting of the fiber leading to increased compactness of the final composites. The variation in degree of improvement of the various composites is possibly due to difference in the cellulose content of the fibers used and also may be due to the difference in types of natural fibers (hard or base fibers) used. Thus, jute composite shows the least improvement as jute has a low cellulose content of about 63% compared to ramie, which has a cellulose content of about 91%.

It is also significant to note the reduction of % C_v of flexural strength and modulus values in case of all the composite samples reinforced with PEAP-treated fibers compared to those with untreated fibers. This is possibly due to the better wetting of the fiber surface by the resin matrix when PEAP was used as the interfacial agent leading to more uniform distribution of the resin in the fibers.

Figure 5 indicates the reduction of flexural strength values of different composites after immersion in boiling water for different periods. It is found that retention of flexural strength is quite considerable in case of composite sample reinforced with treated degummed ramie fiber (DRTP). The percentage of water uptake is also the lowest (15.8%) in the sample.

Fracture Studies by Scanning Electron Microscopy (SEM)

Fracture modes of jute/polyest (JP) composite samples have been examined in SEM, and it has been observed from Figure 6 that JP composites show a

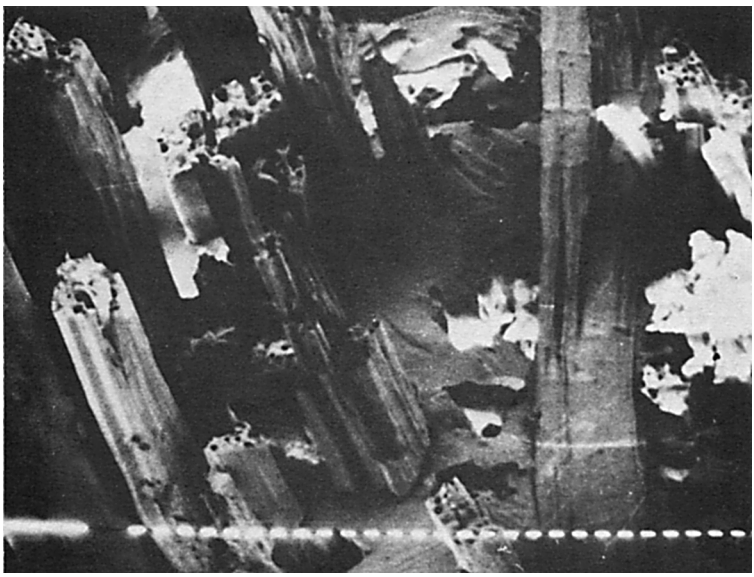

Fig. 8. (200×) SEM of JP composite specimen (dry, no interfacial agent, 53.1% fiber volume) after flexural strength testing, illustrating poor bonding between resin and fiber.

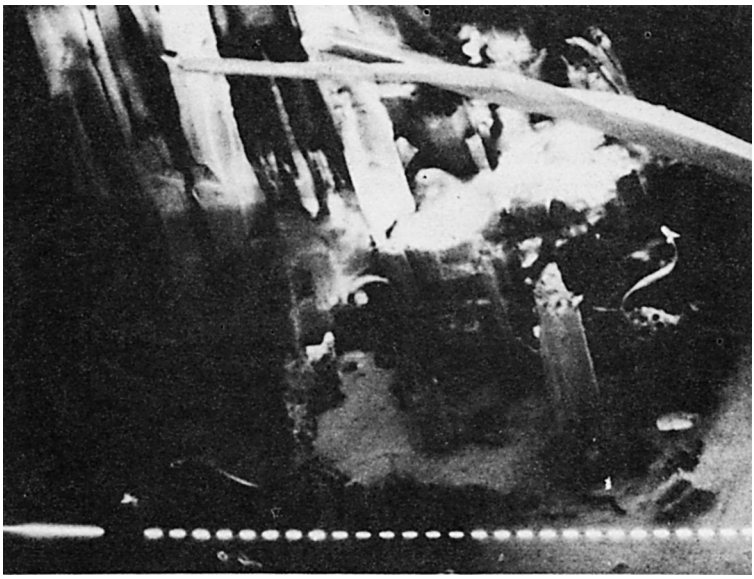

Fig. 9. (200×) SEM of JP composite specimen (dry, with PEAP as interfacial agent, 53.7% fiber volume) after flexural strength testing, showing improved bonding between resin and fiber.

transverse fracture with little fiber pullout and damage at low fiber volume fractions. This may be attributed to the fracture of JP composites at low stress levels. As the fiber volume is increased, there is increased fiber pullout in addition to transverse fracture. This may be due to lack of proper penetration of resin into the fiber matrix at high fiber volume (Fig. 7).

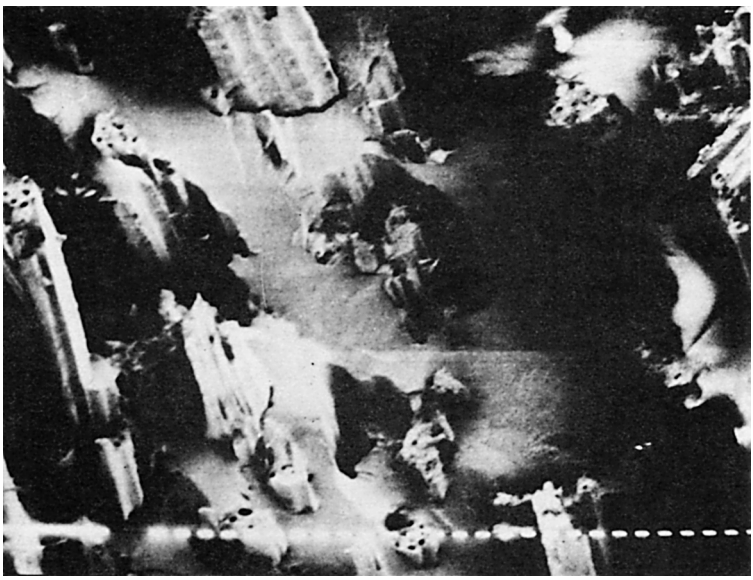

Fig. 10. (200×) SEM of JP composite specimen (after immersion in boiling water for 72 h, no interfacial agent, 52.8% fiber volume) after flexural strength testing. Debonding between resin and fiber is prominent.

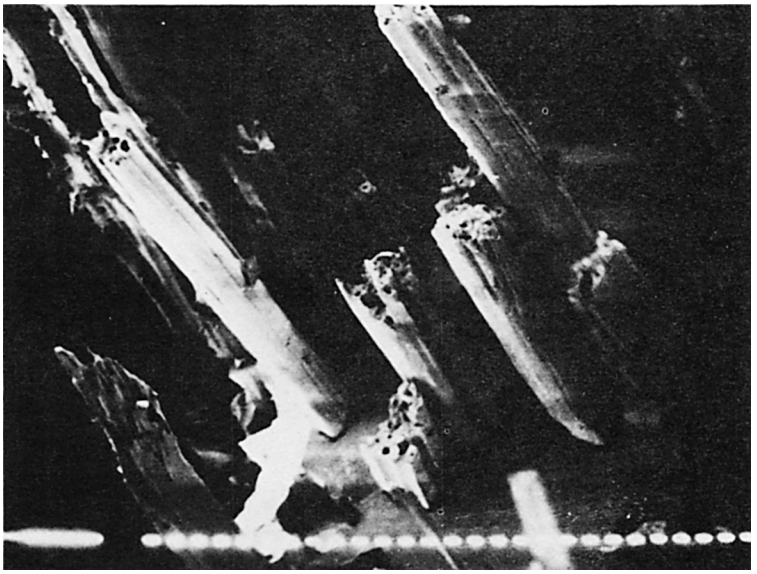

Fig. 11. (200×) SEM of JP composite specimen (after immersion in boiling water for 72 h, with PEAP as interfacial agent, 53.4% fiber volume) after flexural strength testing. Debonding is less prominent, indicating improved bonding between resin and fiber.

Fracture surfaces of untreated and PEAP-treated JP composites samples have been examined in SEM to study the nature of interfacial bonding on fiber treatments with PEAP. A qualitative improvement in bonding in case of PEAP-treated JP composites is evident from SEM photographs (Figs. 8 and 9). Fracture surfaces of these samples after immersion in boiling water for 72 h have also been examined in SEM (Figs. 10 and 11). It is seen that, in case of untreated fibers, the fibers got debonded from the resin matrix, while, in the case of PEAP-treated samples, such debonding is much less and layers of resin can be seen on some fiber surfaces, indicating better bonding even after 72 h of boiling in water. Thus it is found that PEAP treatment improves bonding to a certain extent, which is also evident from the improvement in strength of these composite samples on such treatment.

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