Effect of Acetylation on Dimensional Stability, Mechanical, and Dynamic Properties of Jute Board

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ABSTRACT: Jute slivers were acetylated in pilot scale following a no catalyst-no solvent method at 120°C for 2 h. The weight % gain was found to be 11.37. Different jute boards were pressed under heat and pressure using acetylated jute sliver and urea formaldehyde resin. Neutral salt (NaCl), acid salt (NH_4Cl), and melamine powder were used separately for curing urea formaldehyde. For comparison purposes, control boards were also prepared using nonacetylated slivers. The boards were tested for water soaking, cyclic water soaking, and cyclic humidity to see the effect of acetylation on dimensional stabilization. This chemical modification was found to improve the dimensional stability to a great extent for NaCl and NH_4Cl cured boards and to a less extent for a melamine-cured one. Tensile and flexural strengths were tested by Instron before and after the cyclic tests. Retention values were found to be as high as 60% after cyclic water tests for acetylated boards and the same was as low as 24% for control boards. Dynamic parameters, such as storage flexural modulus (E'), loss flexural modulus (E''), and loss factor or damping efficiency (tan δ) were determined in a fixed-frequency mode. Dynamic mechanical study revealed that tan δ peaks were lowered due to increased bulkiness of the fiber after acetylation and thus restricted mobility. A tiny additional peak was also visible at ~90°C beside the main peak at ~125°C for boards with modified slivers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 935–944, 1999

Key words: jute; acetylation; jute composite; dimensional stabilization; dynamic mechanical thermal analysis

INTRODUCTION

Jute, like other natural fibers, is hygroscopic and exhibits a tendency to be in moisture equilibrium with the relative humidity (RH) of the surrounding atmosphere, either by taking up moisture from or giving out moisture to the atmosphere.[1] This aspect is important in textiles in regard to their ability to transfer water vapor from the human body. However, for applications like composites, this aspect is detrimental insofar as its dimensional stability is concerned.

On the other hand, it is also observed that there is a growing interest of natural fiber-based composites mainly due to its high specific modulus,[2] light weight, low cost, and resistance to deforestation in addition to other usual advantages. Moreover, natural fibers possess fairly reactive cell walls that allow chemical modification on the surface.

Unfortunately, factors like dimensional stability limit the use of jute composites due to swelling and shrinkage in moist and dry atmospheres, re-

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Table I Formulation of Resin Solutions

Ingredient	Amount (g)		
UF	99.00	99.0	95.00
Melamine	—	—	5.00
NaCl	1.00	—	—
NH_4Cl	—	1.00	—
Water	300.00	300.00	300.00
Total	400.00	400.00	400.00
ID of composites	CNa/ANa	CNH/ANH	CMF/AMF

C = control jute sliver and A = acetylated jute sliver

spectively. This is due to adsorption of water molecules with the other polar groups, such as (—OH), (>CO), (—COOH), (—CH_2OH), (>NH_2), (—$CONH_2$), and (—NH) present in the cell wall of the jute fiber. To increase the scope of its utilization, modification of the fiber is essential. Acetylation, methylation, cyanoethylation, etc., are such methods. Jute contains 21–23% hemicellulose, 13–14% lignin, and 61–64% cellulose. Taking advantage of the plentiful hydroxyl groups present in the different constituents, acetylation of jute was done after a simplified procedure and using a no catalyst-no solvent method.[3,4]

The process, acetylation for reducing water absorption and in turn increasing dimensional stability, is already established in different published literature using wood fiber and flake.[5,6] Of these various processes available, a simplified procedure using a no catalyst-no solvent method initially created a lot of interest for its commercialization. With time, due to an increase in operational, as well as chemical cost, perhaps it was not justified to do so. In our recent communication on acetylation of jute fiber at various times and temperatures, we found that 2 h at 120°C is the optimum condition. After this procedure, a pilot scale study was done. Because the acetylation process always added to cost, its effectiveness is also compared with the control using three curing systems with urea formaldehyde (UF).

The aim of this article was to study the effect of acetylated jute board on dimensional stability measured by swelling rate, cyclic water soaking,

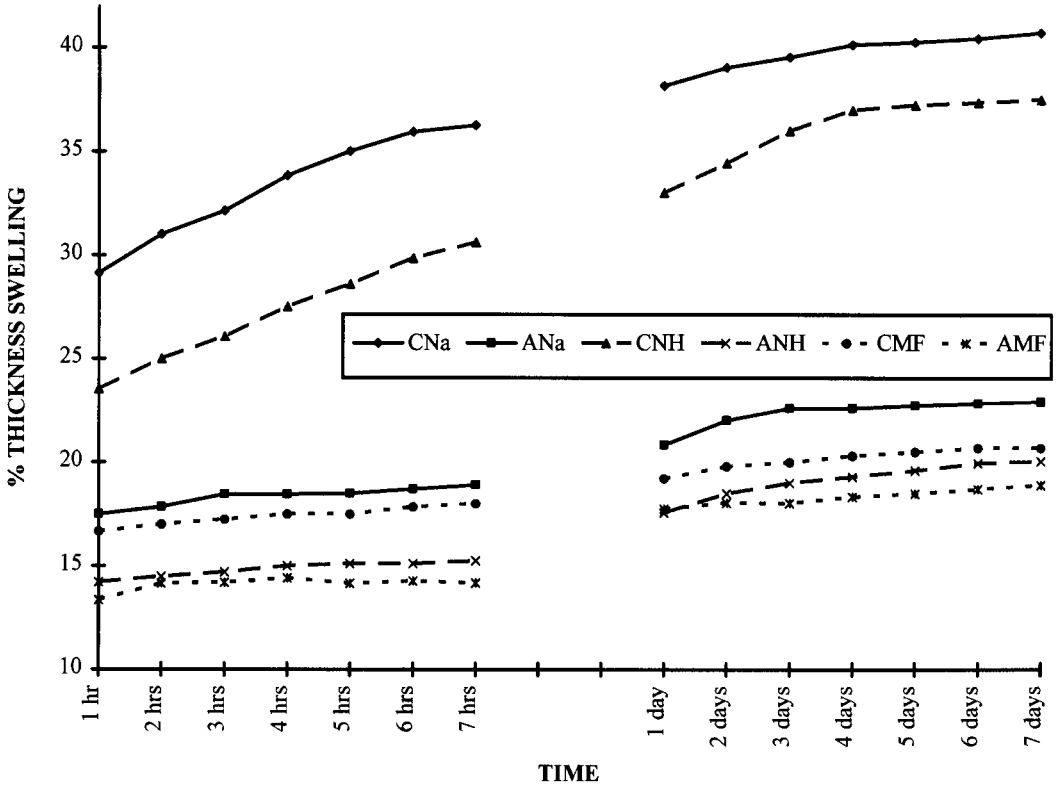

Figure 1 Variation of thickness in water with time of different types of jute boards.

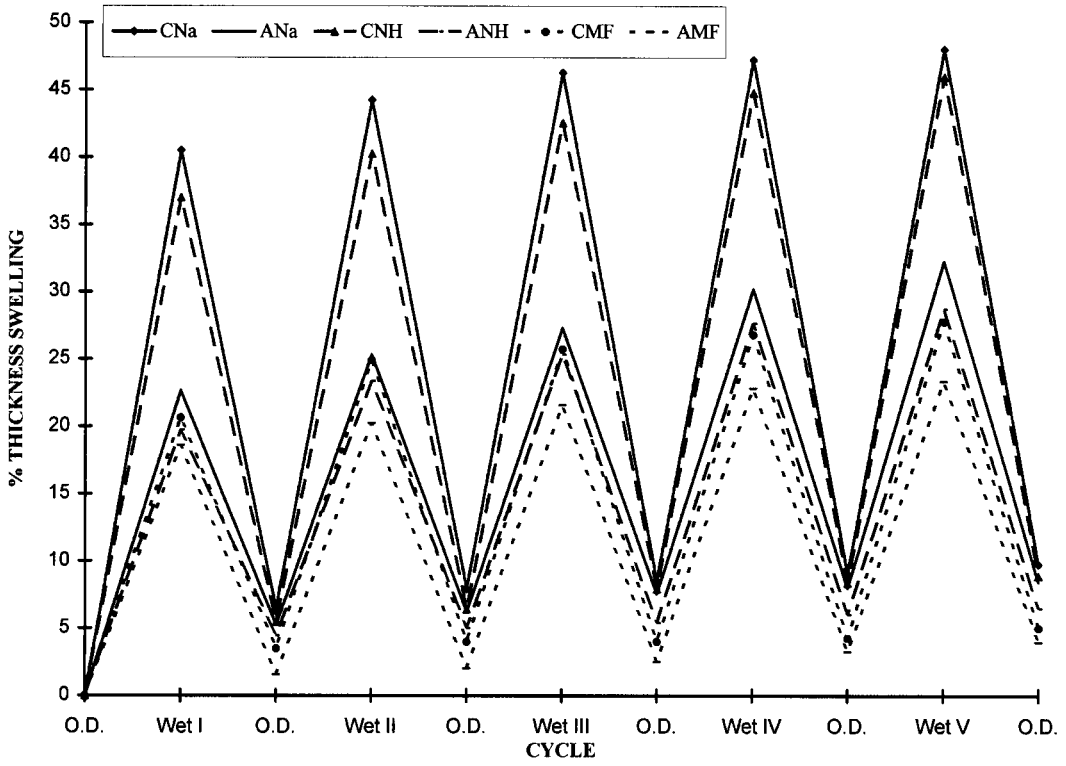

Figure 2 Variation of thickness with alternate dry and wet cycles of different types of jute boards. O.D., outside diameter.

and cyclic humidity tests, using UF resin as binder and cured by three different systems—a neutral salt (NaCl), an acid salt (NH_4Cl), and a crosslinking agent, melamine powder. The results were also compared with the corresponding non-acetylated systems. The mechanical and dynamic properties were also compared.

EXPERIMENTAL

Acetylation

Materials

Jute sliver was made from W2. Corchorus Capsularies were collected from Hastings Jute Mill (Calcutta, India). Acetic anhydride (BP Chemicals) was AR grade.

Methods

Oven-dried jute sliver (dried at 105°C for 24 h) and acetic anhydride were preheated to 120°C. Jute sliver was then completely soaked with sufficient acetic anhydride for 3 min. The excess acetic anhydride was then taken out by vacuum. Acetylation of impregnated material in the heated stainless-steel chamber at 120°C was done for 2 h. Recovery of unreacted acetic anhydride and the byproduct, acetic acid, formed during acetylation was collected by vacuum. Finally, acetylated slivers were oven-dried at 105°C for 10 h. Weight % gain (WPG) was calculated based on oven-dried and unreacted sliver.

Board Preparation

Materials

UF powder resin (plywood grade; Hindustan Ciba, India), melamine powder (GSFC, India), NaCl (E. Merck, AR grade), NH_4Cl (IDPL, AR grade), and acetylated jute sliver were prepared as previously described.

Method

Resin solutions were prepared using ordinary tap water, and the formulations are shown in Table I.

Jute slivers were completely immersed in the resin solution (25% solid content) for 3 min and then squeezed between the two rollers so that its

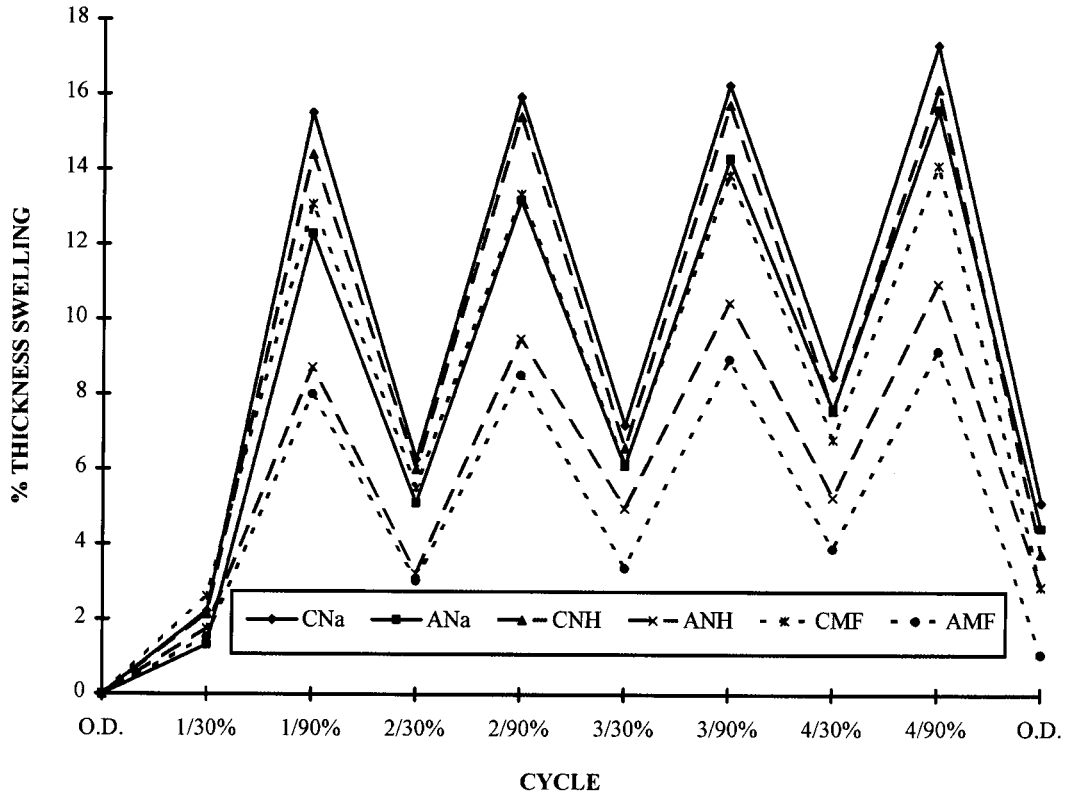

Figure 3 Variation of thickness with alternate 30% and 90% RH of different types of jute boards. O.D., outside diameter.

weight became double from its initial oven dry weight (i.e., the solid add-on became 25% on a w/w basis). These wet slivers were then dried in an air-circulated oven to a volatile content of 12–15% measured at 160°C for 10 min.

Boards (15 cm × 15 cm × 3 mm) were prepared by placing four layers of the impregnated slivers in the same fiber direction between the two mirror finish plates and pressed at 160°C for 5 min under a specific pressure of 400 psi. Platens were cooled to 40°C before removed from the press.

Water Soaking Test

Test samples (5 cm × 5 cm) were cut from the board. Tests were performed following the previously described procedure. All measurements were taken at the center of the each specimen every hour for 7 h and every day for 7 days. Thickness swelling was calculated as a percentage of the original oven-dried thickness. All tests were performed in triplicate.

Cyclic Water Soaking Test

This test was conducted with specimen size as previously described. Specimens were soaked in water at 25°C for 4 days and then oven-dried at 105°C for 24 h. This cycle was repeated five times and finally oven-dried at 105°C for 24 h. Thickness swelling was calculated as a percentage of the original oven-dried thickness.

Cyclic Humidity Test

In this test standard, oven-dried specimens were kept alternatively for 14 days at 30% and 90% RH at 25°C for reaching equilibrium.[5] Thickness swellings were calculated as a percentage of oven-dried original thickness. Four cycles of 30% and 90% RH were repeated. Finally, specimens were oven-dried and thickness measured.

Mechanical Test

Mechanical properties were measured using Instron 4303 (125 mm × 12.5 mm × 3.0 mm). Specimens were tested at 5.0 mm min^{-1} at room temperature after keeping at 65% RH for 24 h.

Dynamic Mechanical Analysis

This test was performed using DMA 983, Dynamic Mechanical Analyzer, TA instruments at a

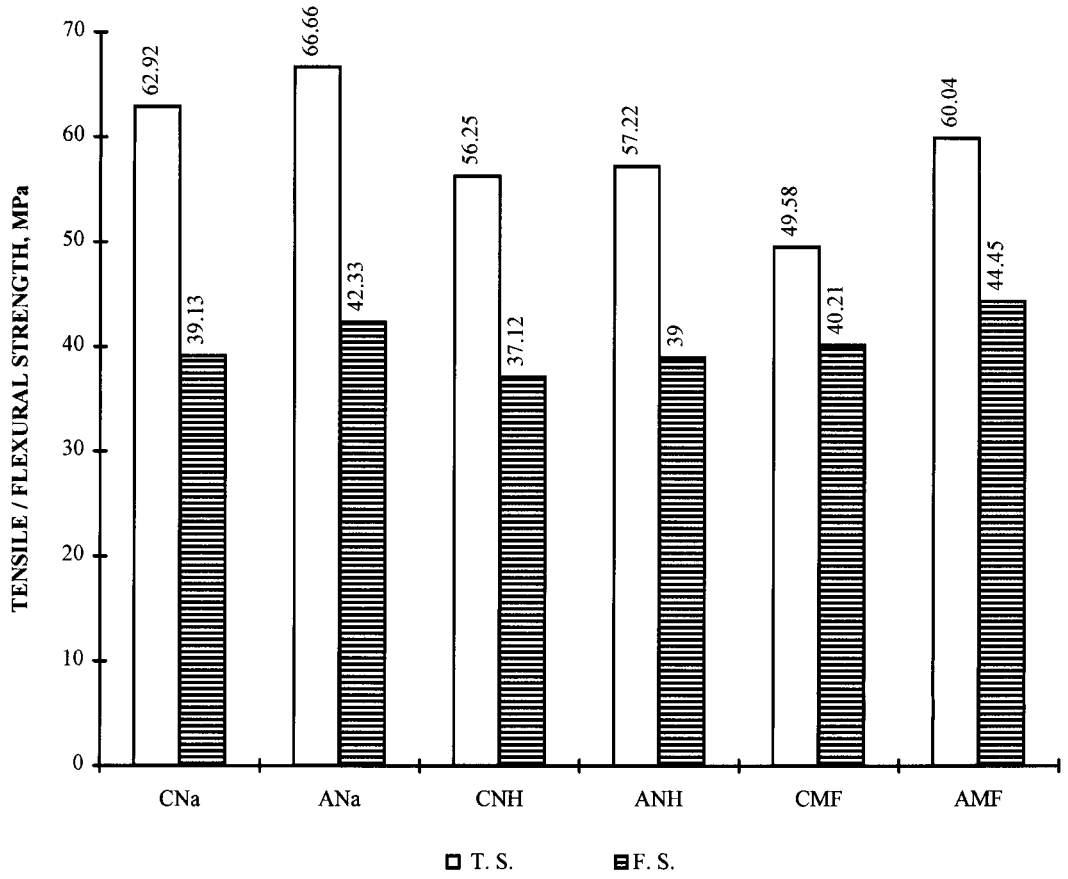

Figure 4 Tensile (T.S.) and flexural (F.S.) strengths of different types of jute boards.

fixed-frequency (1-Hz) mode. Data so obtained were analyzed with the help of computer software DMA V4.2. Each specimen was equilibrated at 35°C; ramp = 5°C min^{-1}; length/thickness = 10; amplitude = 0.30 mm; and temperature range = 35°–180°C. All specimens were cut along the direction of the fiber. In all cases, four specimens were tested and average values were reported.

RESULTS AND DISCUSSION

Acetylation

In our previous communication,[4] we found that, with a rise in temperature and time, weight % gain (WPG) increased. It was also found that 2 h at 120°C for a noncatalyst, nonsolvent system was optimum. In this pilot scale study, we obtained a WPG value of 11.37, compared with our earlier experimental WPG of 10.6 at the same reaction condition. The small increase in WPG may be due to the bulk trial of 2.0 kg jute sliver instead of only 1 g during the experiment, because the bulk reaction is often faster due to slow dissipation of heat.

Water Swelling Test

Test results are graphically represented in Figure 1 as % swelling *versus* time. Maximum and minimum swellings were found in CNa (29.14% in 1 h, 40.79% in 7 days) and in AMF (13.36% in 1 h, 18.79% in 7 days). During the first 7 h, the control boards CNa, CNH, and CMF swelled 36.26%, 30.61%, and 18%, respectively. The corresponding acetylated boards swelled only 18.9%, 15.25%, and 14.17%. From the figure, it is also found that the effect of acetylation toward dimensional stability was more prominent when NaCl and NH_4Cl were in the resin system. On the contrary, it was least prominent when melamine was present in the system.

After 7 days the control boards CNa, CNH, and CMF swelled 40.79%, 37.55%, and 20.7% in comparison with acetylated boards 22.92%, 20.05%,

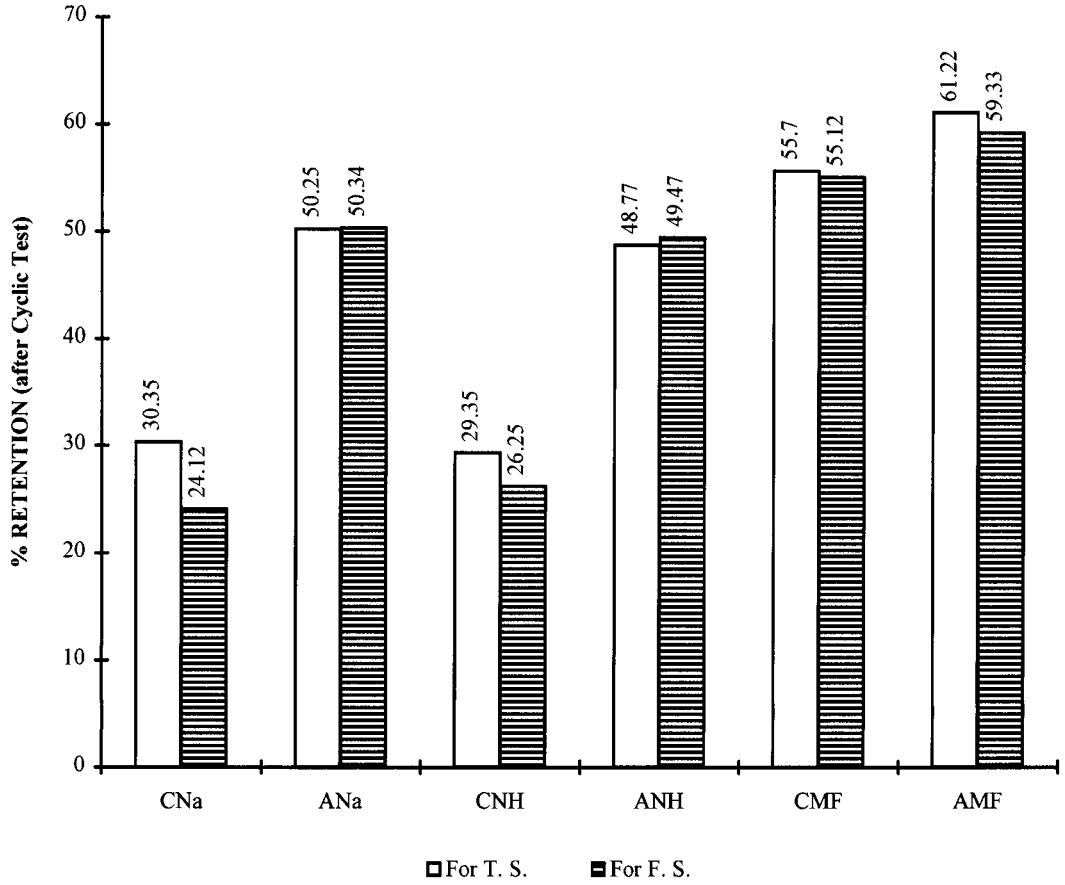

Figure 5 % retention of tensile (T.S.) and flexural (F.S.) strengths of different types of jute boards after the cyclic test.

and 18.9%, respectively. Control of swelling by acetylation may be compared by the relative swelling rate where,

Relative swelling rate = % swelling

of (control − acetylated)/% swelling of control.

The values are found to be 43.81, 46.60, and 8.70 after 7 days using NaCl, NH_4Cl, and melamine in the system. So, we found that acetylation has a tremendous effect on dimensional stabilization when NaCl and NH_4Cl are used as catalyst for UF, whereas melamine has a dramatically lesser effect. The reason may be attributed to its own crosslinking action and resistance to water. That is why a further effect of acetylation was less evident.

Cyclic Water Soaking Test

Thickness changes in the cyclic water soaking test is shown in Figure 2. The boards made from acetylated and control sliver behaved similarly as in the water swelling test. Both in the oven-dried sample and wet samples, an upward trend was observed with an increase in the number of cycles. After the 5th cycle, % thickness swelling for CNa, CNH, and CMF were 48.06, 46 and 27.82, respectively, for wet samples. The corresponding values for oven-dried samples were 9.8, 8.93, and 5.03, respectively. After acetylation, there was considerable improvement in the thickness swelling. The corresponding values for wet samples were 32.29, 28.75, and 23.36; for oven-dried samples, they were 8.46, 6.49, and 3.97.

Cyclic Humidity Test

Figure 3 shows the thickness change at 30% RH and 90% RH of acetylated and nonacetylated boards. In all cases, the extent of swelling decreased due to acetylation. An upward trend of increase in swelling with an increase in the number of cycles were also noted in this case. This was much more so in control boards.

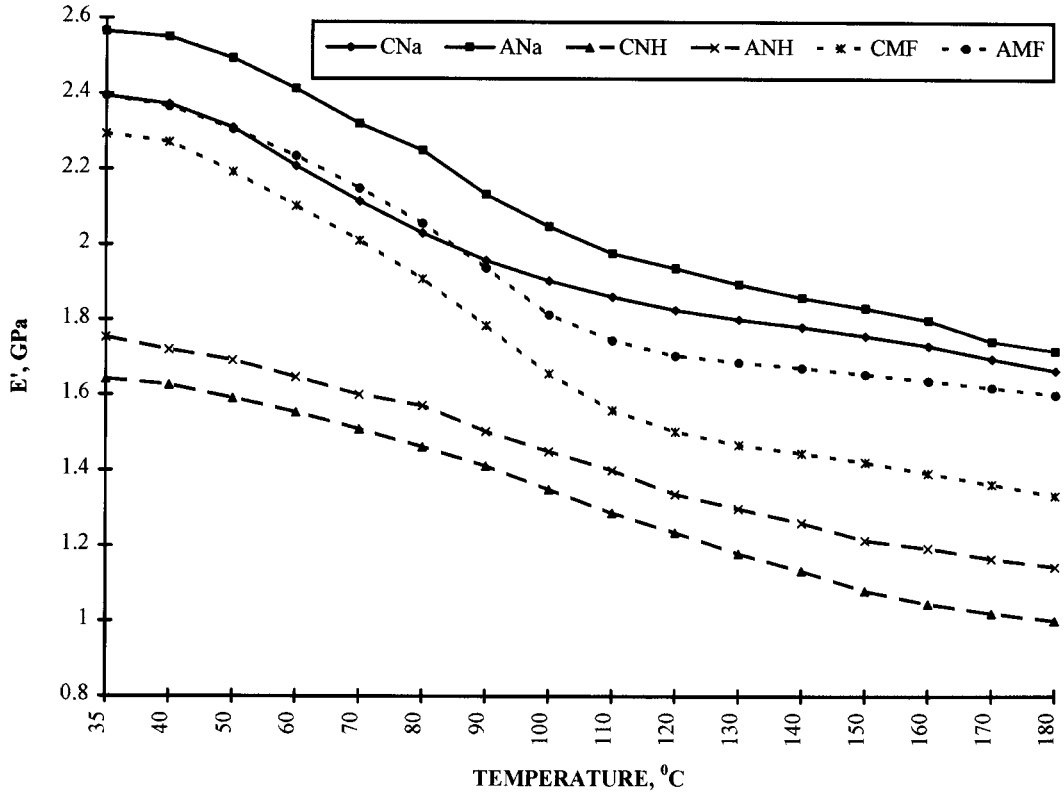

Figure 6 Variation of storage flexural modulus of different types of jute boards with temperature.

In both the cyclic humidity tests and cyclic water soaking tests, an irreversible swelling was evident. This was more prominent in the nonacetylated boards. There was always some permanent swelling, and this was more prominent in control boards. This may be attributed to the adhesive failure resulting from the accelerated test conditions. The least permanent swelling was noted in AMF.

Mechanical Properties

Tensile and flexural strengths are shown in Figure 4. Improvement in tensile strengths were observed for AMF over CMF by 20%, ANa over CNa by 10%, and negligible for ANH over CNH. Improvement in mechanical properties were also observed for dry acetylated particle boards by Mallari and colleagues.[7,8] However, significant strength losses of fiber boards were also reported at a higher level of acetylation and for severe reaction conditions in the presence of a strong catalyst.[3] In contrast, for flexural strengths, there was no appreciable change in values between acetylated and nonacetylated, except an increase of 10% strength in AMF over CMF.

Percent retention of strengths after the cyclic test is plotted in Figure 5. It is noted that there was appreciable gain in the retention values for both tensile and flexural strengths after acetylation. The maximum gain was found in AMF (61.22% for tensile and 59.33% for flexural strength), and it was ~ 10% higher than the nonacetylated board. The significant effect of acetylation on the retention of strength in ANa over CNa and ANH over CNH are also observed from Figure 5.

Dynamic Mechanical Study

The variation of E' for different samples is shown in Figure 6 as a function of temperature. It can be seen from the figure that E' of the NH_4Cl-based system was much lower than the other two. This might be due to the modulus imparted by the respective binding system. E' values were decreased sharply with temperature. It is also found that E' of acetylated samples were much higher

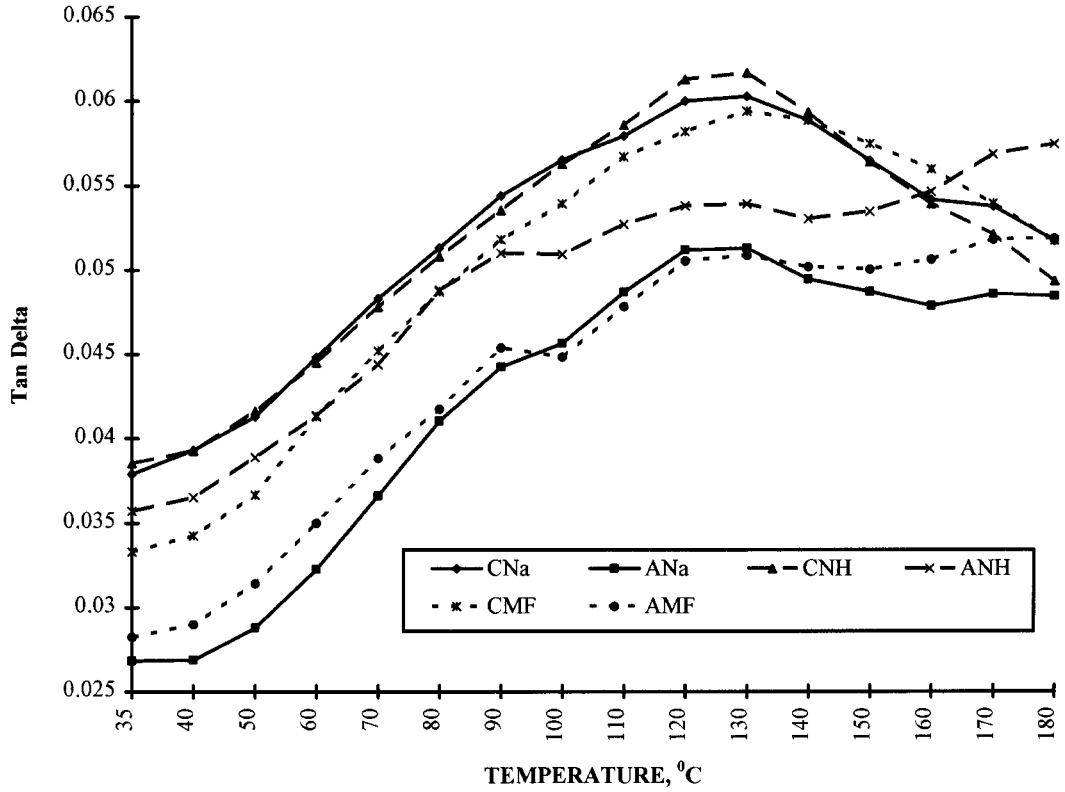

Figure 7 Variation of tan δ of different types of jute boards with temperature.

than that of the nonacetylated one at a particular temperature.

Figure 7 shows the variation of the tan δ with temperature for different acetylated and nonacetylated jute boards. It is observed that acetylated boards have reduced peak height (i.e., tan δ is lowered due to increased bulkiness of the acetylated fiber). The reason might be due to the restriction of mobility of the fiber due to the pendent acetyl group on the fiber cell wall. Reduction of peak height due to restriction of mobility was also observed by the earlier workers.[9,10] The other prominent effect was that, instead of shifting, an additional tiny peak at ~ 90°C was visible for acetylated boards. The appearance of this peak may be attributed to what is called the second relaxation process or the "β relaxation process," which is caused by the introduction of acetyl groups in the cell wall. An analogy might be drawn with the effect of grafting butyl rubber onto polyethylene and its tan δ plot with temperature giving two distinct peaks.[11]

The main difference between the acetylated and nonacetylated sample peaks at ~ 125°C was that the latter was more broader and the former was more sharp. This might be due to the inhibition of the relaxation process (or α relaxation) within the composites upon chemical modification of the fiber by acetylation. The presence of acetyl groups could create strong intermolecular interactions of the H-bonding type within the composites, and these interactions could likely act as a physical crosslinking that yielded, to some extent, a similar effect on the relaxation process as a chemical crosslinking did, such as the case where melamine powder was used. This phenomenon could be a key factor contributing to improvements in many physical and mechanical properties of acetylated jute sliver boards when NaCl or NH_4Cl was in the resin system. The least value of tan δ at ~ 125°C was for the system having melamine as the curing agent. The reason may be attributed to a further decrease in mobility due to its powerful crosslinking abilities.

Figure 8 shows the variation of E'' with temperature for different samples. If the applied mechanical energy (work) is not stored elastically, it must be lost-converted to heat through molecular friction (i.e., viscous dissipation) within the material. This is precisely the loss modulus.[12] More or less the same observations as tan δ is observed through the peaks were not as sharp as those.

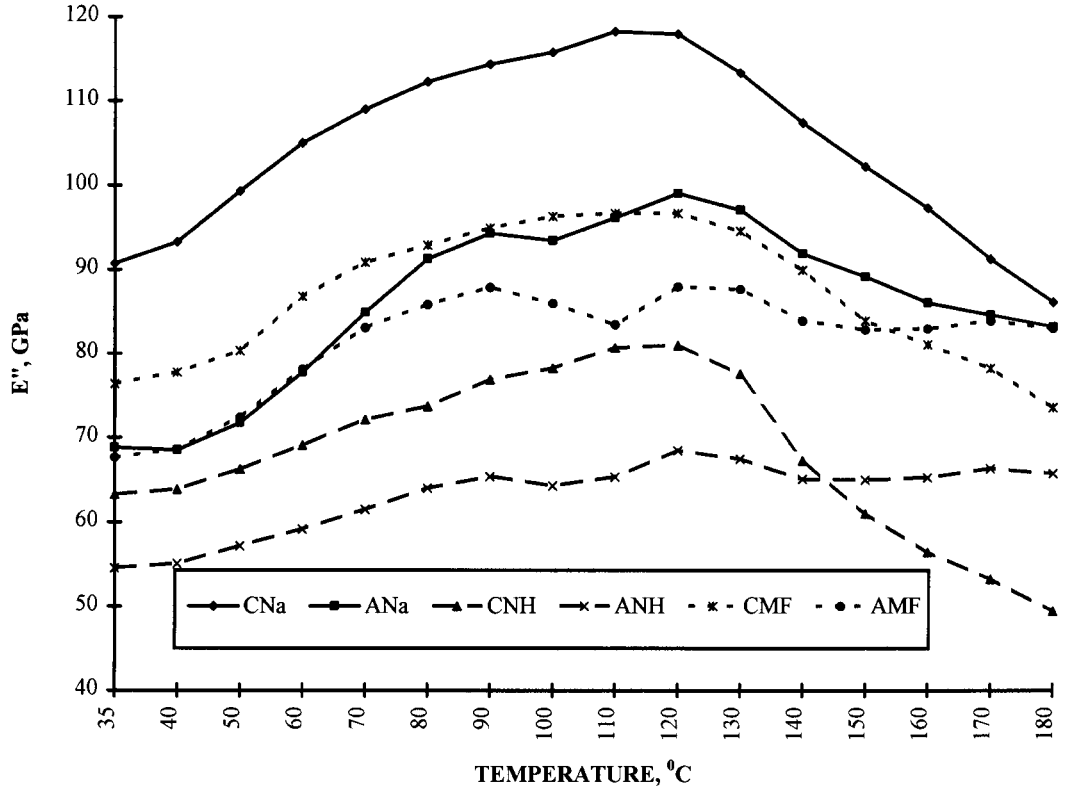

Figure 8 Variation of loss flexural modulus of different types of jute boards with temperature.

CONCLUSIONS

1. Earlier experiments on the nonsolvent and noncatalyzed acetylation system[4] and present pilot scale study was in close agreement, so far as WPG was concerned.
2. The difference in dimensional stability between control and acetylated board using melamine as crosslinking agents in UF resin was found to be very marginal when the extent of acetylation was ~ 12 WPG. However, this difference was much higher when NaCl and NH_4Cl were present in the system.
3. The retention of tensile and flexural strength after acetylation was found to be as high as 60% after the cyclic water test; for control boards, it was as low as 24%.
4. The effect of melamine as the crosslinking agent in UF was found to be very good, so far as dimensional stability was concerned. Although acetylation of the sliver further increased the dimensional stability, the cost of acetylation did not economically justify the marginal better performance.
5. The dynamic mechanical study revealed that E' of acetylated boards was much higher than that of the nonacetylated one at a particular temperature. E'' and tan δ peaks were lowered due to increased bulkiness of the fiber after acetylation. A tiny additional peak was also visible at 90°C beside the main broad peak at 125°C.

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REFERENCES

1. Mookherjee, R. R. Tex Digest 1955, XVI, 86.
2. Wells, H.; Bowen, D. H.; Macphail, I.; Pal, P. K. 35th Annual Technology Conference 1980, Reinforced Plastics/Composites Institute, SPI, Sect. I-F, 1980.

3. In Paper and Composites from Agrobased Resources; Rowell, R. M.; Young, R. A.; Rowell, J. K., Eds.; Lewis Publishers: New York, 1996.
4. Rana, A. K.; Basak, R. K.; Mitra, B. C.; Lawther, M.; Bannerjee, A. N. J Appl Polym Sci 1997, 64, 1517.
5. Rowell, R. M.; Tillman, A. M.; Simonson, R. J Wood Chem Technol 1986, 6, 427.
6. In Handbook on Wood and Cellulosic Materials; Hon, D. N. S.; Shirashi, N., Eds.; Marcel Dekker, Inc.: New York, 1991.
7. Mallari, V. C.; Fukuda, K.; Morohoshi, N.; Haraguchi, T. Mokuzai Gakkaishi 1989, 35, 832.
8. Mallari, V. C.; Fukuda, K.; Morohoshi, N.; Haraguchi, T. Mokuzai Gakkaishi 1990, 36, 139.
9. Saha, N.; Bannerjee, A. N.; Mitra, B. C. J Appl Polym Sci 1996, 60, 657.
10. Saha, N.; Bannerjee, A. N. J Appl Polym Sci 1996, 62, 1199.
11. In Handbook of Thermoplastic Elastomers; Walker, B. M., Ed.; Van Nostrand Reinhold Company: New York, 1979.
12. In Fundamental Principles of Polymeric Materials; Rosen, S. L., Ed.; John Wiley & Sons: New York, 1982.