Study of Jute Fiber Reinforced Polyester Composites by Dynamic Mechanical Analysis

A. K. SAHA,¹ S. DAS,¹ D. BHATTA,² B. C. MITRA³

¹ Indian Jute Industries' Research Association, 17 Taratola Road, Calcutta 7000 88, India

² P.G. Department of Chemistry, Utkal University, Bhubaneswar

³ National Institute of Research on Jute and Allied Fibre Technology, Calcutta 700040

Received 11 March 1998; accepted 25 July 1998

ABSTRACT: Cyanoethylation of jute fibers in the form of nonwoven fabric was studied, and these chemically modified fibers were used to make jute-polyester composites. The dynamic mechanical thermal properties of unsaturated polyester resin (cured) and composites of unmodified and chemically modified jute-polyester were studied by using a dynamic mechanical analyzer over a wide temperature range. The data suggest that the storage modulus and thermal transition temperature of the composites increased enormously due to cyanoethylation of fiber. An increase of the storage modulus of composites, prepared from chemically modified fiber, indicates its higher stiffness as compared to a composite prepared from unmodified fiber. It is also observed that incorporation of jute fiber (both unmodified and modified) with the unsaturated resin reduced the tan δ peak height remarkably. Composites prepared from cyanoethylated jute show better creep resistance at comparatively lower temperatures. On the contrary, a reversed phenomenon is observed at higher temperatures (120°C and above). Scanning electron micrographs of tensile fracture surfaces of unmodified and modified jute-polyester composites clearly demonstrate better fiber-matrix bonding in the case of the latter. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1505–1513, 1999

Key words: composite; storage modulus; loss modulus; tan δ ; creep

INTRODUCTION

Fiber-reinforced composite materials¹⁻⁴ consist of fibers of high strength and modulus embedded in or bonded to a matrix with a distinct interfaces between them. In this form, both fibers and matrix retain their physical and chemical identities, yet they provide a combination of properties that cannot be achieved with either of the constituents acting alone. In general, fibers are the principal load-bearing materials, while the surrounding matrix keep them in the desired location, and orientation acts as a load transfer medium between them and protects them from environmental damage.

The importance and popularity of fiber-filled composites are due to their unusually high strength and stiffness for a given weight of material. Moreover, both the properties, that is, strength and stiffness can be altered according to our requirement by altering the composition of a single fiber-resin combination. Again, fiber-filled composites find uses in innumerable applied areas by judicious selection of both fiber and resin.

In recent years, greater emphasis has been rendered in the development of fiber-filled com-

Correspondence to: D. Bhatta.

Journal of Applied Polymer Science, Vol. 71, 1505-1513 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/091505-09

Consta	Moisture Regain	Tensile Strength	Tensile Modulus	Flexural Strength	Flexural Modulus	Bundle Tenacity
Sample	(65% KH at 25°C)	(MPa)	(GPa)	(IMPa)	(GPa)	(g/Tex)
Unmodified jute fiber	12.5	565	27.2	—	—	21.26
Modified jute fiber (RT, 1 h)	9.02	453	26.3	—	—	17.66
Modified jute fiber (RT, 2 h)	8.89	442	26.2			15.70
Modified jute fiber (RT, 3 h)	8.45	409	26.1			15.36
Modified jute fiber (RT, 4 h)	8.26	402	26.00			15.30
Modified jute fiber (RT, 5 h)	8.12	396	25.1	—	—	15.19
USP resin (cured)	—	69	3.2	122.6	3.6	—

Table I Properties of Fibers and Unsaturated Polyester Resin (Cured)

RT denotes the reaction time for cyanoethylation.

posites based on natural fibers 5-12 with a view to replace glass fibers either solely or in part for various applications. The scope for using jute fiber in place of the traditional glass fibers stems from the lower specific gravity and workable specific modulus of the jute fiber (1.45 and 19 GPa, respectively) compared to those of glass (2.56 and 29 GPa, respectively). Moreover, the much lower cost and the renewable nature make it an attractive fiber for use as a reinforcing material in the fiber-filled composite. Again the nonabrasive nature of the jute fiber permits the use of high fiber content in the composite without the fear of extensive damage to compounding and molding equipment that occurs when much harder glass fiber is used.

In spite of the various desirable properties of the jute fiber to act as a reinforcing material, its commercial utilization in the fiber-filled composite has not gained much success. The main reasons of the failure are poor wettability and adhesion characteristics of the jute fiber towards many commercial synthetic resins, resulting in poor strength and stiffness of the composite as well as poor environmental resistance.^{13–17} Therefore, an attempt has been made to overcome the limitations of the jute fiber through its chemical modification.

Dynamic mechanical tests, in general, give more information about a composite material than other tests. Dynamic tests, over a wide range of temperature and frequency, are especially sensitive to all kinds of transitions and relaxation process of matrix resin and also to the morphology of the composites. Dynamic mechanical analysis (DMA) is a sensitive and versatile thermal analysis technique, which measures the modulus (stiffness) and damping properties (energy dissipation) of materials as the materials are deformed under periodic stress. DMA also provides reliable information about the T_g of a fiberfilled composite.

The object of the present article is to study the effect of chemical modification (cyanoethylation) of the jute fiber for improving its suitability as a reinforcing material in the unsaturated polyester resin-based composite by using a dynamic mechanical thermal analyzer. Attempts have been made to compare the flexural modulus and mechanical damping properties as a function of temperature of unmodified jute-polyester composite with chemically modified samples. In addition, the time-dependent aspects of load-bearing capabilities have been studied by using the data obtained from the creep experiment.

MATERIALS AND CHEMICALS

General purpose unsaturated polyester resin (USP) was obtained from M/S Ruia Chemicals Pvt. Ltd., which was based on orthophthalic anhydride, maleic anhydride, 1,2-propylene glycol, and styrene. The styrene content was about 35%.



Figure 1 Storage modulus (E') profiles of neat resin (cured), one unmodified jute-polyester composite (NJC), and five chemically modified (cyanoethylated) jute-polyester composites (MJC).

Uniaxially oriented, jute-based, needle-punched, nonwoven (750 gm/cm²) fabric was procured from M/S Birla Corporation Ltd. Laboratory reagentgrade acrylonitrile of S.D.Fine Chemicals was used in this study without further purification.

CYANOETHYLATION OF JUTE NONWOVEN

Cyanoethylated jute nonwovens were prepared by using the procedure reported earlier.¹⁸ Uniaxially oriented, needle-punched, nonwoven (felt) jute was cut to a 30×30 cm size, and the pieces were padded twice in 4.0% (w/w) sodium hydroxide solution at room temperature. The wet pickup was adjusted to 90%, and the alkali-soaked nonwovens were again padded with acrylonitrile to the same wet pick-up, that is, 90%. The acrylonitrile impregnated felts were held for different periods of time, namely, 1-5 h at room temperature wrapped with polyethylene sheet. After the stipulated time of reaction, the felts were washed with 5.0% formic acid, then with distilled water, and were dried in a vacuum oven at 80°C.

Some properties of unmodified jute, chemically modified (cyanoethylated) jute, and neat unsaturated polyester resin (cured) are given in Table I.

FABRICATION OF COMPOSITE SHEETS

A weighed amount of polyester resin, admixed with catalyst (tertiary butyl perbenzoate), was applied on one side of the nonwoven jute by a hand lay-up technique. Several layers were pressed together in a hydraulic press at 610 psi pressure and 150°C temperature, and pressing was continued for 15 min. Myler film on both sides of the stack



Figure 2 Loss modulus (E'') profiles of neat resin (cured), one unmodified jute-polyester composite (NJC), and five chemically modified (cyanoethylated) jute-polyester composites (MJC).

was placed for easy release and to obtain superior surface finish of the pressed laminates. After the stipulated time of pressing, the temperature of the press was brought down under the same pressure by circulating cold water, and the laminate was taken out and trimmed. In all the experiments, a resin content of 30% by weight was maintained.

MEASUREMENTS

Tensile and flexural strength of the fibers and the cured resin were measured by Instron Universal Testing Machine (Model No. 4303). DMA measurements were carried out on a TA Instruments DMA 983. Test samples ($60 \times 11 \times 3.2 \text{ mm}$) were cut from jute-polyester laminated sheets and were postcured at 110°C for 1 h and conditioned at 65% relative humidity (RH) at 25°C for 15 days.

In DMA, the test specimen was clamped between the ends of two parallel arms, which are mounted on low-force flexure pivots allowing motion only in the horizontal plane. The samples in a nitrogen atmosphere were measured in the fixed frequency mode, at an operating frequency 1.0 HZ (oscillation amplitude of 0.2 mm) and a heating rate of 4°C per min. The samples were evaluated in the temperature range from 40 to 200°C.

In the creep mode of DMA, the samples were stressed for 30 min at an initial temperature of 40°C and allowed to relax for 30 min. The temperature was then increased in the increments of 40°C, followed by an equilibrium period of 10 min before the initiation of the next stressrelax cycle. This program was continued until it reached the temperature of 160°C. All the creep experiments were performed at stress level of 20 KPa (approximate). The tensile fracture surfaces of the composite samples were studied with a scanning electron microscope (Hitachi Scanning electron Microscope, Model S-415 A) operated at 25 keV.



Figure 3 Tan δ profiles of neat resin (cured), one unmodified jute-polyester composite (NJC), and five chemically modified (cyanoethylated) jute-polyester composites (MJC).

DYNAMIC MECHANICAL ANALYSIS

Dynamic storage modulus (E') is the most important property to assess the load-bearing capability of a composite material, which is very close to the flexural modulus, as measured by ASTM D-790. The ratio of the loss modulus (E'') to the storage modulus (E') is known as a mechanical loss factor (tan δ). This quantity is the measure of balance between the elastic phase and the viscous phase in a polymeric structure. This can relate to impact properties of a material. Generally, the tan δ peak (at low frequency) is at a temperature 10–20°C above the T_g , as measured by dilatometry or differential thermal analysis (DTA). The temperature of maximum loss modulus (E'') is very close to T_{g} . Figure 1 depicts the DMA curves of storage moduli (E') versus temperature of neat resin (cured), one unmodified jute-polyester composite (NJC), and five modified jute-polyester composites (MJC). The curves indicate that the initial storage modulus value (E') of all the five modified jute-polyester composites have been

enormously improved compared to unmodified jute-polyester composite, and the degree of modulus loss due to thermal transition is markedly reduced in all the five modified jute-polyester composites. It is also evident that the degree of modulus loss between 40 and 100°C for NJC is around 38%; but for MJC, they are only around 16%. It is also evident from the Figure 1 that, in all cases, the storage moduli (E') values of modified jute-polyester composites at any temperature are higher than that of unmodified jutepolyester composite.

It is seen from the Table I that there are no large differences in modulus values between modified and unmodified jute fiber. The much improved moduli of the five chemically modified jute-polyester composites might be due to the greater interfacial bond strength between the matrix resin and the fiber. The hydrophilic nature of jute induces poor wettability and adhesion characteristics with USP resin, and the presence of moisture at the jute-resin interface promotes the formation of voids at the interface. Thus, the presence of moisture and voids at the interface weaken the bonds and produce composite of lower stiffness and strength. The presence of moisture in the system may result from diffusion of atmospheric moisture through the matrix on subsequent aging. On the other hand, owing to cyanoethylation, the moisture regain capacity of the jute fiber is much reduced; also, the compatibility with unsaturated polyester resin has been improved and produces a strong interfacial bond with matrix resin and produces a much stiffer composite.

Figure 2 plots loss moduli (E'') versus temperature of neat resin (cured), one NJC and five MJC. It can be seen from Figure 2 that the loss modulus peak temperature for the unmodified jute-polyester composite has been reduced compared to neat resin, while the same has been increased for all the 5 chemically modified composites. As the loss modulus peak temperature is very close to T_g of the polymeric system, it may be concluded that the composites prepared from cyanoethylated jute shift the T_g value to the higher temperature.

Figure 3 shows tan δ versus temperature plots for neat polyester resin (cured), one NJC and five MJC composites. It has been reported $^{19-21}$ that the incorporation of stiff fibers reduce the tan δ peak height by restricting the movement of polymer molecules. It is also seen that the tan δ peak height of all the six composites are reduced markedly compared to neat resin. It is evident from Figure 3 that there is not much difference in the height of the tan δ peak for all the six composites, including NJC. This indicates that all the six composites possess the same order of damping capabilities. It is observed in many cases that the improvement of stiffness markedly reduces the ductility. But through cyanoethylation of jute, it is possible to manufacture composites with increased stiffness without sacrificing its ductility. The increased transition temperature of composites, prepared from cyanoethylated fiber over unmodified jute-polyester composite suggests an increase in rigidity of the fibermatrix interfacial zone due to improved fiber-matrix interaction,²² which reduces molecular mobility in the interfacial zone.

Scanning electron micrographs^{23,24} of fractured surfaces of both unmodified and one chem-



(a)



(b)

Figure 4 Scanning electron micrographs $(200 \times)$ of tensile fracture surfaces of (a) unmodified and (b) chemically modified jute-polyester composites.

ically modified jute–polyester composite are shown in the Figure 4. The modified jute-polyester composite shows excellent retention of resin on broken fiber ends, while an unmodified one shows uncoated fibers and holes in the matrix. Thus, the indication of better fiber–matrix bonding in the case of cyanoethylated jute is further supported by a scanning electron microscopy (SEM) study.

Figure 5 denotes the creep behavior of one unmodified and five modified jute-polyester composites at the following four different temperatures:

Figure 5 Comparison of creep percentages for one unmodified jute–polyester composite (NJC) and five chemically modified jute–polyester composites (MJC) at the following four different temperatures: (a) 40, (b) 80, (c) 120, and (d) 160°C.







40, 80, 120, and 160°C. It is observed that composites prepared from cyanoethylated jute possess less creep compared to that prepared from unmodified (normal) jute when the creeps are measured within 80°C. A reversed trend is observed when the creeps are measured at 120 and 160°C. Better creep resistance of composites, prepared from chemically modified jute at comparatively lower temperature (up to 80°C), may be due to better fiber-matrix bonding. Rowell and his coworkers²⁵ showed that kenaf (bast) fiber attains thermoplasticity, and the first transition temperature drops to 135 from 170°C when the fiber constituents are esterified with succinic acid. Hon and his coworkers $^{\rm 26}$ produced a thermomoldable wood by benzoylation of wood powder. Probably, in the same manner, thermoplasticity of jute develops, owing to cyanoethylation, and the corresponding composites give higher creeps at elevated temperatures, that is, at 120 and 160°C.

CONCLUSIONS

- 1. When jute fiber is chemically modified (cyanoethylated) to a different extent, the storage moduli and thermal transition temperatures of the composites shift to higher values.
- 2. It is possible to produce much stiffer and stronger jute-polyester composites by partial cyanoethylation of fiber before it is converted to composite.
- 3. The degree of modulus loss with the increase of temperature is drastically reduced when the cyanoethylated jute is used to make jute-polyester composite.
- 4. To obtain the desired effect of cyanoethylation, 2 h of batching time is quite sufficient.
- 5. At a comparatively lower temperature (up to 80°C), cyanoethylated jute fiber-filled composites show much more creep resistance than the same fabricated with untreated jute.
- 6. At a comparatively higher temperature (120°C and above), cyanoethylated jute fiber-filled composites show higher creep than when it is prepared from untreated fiber.
- 7. The scanning electron micrographs of the fracture surface of the samples reveal the improved bonding at the interface between the cyanoethylated fiber and the polyester resin.

The first two authors are thankful to Dr. K. Jayachandran, Director, Indian Jute Industries' Research Association, for his keen interest and for permission to publish the work.

REFERENCES

- Mallick, P. K. Fiber-Reinforced Composites: Materials, Manufacturing and Design; Marcel Dekker: New York, 1988.
- Weatherhead, R. G. FRP Technology: Fibre-Reinforced Resin Systems; Applied Science Publishers Ltd.: London, 1980.
- Broutman, L. J.; Kroek, R. H. Modern Composite Materials; Addison Wesley: Reading, MA, 1967.
- Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and composites, 2nd ed.; Marcel Dekker: New York, 1994.
- Owolabi, O.; Czvikovszky, T.; Kovacs, I. J Appl Polym Sci 1985, 30, 1827.
- Belmares, H.; Barrera, A. Ind Eng Chem Prod Res Dev 1981, 20, 555.
- Usmani, A. M.; Ball, G. L. J Elastomers Plast 1980, 12, 18.
- Usmani, A. M.; Ball, G. L. J Elastomers Plast 1981, 13, 46.
- Salyer, I. O.; Usmani, A. M. Ind Eng Chem, Prod Res Dev 1982, 21, 17.
- 10. Murty, V. M.; De, S. K. J Appl Polym Sci 1982, 27, 4611.
- Murty, V. M.; De, S. K. Rubber Chem Technol 1983, 55, 287.
- 12. Setua, D. K.; De, S. K. Rubber Chem Technol 1983, 56, 808.
- Mukherjee, R. N.; Pal, S. K.; Sanyal, S. K. J Appl Polym Sci 1983, 28, 3029.
- Bhatnagar, S. S.; Khan, G. A. R.; Verman, L. C. Ind Pats. 28,281 and 28,427, 1926.
- 15. Philip, A. R. Eng Mater Des 1965, 8, 475.
- Bowen, D. H.; Wells, H. Paper presented at the SPI Reinforced Plastics and Composites Conference, New Orleans, LA, Feb. 4, 1980.
- Saha, A. N.; Lakkad, S. C. Fiber Sci Technol 1981, 14, 319.
- Saha, A. K.; Mitra, B. C. J Appl Polym Sci 1996, 62, 733.
- Harris, B.; Braddel, O. G.; Almond, D. P.; Lefebvre, C.; Verbist, J. J Mater Sci 1993, 28, 3353.
- Dibcnedctto, A. T.; Lex, P. J. Polym Eng Sci 1989, 29, 543.
- 21. Thomson, J. L. Polym Compos 1990, 11, 105.
- 22. Chua, P. S. Polym Compos 1987, 8, 308.
- 23. Hartlein, R. C. Ind Eng, Chem Prod Res Dev 1971, 10, 92.
- 24. Toy, A.; Engquist, R. D. Scanning Electron Microscopy Proceedings, 3rd Symposium, Chicago, IL; 1970.
- Rowell, R. M.; O'dell, J. L.; Rails, T. G. Proceedings of the 2nd Pacific Rim Biocomposites Symposium, Vancouver, Canada, Nov. 6–9, 1994.
- Hon, D. N. S.; Ou, N. H. J Polym Sci, Part A, Polym Chem 1989, 27, 2457.