JOURNAL OF MATERIALS SCIENCE **39** (2004) 2961 – 2964

Effect of novel sizing on the mechanical and morphological characteristics of natural fiber reinforced unsaturated polyester resin based bio-composites

G. MEHTA, A. K. MOHANTY, M. MISRA, L. T. DRZAL
Composite Materials and Structures Center, Michigan State University, 2100 Engineering Building, East Lansing, MI 48824, USA
E-mail: mohantya@egr.msu.edu

Bio-composites are the smart materials of the future. It is only through these materials that the balance of ecology and economy can be maintained. In the past decade the interest and research in this area has grown exponentially. There is a growing interest in the use of natural/bio-fibers as reinforcing components for thermoplastics and thermosets. Although thermoplastics have added advantage of recycling possibility, thermosets are targeted to obtain much improved mechanical properties as compared to thermoplastics in the resulting bio-composites. Natural/bio-fibers offer many advantages such as energy efficiency, low cost, low density, high toughness, acceptable specific strength, and bio-degradability [1, 2]. However they do suffer from a few limitations as well. Bio-fibers are hydrophilic in nature, and thus have lower compatibility with relatively hydrophobic polymer matrices. The hydrophilic nature of biofiber is also responsible for water absorption characteristic of the biocomposite thus limiting its application where water absorption is a major hurdle. Since mechanical properties of the composites are related to the compatibility and interaction between the components, improvement of the interface and interphase interactions in natural fiber/polyester composites is essential.

In this paper, bio-composites were made using a hemp fiber as reinforcement and unsaturated polyester (UPE) as the matrix. Hemp fiber is a "bast fiber," meaning that it is obtained from the stem of the plant. It has 70.2–70.4% (by wt.) cellulose, 3.7–5.7% lignin, 17.9–22.4% hemicellulose, 0.9% pectin, 0.3% wax and 8.0% moisture [1, 3]. Hemp fiber has tensile strength of 690 MPa and Young's modulus of 20 GPa [1, 3]. A non-woven mat containing 90% hemp and 10% low molecular weight polyester binder was used as the reinforcement for the bio-composites fabricated in this work. As a polymer matrix, UPE finds widespread use and enjoys a 40% market share of all thermoset composites [4]. In this work, composites were made using untreated and chemically treated hemp mats and fabricated using compression molding. A control made from only neat UPE was cured in a conventional oven since it could not be compression molded as it shrank during curing. The optimum fiber content was determined by making bio-composites with different fiber volume fractions (10, 20, 30 and 40%), and testing them for mechanical properties. Bio-composite with highest mechanical properties was the one with optimum fiber content (30%).

The required amount of fiber mats was vacuum dried prior to sizing. The dried fiber mats were soaked in a solution containing 3.0% acrylonitrile (AN), 0.5% dicumyl peroxide and 96.5% ethanol for 15 min. The excess solution was drained from the mats and they were dried overnight in a hood followed by vacuum drying. The polyester resin (UPE) was mixed well with the initiator, methyl ethyl ketone peroxide (MEKP) and the accelerator, cobalt naphthenate (CoNp), in required amounts and then degassed under vacuum at room temperature for 5 min. The fiber mats were individually coated with the degassed resin. They were then placed between two aluminum plates covered with teflon release sheets. The plates were placed in a compression molding press (Carver® Laboratory Press) and composites were cured at 560 kPa for 2 h at 100 °C followed by 2 h at 150 °C. The bio-composite using untreated fiber mats was made in same way. The resulting composite plaques were cut into required shapes for various tests. For making the control panel from neat resin, degassed UPE solution was poured over degassed silicone moulds and cured in a conventional oven using the same temperature profile.

The bio-composites and neat polyester samples were used for tensile, flexural and notched Izod impact test complying with ASTM D638, ASTM D790 and ASTM D 256 standards respectively. The tensile fractured surfaces of the composites were examined using Environmental Scanning Electron Microscopy (ESEM). Dynamical mechanical analysis (TA Instruments DMA 2980) was used to measure the storage modulus, loss modulus and tan delta. For this test, rectangular sample bars were placed on the 3 point bending clamp in the furnace and heated at 4 °C/min from room temperature to 150 °C.

Bio-composite made from acrylonitrile treated hemp fiber gave the highest tensile strength and tensile modulus, (Fig. 1). By this treatment, the tensile strength was enhanced by 160% as compared to that of the neat polyester control, and 80% when compared to the raw hemp-UPE bio-composite. In the case of the modulus, the bio-composite made with chemically treated hemp gave an improvement of 430% compared to the polyester control and 25% when compared to untreated hemp-UPE. Flexural properties follow the same

0022–2461

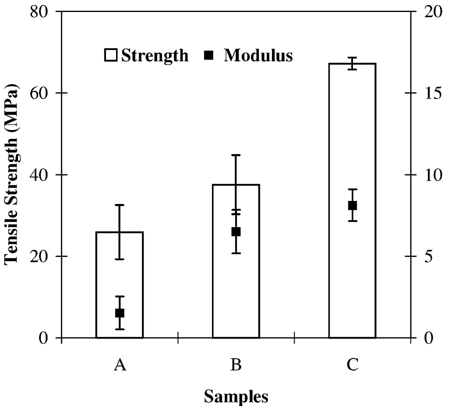


Figure 1 Effect of acrylonitrile treatment on tensile properties of hemp fiber-unsaturated polyester composites: A = neat resin, B = untreated hemp-polyester composite, and C = acrylonitrile treated hemp-polyester composite.

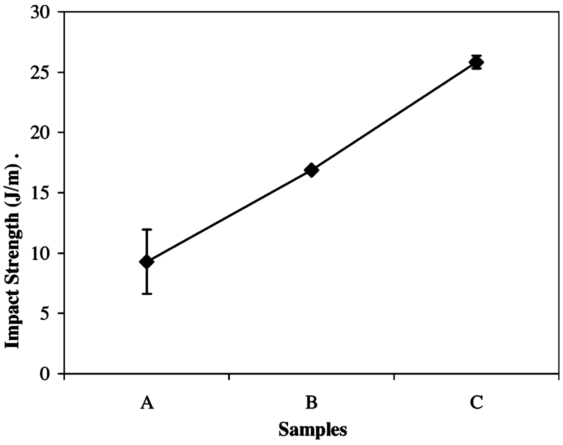


Figure 2 Effect of acrylonitrile treatment on Izod impact properties of hemp fiber-unsaturated polyester composites: A = neat resin, B = untreated hemp-polyester composite, and C = acrylonitrile treated hemp-polyester composite.

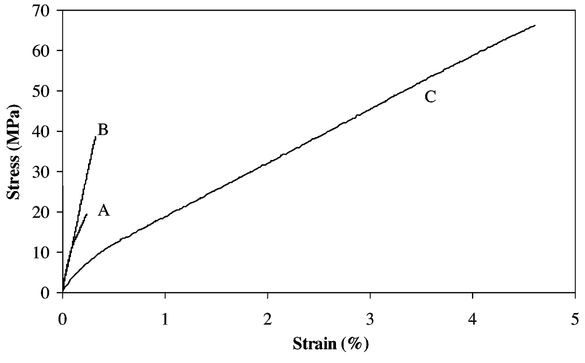


Figure 3 Stress-strain plot from tensile test: A = neat resin, B = untreated hemp-polyester composite, and C = acrylonitrile treated hemp-polyester composite.

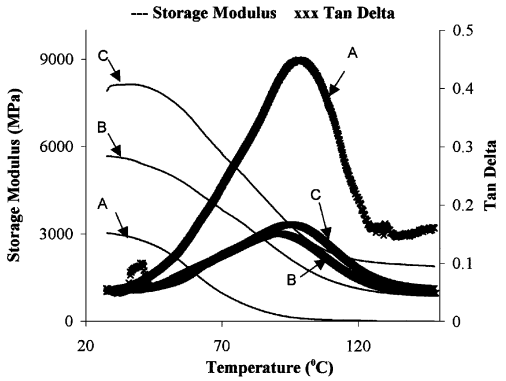


Figure 4 Effect of acrylonitrile treatment on storage modulus and tan delta of hemp fiber-unsaturated polyester composites: A = neat resin, B = untreated hemp-polyester composite, and C = acrylonitrile treated hemp-polyester composite.

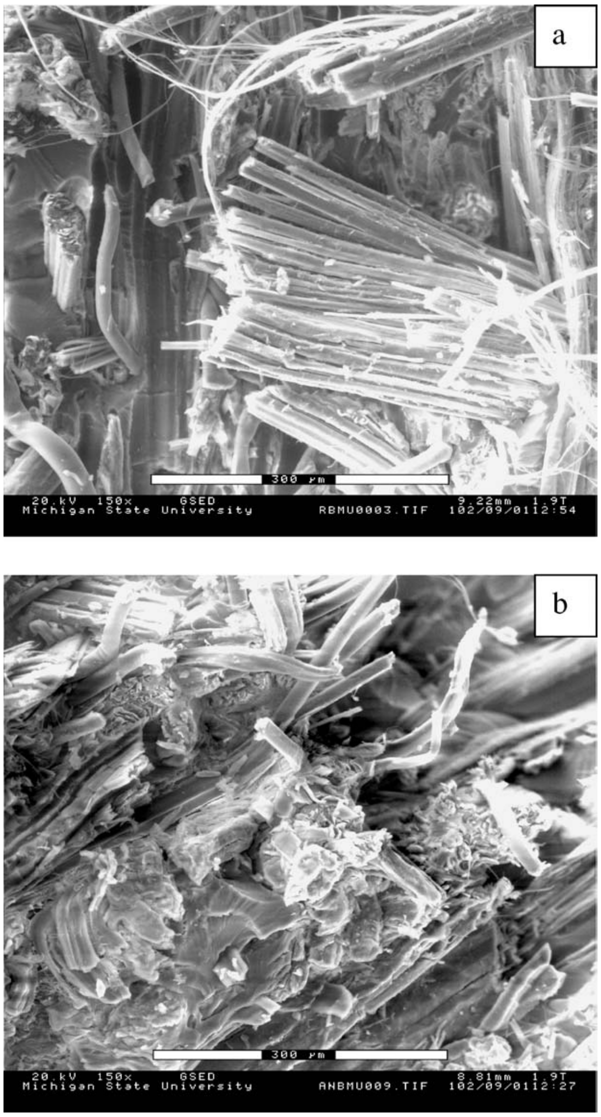


Figure 5 ESEM micrographs (magnification150×, scale 300 μm) of tensile fractured surfaces of: (a) untreated hemp mat-UPE composite and (b) acrylonitrile treated hemp mat-UPE composite.

trend as tensile properties. The highest bending strength and MOE are exhibited by acrylonitrile treated hemp-UPE composites, (figure not shown). As compared to neat UPE plastic, the bending strength of acrylonitrile treated hemp-UPE composite increased by 15%. The elastic modulus of acrylonitrile treated hemp-UPE biocomposite increased by 225% as compared to that of neat UPE, and by 30% as compared to that of untreated hemp-UPE composite. The improvement in the flexural and tensile properties of the treated fiber composite is attributed to the modifications at the molecular level of the fiber, which lead to fiber-matrix bonds, increased adhesion and more effective stress transfer.

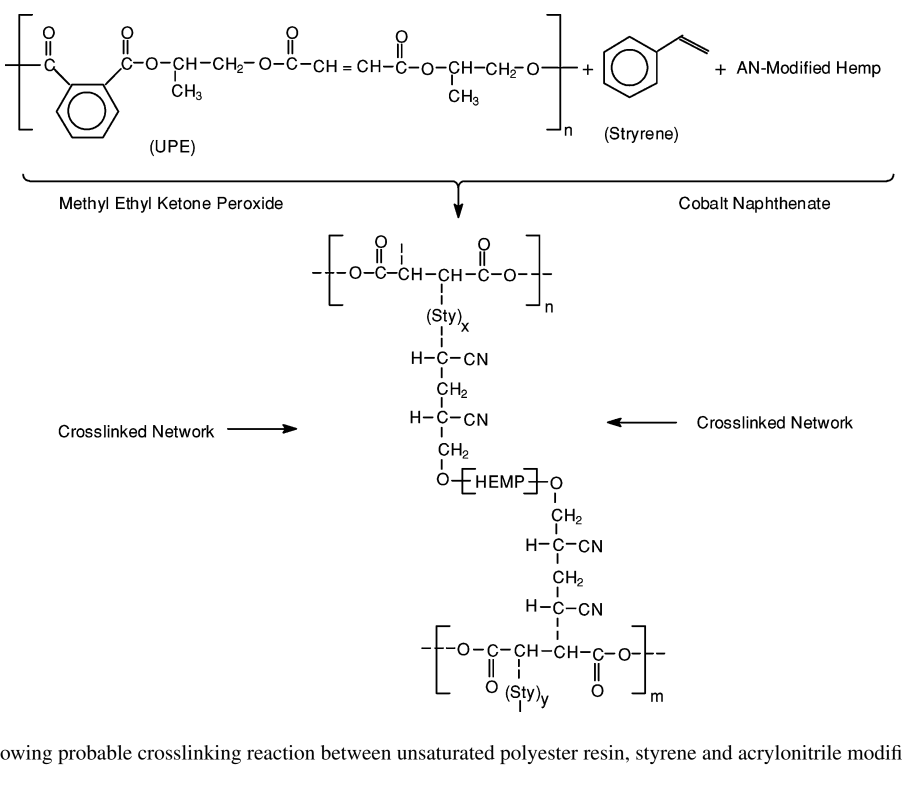
Composite fracture toughness is influenced by interlaminar and interfacial strength parameters. The fibers play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. It is a common observation that with most of the effective surface treatments, the flexural and tensile properties of the composite increase, but the impact strength decreases. But with the acrylonitrile treatment of hemp fibers, not only do the flexural and tensile properties of the composite increase, but the impact strength increases as well (Fig. 2). The enhancement in notched Izod impact strength is 180% as compared to the polyester control, and 50% as compared to raw hemp-UPE bio-composite. Here, the impact strength increases because of the flexibility of the interface molecular chains. There is greater energy absorption in the bio-composite containing treated fibers. When the cracks moves forward, the chain motions change due to their flexibility and create a barrier to the crack growth. The tensile stress-strain plot to failure for chemically treated fiber based composites has a greater area under the curve than the other materials (Fig. 3). Therefore, the acrylonitrile treated fiber based composite is expected to have the highest impact strength, because the area under the curve in the stress-strain plot is generally related to the impact strength of the material.

The storage modulus (Fig. 4) tracks the trend in flexural and tensile moduli. The composites prepared with the treated fibers showed improved wetting behavior of the fibers with the resin, producing a stronger bond at the interface and higher mechanical strength. At 30 °C, the increase in the storage modulus of the treated hemp-UPE composite as compared to untreated hemp-UPE bio-composite was 45%, at 80 °C this increase was 50%, and at 150 °C, it was 110%. The loss modulus of composite containing chemically modified hemp fibers is higher than the composite with untreated hemp, (figure not shown). At 30 °C, the loss modulus of the bio-composite with chemically treated fibers was 55% higher than untreated, at 80 °C it was 60% higher, and at 140 °C it was 75% higher than that of the composite made with untreated fibers. This follows the trend found previously for natural fiber-thermoset composites, where the loss modulus increased after addition of fibers to the plastic [5].

Tan delta (Tan δ) is the ratio of loss modulus to the storage modulus. The temperature corresponding to the maximum tan delta value is often taken to be the glass transition temperature, T_g. The T_g for untreated hemp-polyester composite is 97 °C, and that of acrylonitrile treated hemp-UPE composite is 95 °C (Fig. 4). Over the entire range of temperature, tan δ was very high for the neat resin due to huge reduction in the storage modulus values at higher temperatures. The lower values of tan δ for the bio-composite made with modified hemp fibers suggest that there is less damping in the chemically treated hemp composite. The tan δ vs. temperature plot for both bio-composites is similar.

The ESEM micrographs of tensile-fractured surface of bio-composites are shown in Fig. 5. The distribution of the fibers in the mat is random, and uneven. Unmodified composites show poor interfacial bonding between the fiber and matrix, resulting in a relatively clean surface over the pulled out fibers due to greater extent of delamination. Shear failure results in a high degree of pull out in the case of untreated fiber/polyester composites. Acrylonitrile treated hemp-UPE composite show a smaller degree of fiber pull-out and good adhesion between fiber and matrix.

The improvement in all mechanical and thermal properties of the bio-composite based on acrylonitrile treatment are because of the possible structure (Scheme 1) that results during the curing reaction. This structure consists of acrylonitrile molecules grafted onto the hemp fiber and cross-linked with styrene as



Scheme 1 Scheme showing probable crosslinking reaction between unsaturated polyester resin, styrene and acrylonitrile modified natural fibers.

well as with UPE resin. In this structure, the polystyrene chains are joined to polyacrylonitrile chains, which in turn are connected to the hemp fiber and UPE resin, giving rise to a highly cross linked network.

In conclusion, an increase in the mechanical and thermal properties is seen for surface treated fiber based bio-composites. Low percent acrylonitrile grafting is quite effective in improving the fiber-matrix adhesion. The ESEM photomicrographs corroborate the claims that adhesion and interfacial bonding between fiber and matrix is improved by this surface modification.

Acknowledgment

We are highly grateful to National Science Foundation—Partnership for Advancing Technologies in Housing (NSF-PATH) 2001 Award No. 0122108 for financial support. The collaborating efforts and many fruitful discussions with our industrial partners from Flaxcraft Inc., Cresskill, NJ and Kemlite Inc., Joliet, IL are gratefully acknowledged.

References

1. A. K. MOHANTY, M. MISRA and G. HINRICHSEN, *Macromol. Mater. Eng.* **276/277** (2000) 1.
2. A. K. MOHANTY, M. MISRA and L. T. DRZAL, *J. Polym. Env.* **10**(1/2) (2002) 19.
3. J. N. MCGOVERN, in "Encyclopedia of Polymer Science and Engineering," Vol. 7, edited by H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, (John Wiley & Sons, New York, 1987) p. 16.
4. M. MALIK, V. CHOUDHARY and I. K. VARMA, *J.M.S.-Rev. Macromol. Chem. Phys.* **C40**(2/3) (2000) 139.
5. A. K. RANA, B. C. MITRA and A. N. BANERJEE, *J. Appl. Polym. Sci.* **71** (1999) 531.

Received 27 March
and accepted 16 July 2003