COMPOSITE NONWOVENS MADE OF COTTON AND OTHER PLANT FIBERS: MECHANICAL AND THERMAL CHARACTERIZATION

Ioan I. Negulescu
Yan Chen
School of Human Ecology, LSU
Baton Rouge, LA
D. V. Parikh
Valeriy G. Yachmenev
SRRC-ARS-USDA
New Orleans, LA
Michael Saska
LSU AgCenter Audubon Sugar Institute
Saint Gabriel, LA

Introduction

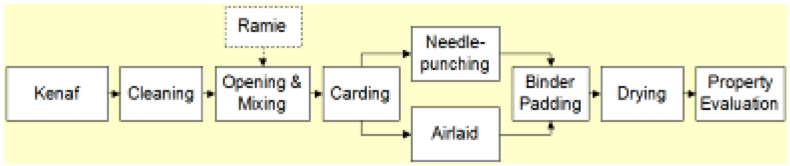
In 2007, the nonwovens industry saw a continued increase in product performance and technology development as well as ongoing investment in capacity expansions to meet customer demands. With a barrel oil price achieving $100, the forecast in the near future on raw material costs are not optimistic. The positive consequence is the need for broadening the prevailing raw material palette. Raw material innovations are occurring in a number of areas that are crucial to the future of the nonwoven industry. The demand for natural fibers continues to increase because of their many outstanding properties, including aesthetics, comfort, and biodegradability. Farmers, fiber producers, and a diversity of scientists worldwide have been exploring the use of alternative fiber crops (kenaf, jute, and hemp), crop residues, and agricultural by-products, which are often underutilized and undervalued. For example, kenaf fibers are biodegradable, environmentally friendly, inexpensive to grow, plus, they will grow almost anywhere and in any soil type. Jute also is a relatively cheap, easy to grow fiber having good mechanical properties. Flax and ramie, textile fibers used for long periods of time in different parts of the world, became cost competitive because of new developments in the fiber extraction process. At the same time, agricultural residues and by-products from major U.S. agricultural commodities (sugarcane, soybeans, wheat, corn, etc.) potentially could be used to produce a multitude of value-added non-food products, ranging from fibers, films, plastics, and composites to resins, finishing agents, and other auxiliary materials. Sugar cane is an important agricultural crop in Louisiana and Florida. The crushed stalks (bagasse), remaining from traditional sugar cane processing, is used mainly for low-value applications. Development of value-added products from the waste or low-value materials such as bagasse could allow mills to migrate to cleaner burning fuels and provide economic benefits, as cane producers compete in a freer trade environment.

The objective of the presentation was to exemplify the preparation of biodegradable nonwoven flexible sheets containing at least 30-50% cellulosic fibers reinforced with synthetic or biobased polymers and to determine their physical properties and biodegradability.

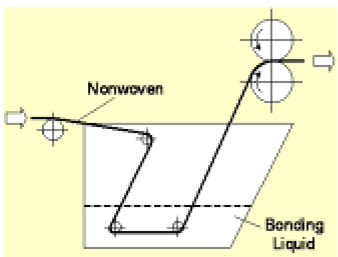
Materials and Methods

Several natural fibers, i.e., cotton, bagasse, kenaf, and ramie, have been considered in the present investigation. Synthetic polymers, viz., polypropylene and polyvinyl alcohol, as well as biobased polyesters were employed for manufacturing of composite nonwovens.

Processing Flow Chart for Kenaf/Ramie PVA Bonded Nonwovens



Padding Procedure



Sample Specifications

Sample	Kenaf/Ramie Ratio	Thickness (mm)	Weight (g/m^2)
Carded	***70/30***	***0.791***	***103.4***
Airlaid	100% kenaf	0.894	109.8
	70/30	0.973	114.3

Figure 1. Processing procedure and sample specifications for kenaf/ramie nonwovens

The carded kenaf nonwovens were produced in the LSU Textile Processing Laboratory [Chen 2004]. The processing procedures are illustrated in Figure 1. The kenaf fibers wee cleaned by a cotton cleaner and mixed with the ramie fiber in a ratio of 70% kenaf and 30% ramie. The kenaf/ramie blend was fed into a lab-scale carding machine to obtain a fiber web. During the carding, the fiber blend was further opened and individual fibers were combed to be relatively parallel. To enhance web uniformity, the fiber blend was carded twice. A needle-punching machine was used for mechanically bonding the kenaf/ramie web. The airlaid kenaf nonwovens were provided by a nonwoven producer.

Composite nonwovens have been prepared also from bagasse and cotton fibers and a poly(hydroxy alkanoate), PHA. In order o obtain the nonwoven composites, cellulosic webs and PHA films have been sandwiched and pressed for seven minutes at 180°C and 139 psi (2 tons/(4x4in) to form a flexible bonded sheet. The architecture before pressing contained 3-4 layers of PHA films intercalated with 3-4 layers of bagasse or bagasse/cotton webs [Negulescu 2007a].

Mechanical Properties. For the investigation of static mechanical properties, the tensile strength of nonwoven composites was determined according to ASTM D5035-95. The machine used was an Instron tester Model 4301. Flexibility of the nonwoven composites was tested in accordance with the ASTM 790-97 for flexural properties of plastics (three-point bending method). A dynamo-mechanical spectrometer (Seiko) was used or determination of viscoelastic parameters in bending mode with a heating rate of 1°C/min.

Thermal properties. The all thermal conductivity and thermal transmittance tests were performed using thermal conductivity meter, FOX 200 from LaserComp Corporation, in accordance with ASTM D1518- 85 standard procedure.

The aerobic and anaerobic biodegradation studies were performed according to ASTM D 5338-98 and ASTM D 5210-92 (Re-approved 2000), respectively [Negulescu 2007b].

Results and Discussion

The extent of nonwoven applications increased dramatically in the last decades. Nonwovens can be found nowadays in automotive manufacturing, building construction, medical applications, petroleum industry (as sorbents), civil engineering, etc. The use of natural fiber composites for automotive interior components is an emerging market with hundreds Ktons of natural fibers annually that are used for reinforced composites in the worldwide automotive production, i.e. passenger cars and trucks (Figure 2). Advantages of natural-fiber nonwovens in automotives are their lower weight, good acoustic properties, versatile and easily tailored properties, the moldability, recyclability, the low process and materials costs and consequently the attractive cost/performance ratio.

There are two important steps in nonwoven manufacturing that are going to influence the characteristics of the final product: (a) the preparation of the fiber web and (b) the bonding of the fibers in the web. In addition to these, a strong influence is exercised by the composition of the nonwoven. It is customary to blend two or more fibers in order to improve the final characteristics. In the web bonding step, the presence of fine synthetic fibers will secure a better bonding, influencing positively the mechanical properties, such as the tensile strength and the flexural rigidity.

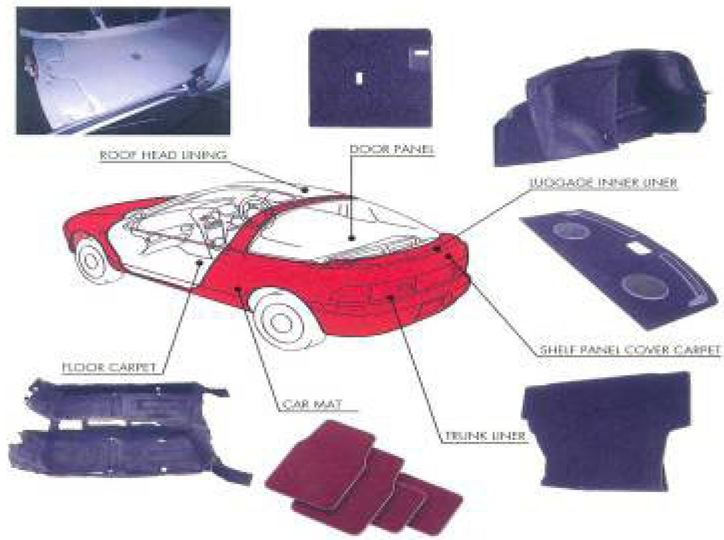


Figure 2. Examples of utilization of nonwoven composites for auto interiors.

If the final product is a board, the synthetic fibers will melt by heating, gluing together the natural fibers in the desired shape. This is particularly important in manufacturing boards and side panels for automotive industry.
In a traditional structural complex of commercial headliner materials two layers of glass fiber mat are used as intermediate substrates for the polyurethane foam. The use of natural fiber mat to replace the glass fiber mat will help reduce the use of glass fiber and enhance biodegradability of the auto headliner materials. Quite recently, automotive components supplier Johnson Controls has unveiled a new “earth-friendly” headliner for car interiors, which is made from natural fibers such as hemp, flax and kenaf and has a soy-based urethane core foam instead of fiber glass (ECOTEXTILENEWS 2008).

Physical and mechanical characteristics of the natural fiber components will also influence the properties of the final products. However, as shown in the following for kenaf/ramie nonwoven composites, the properties are also influenced, among other factors, by the padding time and direction. On most industrial-scale padding machines, there is usually more than one pair of nip rollers for padding. This means nonwoven webs may be padded more than once upon different requirements for products. To evaluate the influence of padding time on nonwoven properties, the experimental 70/30 kenaf/ramie nonwoven samples were padded once and twice respectively. Tested tensile modulus (E), tensile breaking stress (σ) and strain (ε), bending rigidity (B), and bending hysteresis (HB) are listed in Table I. It can be seen that after padding twice, the tensile strength and modulus are increased. The ANOVA analysis indicated that only the tensile modulus and strength in the cross-machine direction were significantly affected by the padding time at the 95% confidence level.

Table 1. Effect of Padding Times on Carded Nonwovens

Padding Time	Direction	E (MPa)	σ (MPa)	ε (%)	B (Gm·cm^2/cm)	HB (Gm·cm/cm)
Once	along machine	255.99	4.12	3.06	0.39	10.05
	cross machine	122.51	1.71	3.11	0.32	8.30
Twice	along machine	309.52	6.18	3.56	0.33	7.79
	cross machine	167.40	2.43	2.84	0.24	9.49

Mechanical properties of the airlaid nonwoven samples are listed in Table 2. Padding direction is an essential parameter for developing the strength. At the same time, the reduction of kenaf content tends to reduce the tensile strength and modulus. According to the ANOVA computation, this influence is significant at the 95% confidence level. For the flexibility, only the bending rigidity in machine direction shows a slight decline as the kenaf content decreases from 100% to 70%. But, this effect was statistically insignificant.

Table 2. Statistical Test for Anisotropy of Mechanical Properties of kenaf composite nonwovens

Sample	Kenaf Content (%)	p-Value				
		E (MPa)	□ (MPa)	□	B (Gm□cm^2/cm)	HB (Gm□cm/cm)
Carded	70	0.001	0.0003	0.072	0.130	0.440
Airlaid	70	0.007	0.006	0.990	0.360	0.960
	100	0.002	0.830	0.920	0.056	0.160

O -- 99% confidence level.
O -- 90% confidence level.

The measured result of thermal conductivity (λ) for the carded and airlaid nonwovens is listed in Table 3. The experimental data also include the sample density (d) and average testing temperature (T). Because the tested samples had different density or different kenaf blending ratio, the thermal conductivity results could not be compared directly. The equation λ/d was used to normalize the λ values. As shown in Figure 3, all the carded samples (except the carded Sample 5) have a lower thermal conductivity than the airlaid samples. This means the carded samples can perform a better thermal insulation as used for the auto headliner. Figure 4 illustrates that the thermal conductivity is generally proportional to the nonwoven density.

Table 3. Thermal conductivity data for kenaf composite nonwovens

Sample	d (g/cm^3)	λW/m.K	λ/d
1	0.159	0.0210	0.132
2	0.158	0.0216	0.137
3	0.148	0.0217	0.147
4	0.135	0.0197	0.146
5	0.154	0.0276	0.179
6	0.148	0.0205	0.139
7	0.168	0.0202	0.120
8	0.124	0.0151	0.122
9	0.157	0.0223	0.142
100 Kenaf	0.119	0.0208	0.174
70/30 K/R	0.140	0.0218	0.156

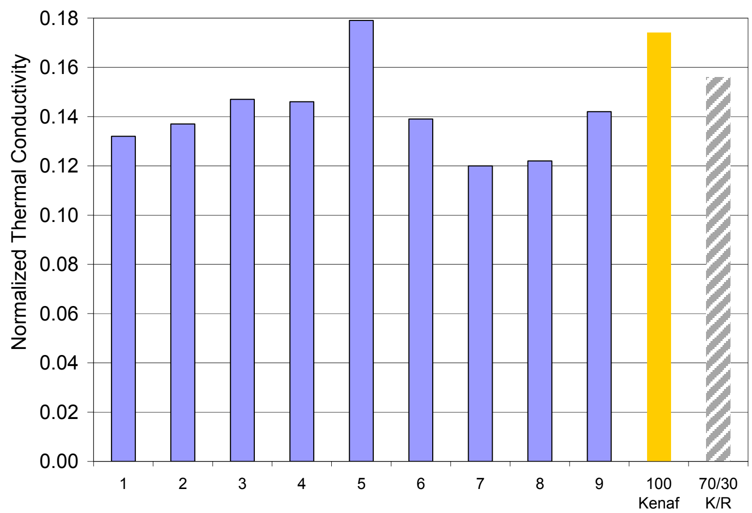


Figure 3. Normalized thermal conductivity of kenaf composite nonwoven samples.

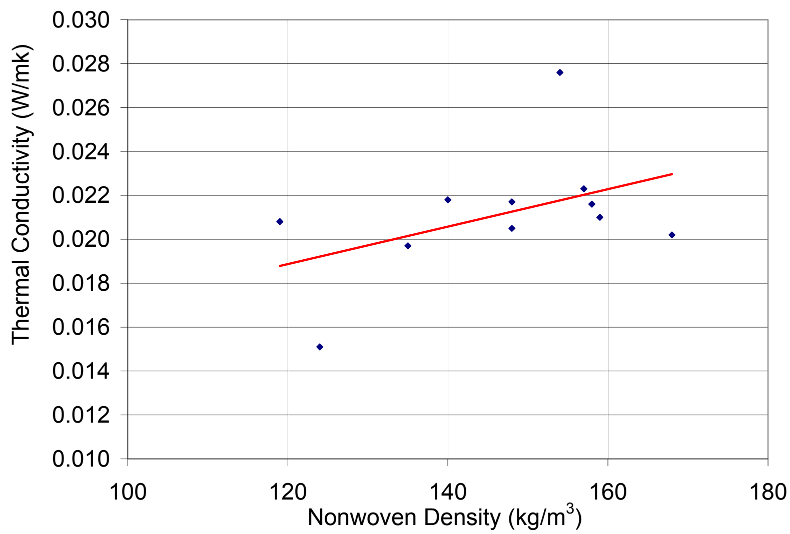


Figure 4. Relationship between Thermal Conductivity and Nonwoven Density

Figure 5 presents the variation of storage modulus for the airlaid and carded samples under tension mode measured at different frequencies. The temperature of material glass-like transition observed 60°C represents the softening of the material after drying. The material retained good viscoelasticity until the temperature reached 150°C, where the tensile strength was totally lost because of the melting of the bonding polymer (polypropylene).

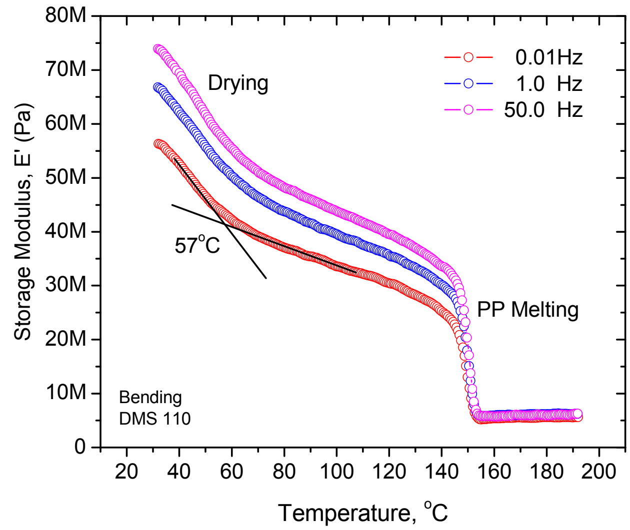


Figure 5. Ramie/Kenaf/PP Nonwoven: Variation of E' with temperature and frequency in bending mode.

The following data refer to a series of composite nonwovens based on bagasse and cotton as cellulosic fibers and stabilized with PHA or a solution of 10% cellulose in N-Methyl Morpholine N-Oxide monohydrate(Lyocel solution), the so-called "all-biobased-composite nonwovens [Negulescu 2003]. As seen from Table 4 mechanical properties are primarily dependent on the nonwoven composition, particularly on the amount of the bonding polymer.

More complex formulations containing PHA plasticizers and fire retardants for cellulosic fibers have been prepared by blending cellulosic fibers with plasticized PHA (Figure 6) followed by a fire-retarding process [Negulescu 2006]. The composition of plasticized samples is listed in table 5. The large oxygen index (OI >> 30. viz., the accepted OI for a material to be considered fire-retarded) of these nonwovens recommends their utilization in applications where fire-retarding is a must.

Table 4. Mechanical Properties of PHA/Bagasse Nonwovens Prepared at High Pressure (434 psi)

Nonwoven structure	PHA Content (%)	Stress at Max. Load (psi)	Strain at Max Load (in/in)	Modulus (psi)
Bagasse	32	1.765	0.051	92,634
Bagasse	38	2,086	0.047	115,740
With 13.5% cotton	55	2,337	0.080	102,091

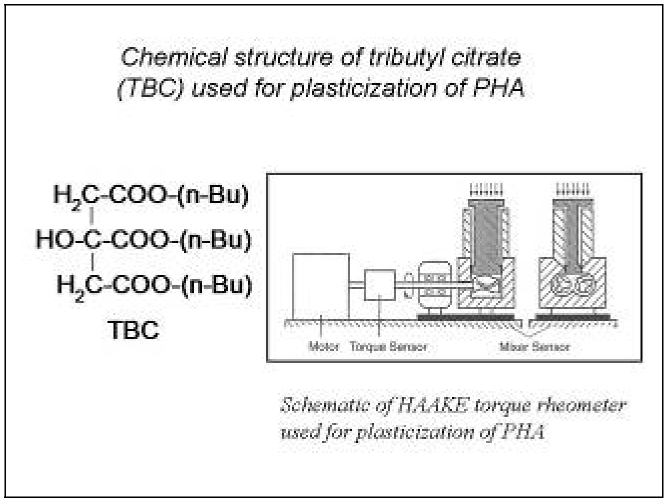


Figure 6. Chemical structure of the PHA plasticizer and the instrument used for polymer plasticization.

Table 5. Composition of bagasse nonwovens containing plasticized PHA and non durable fire retardant.

Sample	% Bagasse	NDFR	TBC plasticizer	Density g/cm^2	Oxygen Index
1	36.8	29.9	33.3	1.06	35
2	39.0	31.6	21.0	1.06	37

Table 6. Mechanical characteristics of FR bagasse nonwovens containing plasticized PHA.

Sample	% Plasticized PHA	Tensile Strength MPa	Strain at Yield %	Young Modulus MPa	Density g/cm^2
1	33.3	8.685	3.0	414.5	1.06
2	21.0	8.354	2.2	465.1	1.06
3	100	21.2	34.1	294.2	1.25

In aerobic environment the organics (cellulosic fibers and PHA) are reduced to carbon dioxide, water and residual C and biomass:

$$C_{polymer} + O_2 \rightarrow CO_2 + H_2O + C_{residue} + C_{biomass} + salts$$

while in anaerobic conditions reduced methane is formed also:

$$C_{polymer} \rightarrow CO_2 + CH_4 + H_2O + C_{residue} + C_{biomass} + salts$$

Anaerobic degradation of samples of TBC plasticized PHA and of FR bagasse nonwoven composites is illustrated in Figures 7 and 8 for a span of time up to 20 weeks in the degrading environment. The PHA degrades more readily as bagasse fibers can be visualized after 12 weeks (Figure 8).

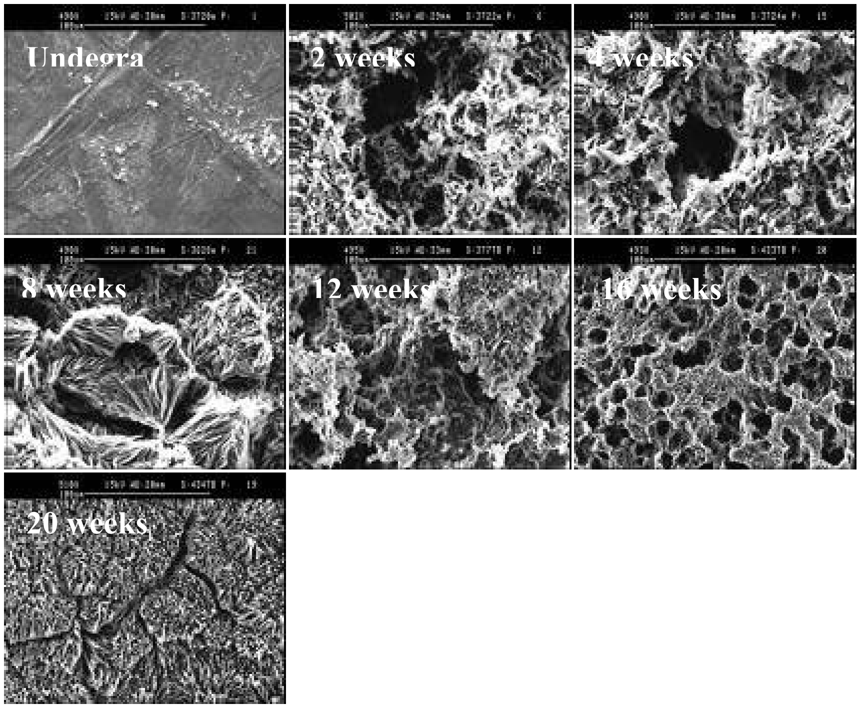


Figure 7. SEM images (500X magnification) of 1.2-mm melt-pressed PHA + 15% TBC plates un-degraded and after 2, 4, 8, 12, 16, and 20 weeks of exposure in the second anaerobic mass loss study. Captions indicate time of degradation.

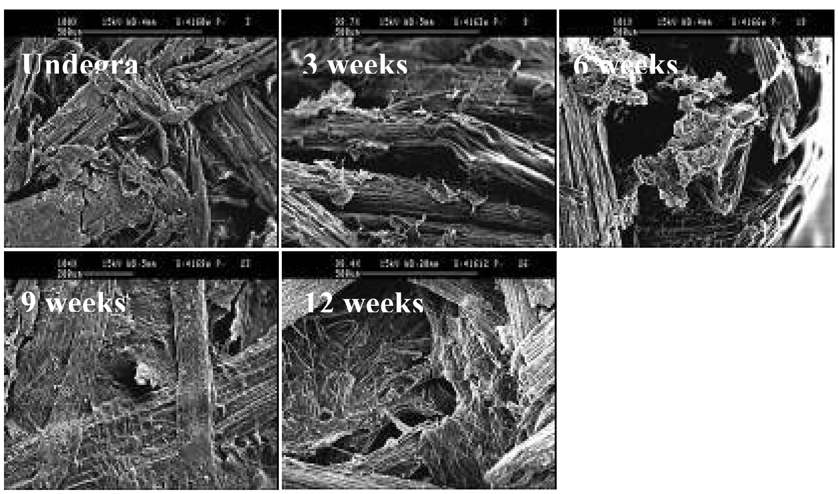


Figure 8. SEM images (~100X magnification) of 3.5-mm plates of pressed composites (76% bagasse / 13.4% NDFR / 10.6% PHB) un-degraded and after 3, 6, 9, and 12 weeks in anaerobic medium.

Conclusions

Biodegradable elastic composite nonwovens have been successfully prepared from annual plant fibers and polymers. Thermal properties of nonwoven composites were related to drying at lower temperatures (T<100°C) and to softening and melting of polymers at T>150°C.

Elastic properties decayed very rapidly after softening and melting of polymers.

Tensile strength was dependent on the nonwoven composition and construction mode.

Plasticization and fire-retardation did not prevent biodegradation of composite nonwovens made of bagasse and PHA.

References

Chen, J. Y., O. I. Chiparus, L. Sun, I. I. Negulescu, J. Kuttruff and V. G. Yachmenev, Comparative Study on Kenaf Nonwoven for Automobile Headliner, in International Development of Kenaf and Allied Fibers, Aimin Liu Editor, CCG International Inc., Minneapolis, MN, 2004, pp. 65-83.

http://www.ecotextile.com/pdf/mediapack2008.pdf

Negulescu, Ioan I., Chen Yan, Xiaoqun Zhang, Liangfeng Sun, Jacquelene Robeck, Valeriy G. Yachmenev, Timothy A. Calamari, Jr., and Dharnidhar V. Parikh, All-Cellulosic Composite Nonwoven Materials, *INDA/TAPPI International Technical Conference, Baltimore, MD, September 15-18, 2003 (CD-ROM).*

Negulescu, Ioan I., Yan (Jonathan) Chen, Xiaoqun Zhang, Michael Saska, Liangfeng Sun, Gita Ramaswami and Dharnidhar Parikh, "Fire Retarded Biobased Non-Woven Composites", *2006 Beltwide Cotton Conferences Ninth Nonwovens Symposium, San Antonio, TX, Jan 5-6, 2006 (CD-ROM).*

Negulescu, Ioan I., Jonathan Chen, Kelly Rusch, Xiaoqun Zhang, Ben Stevens, Maria T. Gutierrez-Wing, and Dharnid V. Parikh. Biodegradability of Environmentally Benign FR Natural Fiber Nonwoven Composites, *International Nonwovens Technical Conference, Nonwovens Symposium, Atlanta, GA, 25-28 September, 2007*

Negulescu, Ioan I., Jonathan Chen, Kelly Rusch, Xiaoqun Zhang, Ben Stevens, Maria T. Gutierrez-Wing, and Dharnid V. Parikh. Biodegradability of Composite Nonwovens Made of Natural Fibers and Bioderived Polymers, *International Nonwovens Technical Conference, Sustainability Symposium, Atlanta, GA, 25-28 September, 2007*

Acknowledgements

The authors (IIN, YC) would like to acknowledge the support of the LSU AgCenter (Projects # 93547 & # 93816) for this work.

The support of the Louisiana Board of Regents for the grant LEQSF(2004-07)-RD-B-03 is also acknowledged by IIN and XZ.

The LSU College of Agriculture is acknowledged for 2006 and 2007 COA Dean's Undergraduate Student Research Grants (2).