

**INVESTIGATION OF BIODEGRADABLE
NONWOVEN COMPOSITES BASED ON COTTON,
BAGASSE AND OTHER ANNUAL PLANTS**

A Thesis

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Abstract

In this study a new method of preparing biodegradable all-cellulosic composite nonwoven materials composed of cotton and kenaf or cotton and bagasse has been developed.

Alkaline extracted kenaf or bagasse fibers were used as the main component of composite nonwovens. Recyclable or low value cotton fibers were used to entangle coarser kenaf or bagasse fibers in a web on which the nonwoven architecture was based. The novel adhesive system developed in this work for the web bonding was cellulose from a solution, in N-methyl morpholine N-oxide monohydrate. The completely biodegradable composite nonwovens were obtained by sandwiching and hot-pressing the cellulosic webs and the adhesive into a bonded sheet. It was shown that synthetic polymers can be substituted for the stabilization of nonwovens by a solution of cellulose that was prepared from recyclable cotton textiles.

Some relevant properties of final nonwoven products, such as strength, viscoelastic characteristics and thermal properties were determined and compared among several compositions. The physical characteristics of all-cellulosic composite nonwovens were comparable to that of the biodegradable composite nonwovens that were prepared earlier at LSU from natural fibers and a biodegradable synthetic polyester.

Practical application of all-cellulosic composite nonwovens will be determined by the economics of delignification of composing fibers.

Chapter 1 Introduction

1.1 Research Objectives

As the application of polymer composites in modern industry has intensified, more attention has been paid to the non-renewable nature of petroleum-based polymer products as well as to the associated problems created by the waste disposal. Woody biomass (agricultural residues, wood fibers, etc.) containing cellulose, hemicelluloses and lignin, is an abundant alternative source of renewable polymers that are also highly biodegradable.

Cotton has long been a dominant natural fiber in the textile industry. Low quality greige fibers or low value textile wastes predominantly consisting of cotton fibers that could not be used directly in the apparel industry, have a high potential in the manufacturing of composite nonwovens that are quite promising materials in the insulation market, especially in the automobile insulation market.

At the same time, scientists and fiber producers are exploring the use of alternative fiber crops (such as kenaf, jute, and hemp) and agricultural by-products (such as sugar cane and rice by-products) which are presently underutilized. For example, in addition to its high strength and porosity, kenaf fiber is biodegradable, environmentally friendly, and able to grow in a wide range of climatic conditions and soil types.

Agricultural residues and by-products of the sugar industry, such as bagasse, could be used to produce a multitude of value-added non-food products, ranging from fibers and composites, to films and resins. Until now, most of the bagasse has been compressed and burned in-house by cane processors as a low calorie generating fuel, or

has been utilized as raw material for producing some low value-added products such as mulch and inexpensive ceiling tiles (Chen, & Negulescu, 2002). Bagasse has also been used to manufacture fiber boards and particle boards, but it was not competitive with products from other woody sources. Bagasse fibers that were alkali extracted from the cane stalk in some previous research conducted at Louisiana State University gave a new prospective solution. If a suitable method will be established to convert bagasse fibers into useful technical nonwovens, this will enhance the profitability of both sugar cane farming and mills.

The utility of nonwoven products increased dramatically in the last decade due to their light weight and low production cost. Nonwovens have found utility in automotive manufacturing, building construction, medical applications, etc. There are two important steps in nonwoven manufacturing that will influence the characteristics of the final product: the first is the forming of the fiber web, and the second is the web bonding method. In the web forming procedure it is customary to blend two or more fibers in order to improve the characteristics of the final product.

The objective of the present research project was to prepare completely biodegradable composite nonwoven materials using inexpensive natural fibers and biodegradable adhesives. Several natural fibers – bagasse, kenaf and greige type cotton were used for this purpose. The composite nonwovens were prepared in two steps. In the first step, a cellulosic web was made using cotton and at least 50% kenaf or bagasse fibers. In the second step, the cellulosic web was cut to smaller webs of desired dimensions which thereafter were assembled (sandwiched) using a biodegradable adhesive to form the final composite nonwoven material.

Alkaline extracted kenaf or bagasse fibers were used as a main component of the cellulosic webs. Waste or greige type cotton fibers were used to entangle the coarser bagasse or kenaf fibers in the web. In order to obtain a completely biobased biodegradable nonwoven material, the adhesive used for the web bonding was lyocell solution that was obtained by dissolving recycled cotton in cellulose solvent. Thus, two types of cotton fibers were utilized in this research: raw cotton fibers used for the entanglement of kenaf or bagasse fibers, and cotton fibers derived from recycled or wasted textiles used for the formation of lyocell solution which acted as the adhesive to bond the webs.

Another type of biodegradable adhesive used for bonding the cellulosic webs was Eastar BioCopolymer (EBC), a petroleum derived synthetic material (Chiparus, 2004). Completely biodegradable nonwoven composites were obtained by sandwiching and hot-pressing the cellulose webs and the adhesive material into a flexible sheet as described in Chapter 3.

Tensile analysis, thermal conductivity, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA) were conducted on selected nonwoven sample(s).

1.2 Definitions

Table 1-1 Definitions

Nonwoven	Structures which consist of a web of fibers joined by chemical or mechanical means.
Bast fibers	Vegetable fibers of the stalks or stems of the plants from which they were derived.
Bagasse	The fibrous residue of the cane stalk from a sugar mill after crushing and extraction of the juice.

Table 1-1 Continued

Kenaf	A warm-season annual fiber crop, the fibers are extracted from their stalks.
Lyocell	Refers to cellulose precipitated from a true cellulose solution.
Tensile analysis	Gives the breaking force, tenacity, strain, toughness, and the modulus of a material.
Thermal conductivity	Is the time rate of unidirectional heat transfer between parallel planes, per unit difference of temperature of the planes.
Dynamic mechanical analysis	Determine the dynamic mechanical properties of materials by measuring the deformation of a sample in response to periodic forces.
Differential scanning calorimetry	Used to characterize materials by studying a wide range of thermal transitions in their system, and to determine the thermodynamic parameters associated with these changes.
Thermogravimetry analysis	A technique for the evaluation of the thermal decomposition kinetics of materials by monitoring the weight loss of the sample as a function of temperature in a chosen atmosphere.

Chapter 2 Literature Review

The present study focused on the formation of biodegradable nonwoven materials using at least 50% extracted kenaf or bagasse fibers as the fibrous web, as well as biodegradable adhesive to bond the cellulose webs. The literature review includes: composites, nonwovens, cellulose fibers, bonding materials and the composite formation, and the application of biodegradable nonwovens and analytical methods.

2.1 Composites

A composite is a material that consists of more than one component, in which at least one of the components remains in solid state during its manufacture. (Weeton, 1987). The light weight and superior mechanical properties of polymer composites have made them good candidates for applications in wide areas of the modern industry that range from transportation, building, to medicine and packaging (Seavey, Ghosh, Davis, & Glasser, 2001).

2.2 Nonwovens

2.2.1 Nonwovens and Their Applications

The major area in nonwovens can generally be split into disposable products such as diapers, sanitary wipes and napkins, and durable products such as materials for apparel, home building, packaging, and industrial applications (Gillies, 1979). This research focused on the durable nonwoven products.

Nonwoven products are taking the place of many woven and knit materials because of their lower cost and lighter weight. In the automotive industry, it was estimated that the yearly demand for nonwoven materials consumed in the automotive

interior component was up to 120,000 tons, and North America shares nearly one third of this global market (Mueller, Krobjilowski, & Muessig, 2001). Recycling automotive interior parts made of petrobased polymer materials with mixed composite structures is very difficult, if not possible at all. As the result of a greater concern in environmental protection, European makers already excluded the use of non-recyclable and harmful materials such as mineral, glass fibers or polymeric foams in car seat and door panel applications (Pelc, 2000).

Nonwoven fabrics are also predominate in the geotextile industry because of their higher permeability, better friction, better conformability and construction survivability compared to that of woven products (Marienfeld, 1995). Biobased nonwoven geotextiles made from bast fibers like hemp, flax, jute, kenaf and bagasse could be used for temporary (several months to several years) applications where biodegradability is required, such as sheet mulch for tree seeding survival and erosion control (Biobased, 1994). There are many other nonwoven materials that utilize natural fibers, such as floor coverings, building materials, and particleboards.

The American Society for Testing Materials defined nonwoven fabric as “a structure of fibers held together with a bonding material”, however, some of the nonwovens do not have a bonding material, being held together just by the entanglement of their fibers produced by some mechanical methods. Gillies (1979) defined nonwovens as “structures which consist of a web of fibers joined by chemical or mechanical means”. Recent authors more broadly defined nonwoven as “a textile structure made directly from fiber rather than yarn” (Wooding, 2001). Nonwoven manufacture is usually made by producing a web of fibers, which is then strengthened by various bonding techniques.

2.2.2 Nonwoven Formation

2.2.2.1 Nonwoven Web Formation

There are various methods of making nonwoven webs: (1) air laid, (2) wet laid, and (3) spun laid. Techniques used to form fiber web are listed in Table 2-1 (B. J. Collier, & Tortora, 2001).

Table 2-1 Techniques used to form fiber web

Air laid	Fibers are opened, suspended by air, and then collected on a moving screen.
Wet laid	A mixture of fibers in water is collected on a screen, then drained and dried.
Spun laid	Hot, continuous synthetic filaments that were just extruded through the spinnerets are blown onto a moving belt where they are bonded together by themselves to a web.

2.2.2.2 Nonwoven Web Bonding

Nonwoven web bonding includes: thermal bonding, mechanical bonding, and chemical bonding. The traditional thermal and mechanical bonding techniques include thermal bonding, hydroentanglement, and needle bonding, as listed in Table 2-2 (Wooding, 2001).

Table 2-2 Traditional thermal and mechanical bonding techniques

Thermal bonding	Bonding of the nonwoven that contains thermoplastic component(s) by application of heat.
Spunlaced or Hydroentanglement	Bonding by entangling the fibers using very fine jets of high pressure water.
Needle bonding	Entanglement of fibers by a set of barbed needles punching through the web.

Chemical bonding include wet and dry chemical bonding, as listed in Table 2-3 (Gillies, 1979). Dry chemical bonding is seldom used because it is difficult to give the composite a uniform strength.

Table 2-3 Nonwoven chemical bonding techniques

Wet chemical bonding	Conducted by saturating fibrous webs with an adhesive, or by applying an adhesive to the surface of the fibrous webs.
Dry chemical bonding	Contact the fibrous web with particles of dry adhesive material, and heat the composite to a temperature above the sticking point of the adhesive.

2.3 Cellulose Fibers

Both natural and regenerated cellulose fibers were used in this research. Cellulose fibers have comparatively high density and relatively low elasticity vs. synthetic fibers, and are good conductors of heat and electricity. Cellulose fibers have good resistance to bases, but are susceptible to damage by mineral acids (Collier *et al.*, 2001).

Natural cellulose fibers widely used are seed hair fibers such as cotton fibers, and bast fibers, such as flax, hemp, and kenaf. Natural cellulose fibers are replacing synthetic fibers in many applications due to their biodegradability, improved acoustics of products, higher processing and operational safety, higher strength and stiffness, lower weight, and lower product cost (Mueller *et al.*, 2002). As more and more attention is paid to the protection of our environment and saving of petroleum resources, there is an increased tendency of using biodegradable natural fibers in manufactured products. The application of natural fiber in the automotive industry as interior components has been developed since 1995, primarily in Europe (Nick, Becker, & Thoma, 2002). One important

advantage of using natural fibers to reinforce products is the possibility of designing the product by arranging (long) fibers in the direction of the applied forces in order to create lightweight components with anisotropic properties, tailored to specific requirements (Mueller *et al.*, 2002).

Currently, an average of 5 to 10 kg of natural fibers are incorporated in each European passenger car as interior parts, such as headliner, trunk liner, kick and door panels, seat backs, insulating materials and air filters (Market, 2000). According to the European Guideline 2000/53/EG administered by the European Commission, 85% weight of the vehicle has to be recyclable by 2005, and this criterion will be increased to 95% by 2015 (Chen, Chiparus, Sun, Negulescu, Kuttruff, & Yachmenev, 2003). Such requirements are not legislated in the U.S.; however, any car maker wanting to export cars to the European market has to comply with this requirement.

2.3.1 Kenaf

2.3.1.1 Introduction of Kenaf

Kenaf, a member of the hibiscus family (*Hibiscus cannabinus* L), is a 4,000 year old annual crop, native to Africa. Mechanical properties of kenaf fibers are similar to those of jute, but kenaf fibers are stronger, whiter, and more lustrous. Kenaf has been used for thousands of years as cordage, canvas, sacking, and fish net due to its mildew resistance (Cook, 1960). Kenaf grows quickly and will achieve 5 to 6 m in height and 2.5 to 3.5 cm in diameter within 5 to 6 months (Smith, 1998). Kenaf is able to be planted in many areas with a temperate or tropical climate, and can grow well in most of the southern areas of America. Studies by the U.S. Department of Agriculture showed that kenaf yields 6 to 10 tons of dry fiber per acre per year. Kenaf seeds require two to three

months of frost free condition to reach the point of germination. Seed production in the U.S. is limited to the frost-free areas of Texas, California, and Florida (Sullivan, 2003).

Each plant of kenaf has a single, straight stem without a branch. The stem consists of an outer fibrous bark and an inner woody core. The outer bark, named bast, is about 40% of the stalk's dry weight, and the inner core is about 60% of the stalk's dry weight. Refined bast fibers measure about 2.6 mm and are comparable to the best softwood fibers. Refined core fibers measure about 0.6 mm and are comparable to the hardwood tree fibers (Smith, 1998). The harvested kenaf plant in whole is processed in a mechanical fiber separator, making possible the independent utility of the bast fibers and core fibers. Both parts of the kenaf have their utilization in the paper making industry. Except paper pulp, long, bast fibers could be used to make products such as burlap and carpet padding; short, core fiber could be made into poultry house bedding, parking material, and mats for oil absorbing (Sullivan, 2003). Even the leaves of the kenaf plant have potential use as livestock feed.

2.3.1.2 Applications of Kenaf

Kenaf's major use for several decades was in the pulp and paper industry as a substitution of wood due to world wide decrease of forest resources. Newspaper made from kenaf pulp is whiter, stronger, smoother, has better ink retention, and does not yellow with age as readily as wood pulp based newsprint (Kador, Karlgren, & Verwest, 1990).

Kenaf by itself, or together with other annual bast plants like flax, hemp and jute could also be used in the making of lignocellulosic boards, such as particleboards or fiber boards, which are the most popular building materials in the furniture and interior

decoration industry. For example, Kozłowski, Mieleniak, Helwig, & Przepiera (1999) found that bast plants such as kenaf could be used as one of the main components to build a special three layer structure flame-resistant lignocellulosic particleboard. Sellers, Miller, & Fuller (1993) found that the woody core of kenaf has potential application as raw material for low-density panels used as thermal resistance or sound absorption building materials.

In addition to its utility in the paper and board industry, kenaf has attracted attention in recent decades as an abundant natural fiber source in the field of fiber-reinforced composites. Many properties of the natural fiber reinforced composites were comparable or superior to those of the glass fiber reinforced composites. It was found that tensile modulus, impact strength and the ultimate tensile stress of the kenaf reinforced polypropylene composites were positive to the fiber content (Wambua, Ivens, & Verpoest, 2003). Kenaf fibers also have a higher reinforcing effect on natural rubber compared with that of synthetic polyester fibers, and improved the rheological properties of the rubber (El-Sabbagh, El-Hariri, & Abd El-Ghaffar, 2001). The major problem raised in the natural fiber reinforced material is the low adhesion between the surface of the filler (natural fiber) and the matrix (synthetic material). Feng, Caulfield, and Sanadi (2001) found in their research that using maleated polypropylene was effective to improve the compatibility between the kenaf fiber and the polypropylene matrix. Scientists are also studying the possible treatment of the fiber surface to enhance the fiber-polymer bonding strength of the natural fiber reinforced composites.

As automakers paid more attention to the recyclability of newly produced vehicles, researchers found that kenaf is ideal for making automotive nonwoven

composites because of its high strength and porosity structure. Incorporating kenaf fibers in the manufacture of automotive nonwovens, not only increased the biodegradability of the nonwovens, but also reduced their weight and enhanced their noise absorbent ability. It was found that nonwovens made of retted kenaf fibers blended with cotton fibers, recycled polyester, and off-quality polypropylene could meet industry specifications of flammability, odor, mildew and strength properties (Parikh, Calamari, Sawhney, Blanchard, Screen, Myatt, *et al.*, 2002).

Kenaf fibers could also found their utilization in the manufacturing of fabrics. Kenaf's strength and resistance to rot and mildew make the fabrics containing kenaf fibers attractive in diverse applications. Fashion designers are always looking for novel textiles, and the characteristics of the retted kenaf fiber made it possible to be applied in the apparel industry. After retting, kenaf fibers are still too stiff to spin. They need to be chemical softened to go through yarn and fabric process. Zhang (2003) studied properties of the softened kenaf fibers that were chemically extracted from the fiber bundle, and found that blending cotton into the pure kenaf yarn can increase the yarn's strength and elongation at break, and make the yarn less stiffer. In her research the yarn was also knitted into fabric and the KAWABATA system was used to test the properties of fabrics made of both pure kenaf and kenaf/cotton blends. If an efficient way of spinning kenaf fiber could be found, the cotton/kenaf blends can provide a new, profitable texture for textile and apparel industry.

2.3.1.3 Processing of Kenaf

Raw kenaf bast fibers have to be mechanically processed because of the coarseness, brittleness, and low cohesion of the fiber bundles. After mechanical

processes, natural or chemical retting is performed and fine fibers are formed for conventional nonwoven producing equipment.

The bast kenaf fibers that already separated most of the core material, need to be mechanically processed to further reduce the core content. Moreau, Bel-Berger, and Tao (1995) found that cotton ginning equipment and a Rando cleaner were effective in reducing the core content to less than 0.2%.

Bound by lignin and pectin, kenaf fiber bundles could be treated with sodium hydroxide to partially extract lignin and separate out the fibers. Kenaf fibers could be chemically extracted through the following steps: (1) boiling in weak alkali solution, (2) acid neutralization, (3) thoroughly rinsing with water, and (4) oven drying. Average fiber dimension after the processing is a major concern, as it affects the final properties of nonwoven products. Alkali concentration and the boiling time significantly affect the result of the treatment. Tao, Moreau, and Calamari (1995) found that finer fibers were obtained with increasing the concentration of sodium hydroxide.

Carding of kenaf is used to further break up the fiber bundles after the chemical processing of kenaf fibers. Softer treatment of the kenaf fibers under neutral condition after alkali extraction helps to get finer fibers to pass the carding machine, with nearly no negative affect on the fiber strength (Yang, Morisawa, Ohtani, & Sameshima, 2001). Tao, Calamari, and Crook (1998) also found a method to modify the traditional carding machine for processing 1 N alkali treated kenaf fibers into pure kenaf mat with good integrate, or into kenaf/polypropylene (95/5) blended fiber mat with much better strength. The oil retention rate of 100% kenaf mat was comparable to that of the traditional

polypropylene mat, while kenaf/cotton blends had a higher oil retention rate than that of the pure kenaf or pure polypropylene mat (Tao *et al.*,1995).

Other than chemical extraction (also called chemical retting), fibers could also be extracted from the kenaf plant by bacterial retting, i.e., anaerobic bacteria fermentation or dew-retting by aerobic fungi (Zhang, 2003). Lignin resists microbial degradation by most organisms, but can be degraded by white rot fungi. Natural retting process is lengthy, but the resulted fibers have many desirable characteristics, such as higher tenacity, better color and luster, as compared with those of fibers retted with chemical methods (Romaswamy, & Boyd, 2004). It was suggested to combine the two methods, whenever possible, in order to reduce the retting time and to retain the fiber quality at the same time.

2.3.2 Bagasse

2.3.2.1 Introduction of Bagasse

One of the most abundant natural fiber resources is the by-product of the sugar industry, viz., the bagasse. U.S. sugar mills produced about 13 million tons of dry bagasse in the year 2001 (Chen, & Negulescu, 2002). Bagasse has been widely used throughout the world in such products as pulp and paper, particle and fiber boards, poultry litter, agricultural mulch and soil conditioner (Manobar Rao, 1997). In the U.S., only a portion of bagasse has been used for power generation or as a raw material for producing low-value products, while large amounts of bagasse went to landfill or were allowed to decay (Chen, & Negulescu, 2002). Disposal of bagasse has become a problem for both agricultural profitability and environmental protection.

The sugar cane stalk is composed of an outside rind and an inner pith. The inner pith consists mainly of short fibers and sucrose, while the outside rind contains longer

fibers, arranged randomly throughout the stem. The fibers are bound together by lignin and hemicellulose (Collier, J. R., Collier, B. J., Thames, & Elsunny, 1995). Defined as the fibrous residue of the cane stalk from a sugar mill after crushing and extraction of the juice, bagasse is a mixture of hard rind fibers and soft pith tissue composed mainly of cellulose fibers, pentosans, lignin, sugar and minerals. The relative proportions of the components of the bagasse's cell wall are showed in Table 2-4 (Manohar Rao, 1997).

During cane harvest time, bagasse is readily available. Other than the harvest time, bagasse has to be stored for use. Special care is needed to prevent bagasse from fermentation due to its sugar content. To increase the storage life, bagasse is usually depithed before storage. The depithed and dried bagasse can be baled and stored outside. Bagasse can also be stored wet for several years if specially handled. In the wet method, large bales of bagasse are specially stacked to ensure adequate air flow; the heat from fermenting sugars will effectively sterilize the bales (Youngquist, Krzysik, English, Spelter, & Chow,1996).

Table 2-4 The relative proportions of the components of the bagasse's cell wall

Cellulose	26% to 43% on dry weight
Hemicellulose	17% to 23% on dry weight
Pentosans	20% to 33% on dry weight
Lignin	13% to 22% on dry weight

2.3.2.2 Applications of Bagasse

Bagasse can be made into soft boards, medium density fiberboards or particleboards, as well as high density hardboards using dry or wet chemical processing. Acetylated bagasse could be used in the manufacture of high density fiberboard with low

water absorption and thickness swelling rate (Rowell, & Keany, 1991). Esterified bagasse fibers could be hot pressed without adhesive into thermoplastic materials with good dimensional stability, and the product has potential applications such as the high-density particleboard (Hassan, Rowell, Fadl, *et al.*, 2000). Stael, Tavares, and d'Almeida (2001) found that bagasse from the sugar cane mills has good surface cleaning that could be directly chopped and used in poly(ethylene-co-vinyl acetate) matrix, forming a completely biodegradable composite which performs like commonly used low-density, low strength particle board.

Another developing application for bagasse fibers is in the manufacturing material products, such as the automobile interior trim parts. Research studies mainly focused on the bagasse fiber reinforced polymer products manufactured by thermal bonding the not-so-easily biodegradable synthetic materials with the bagasse fibers (Mueller, & Krobjilowski, 2003; chen *et al.*, 2003; Rowell, & Keany, 1991). Polypropylene or polyester were the most frequently used polymeric matrices for the preparation of thermo setting fiber-reinforced composites having bagasse fibers as the reinforcing fillers (Hassan, *et al.*, 2000; Ismail, Ismail, Turkey, & Nada, 2000; Chen *et al.*, 2003). Bagasse-phenolic composite is a material with good heat and moisture resistance that could be used as a fire retardant material (Paiva, & Frollini, 2002). For their processing economy and design flexibility, bagasse could also be used as a suitable alternative to cord as the reinforcement material for natural rubber to improve the rubber's aging resistance (Ismial *et al.*, 2000). In the previous research studies, the major problem was how to enhance the adhesion between the hydrophilic bagasse fibers and the hydrophobic polymer matrix of the composite. Although the fiber-matrix interfacial strength will be enhanced by an

effective removal of the lignin from the bagasse, the over-treatment would weaken the fibers, thus decreasing the mechanical properties of the composite material (Stael *et al.*, 2001). Researchers are investigating this problem, searching for a coupling agent able to chemically modify the polar nature of the cellulose surface to render it more compatible with the non-polar natured polymer matrix.

Last but not least, bagasse could also be converted into many other value-added industrial products, such as liquid fuels (Dellepiane, Bosio, & Arato, 2003) and activated carbon (Aguilar, Bonelli, & Cassanello, 2003).

2.3.2.3 Processing of Bagasse

In addition to cellulose fibers, sugar cane rind contains about 18% lignin and 30% hemicelluloses (Paturau, 1989). Thus, cane rind needs to be alkaline-extracted to remove these encrusting substances before its use in textile and geotextile applications. Fibers in sugar cane rind are similar to those in jute, the ultimate fibers in both plants being 2-4 mm long, a length too short to be processed as textile fibers. Useful fibers are bundles of these ultimate fibers held together by lignin and hemicelluloses (B. J. Collier, & Arora, 1996). B. J. Collier, J. R. Collier and their research group at Louisiana State University for many years studied the alkaline extraction of fibers from sugar cane rind. In their study, instead of using the crashed and squeezed bagasse from sugar mill, the Tilby separation process was used to separate the cane rind segments longitudinally from the stalk, remove the soft pith, and get uncrushed rind portion in a strip form. Cane fibers were chemically extracted by treating the rind segments with low concentration solution of sodium hydroxide, followed by high pressure steam explosion. The amount of lignin removed depended on the alkaline concentration, together with the time and pressure of

the treatment; agitation and vigorous boiling also affected the lignin removal. The more severe the treating conditions, that is, higher alkali concentration, higher pressure and longer treating time, yielded the finest fiber bundles with lower tenacity, toughness, linear density, bending rigidity and hysteresis (B. J. Collier, & Manpreet, 1996). Based on their study, the extracted fibers were still too stiff to go through the cotton equipment, but could be formed into nonwoven geotextile mats. Sugarcane fiber mats used for erosion control had higher water resistance, lower light penetration, and were less flammable than traditional products made from coconut, straw, or wood (J. R. Collier, *et al.*, 1995).

2.3.3 Regenerated Cellulose Fibers and Lyocell Solution

Regenerated cellulose fiber is a kind of manufactured cellulose fiber made from natural fiber that can not be utilized in its original form, but can be re-formed into a usable fiber by chemical processing. The most common regenerated cellulose fiber is rayon.

Rayon is produced by dissolving pulp of wood or other natural cellulose in chemicals that break down the molecular structure of the fiber somewhat, while still retaining a substantial quantity of polymer molecules. Continuous rayon filament could be spun from solutions of the chemical treated cellulose (Collier, & Tortora, 2001).

Because of its complexity and the pollution it causes, the viscous process of producing rayon is being abandoned in the western countries in recent years. Scientists around the world had made great efforts to find a new method to prepare cellulose solutions that are more environmentally friendly than rayon. It was found that N-methylmorpholine-N -oxide (NMMO) was the best solvent to directly dissolve cellulose.

The cellulose solution prepared by dissolving wood pulp and other natural cellulose in this amine oxide solvent was called a lyocell solution, and new cellulose fiber named lyocell could be spun from it. The name “lyocell” was derived from “lyo”, meaning solution, and “cell”, meaning cellulose (Collier, & Tortora, 2001). Lyocell has all the advantages of regenerated cellulose fibers: it has high strength in both wet and dry states, has high absorbency, is fully biodegradable and is easy processed (Wooding, 2001). Because of its physical properties, lyocell has excellent blending characteristics with many other commercially available staple fibers (Collier, & Tortora, 2001). In addition, the process for making lyocell is environmentally friendly: the NMMO·H₂O solvent used to dissolve the cellulose is non-toxic, and can be nearly completely recycled.

Lyocell solutions obtained from dissolving recycled cellulose fibers in NMMO·H₂O may also be used as an adhesive to stabilize nonwoven composites. This technique had never been used by previous researchers and was investigated in this work.

2.4 Property Testing of the Polymer Composite

The testing methods used in this research were the standardized methods by the American Society for Testing and Materials (ASTM).

2.4.1 Tensile Analysis

Tensile testing determines the Young's modulus of elasticity which is used to figure out the load-carrying ability and the amount of deformation of a sample before fracture.

Under light stress, a material will undergo a temporary deformation, which is an elastic displacement of the atoms in the space lattice. If the stress is removed, the material

will return to its original shape and dimensions. Thus, in the elastic range of a material, the strain is proportional to the stress. Hooke's experimental law gives the relationship

between the load (force) and the extension: $\delta = \frac{pl}{AE}$.

p : load producing extension of the sample (N).

l : original length of the sample (m).

A : cross-sectional area of the sample (m²).

δ : total extension of the sample (m).

E : the modulus of elasticity or young's modulus (N/m²).

From the above formula we can see that the extension of the sample is directly proportional to the load and the length of the sample, and is inversely proportional to the cross-sectional area of the sample and the modulus of elasticity.

The tensile stress was defined as the load applied per cross-sectional area perpendicular to the load: $\sigma = \frac{P}{A}$, where σ is stress (N/m² or Pa). The tensile strain, or

the extension of a bar per unit length, is determined by: $\varepsilon = \frac{\delta}{l}$, where ε is strain (m/m).

Thus, $E = \frac{\sigma}{\varepsilon}$. In other words, the Young's modulus is the stress, below the proportional limit, divided by the corresponding strain. The stress and the strain introduced above are sometimes called "engineering stress and strain." They are not true stress and strain. The true strain is the natural logarithm of the ratio of the length at any instant to the

original length, that is: $\ln(l/l_0)$. Below the elastic limit, the engineering stress and the true stress are almost identical.

In the tensile test, a gradually increasing load of tension is applied at one end of a sample, and the other end is anchored in a rigid support so that the sample is slowly pulled apart. A device attached to the testing machine records the magnitude of the load applied on the sample throughout the test. At the same time, measurements are made of the increasing length of a selected portion of the sample, which is usually located in the middle of the sample, called the gage length. Measurements of load and elongation will stop shortly after the plastic deformation begins; however, the maximum load reached is always recorded.

The tensile test mainly gives three factors about a material: the load at which the plastic deformation or "yielding" begins, the maximum tensile strength or the maximum load that can be carried by a sample, and the percent of extension or the strain.

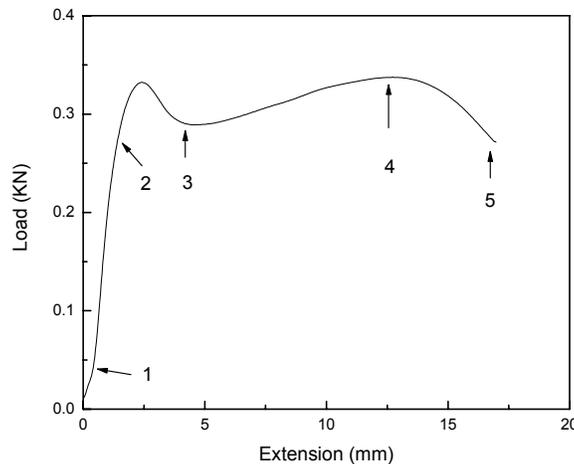


Figure 2-1 Load-Extension Curve

Figure 2-1 shows the Load-Extension Curve. The area between Points 1 and 2 is called the elastic region. If the load is removed, the material will return to its original length. Point 2 is the elastic limit, and point 3 is the yield point. The area between points 2 and point 5 is the plastic region where the sample will not be able to return to its original length. Point 4 is the point of the ultimate strength, and point 5 is the fracture point at which failure of the sample occurs (Tensile, 2004).

2.4.2 Thermal Conductivity and Thermal Transmittance

The thermal conductivity (λ) is the heat flow in unit time that passes through unit area of a plate, induced by unit temperature gradient (i.e. one temperature difference across parallel planes separated by unit distance). It could be expressed as: $\lambda = Q/[A(dt/dx)]$. Where A is the area of the test plate; dt/dx is the temperature gradient. The normalized thermal conductivity refers to normalization by density (λ/d).

Thermal transmittance is the heat flow in unit time and in unit test plate area, induced by unit temperature difference of the plates. It could be expressed as: $U = Q/[A(T_p-T_a)]$. Where U is thermal transmittance (W/m^2K); Q is power loss or heat flow rate from test plate (W); A is the area of the test plate (m^2); T_p is test plate temperature ($^{\circ}C$); T_a is air temperature ($^{\circ}C$).

2.4.3 Dynamic Mechanical Analysis (DMA)

All materials have viscoelasticity, which is a combination of viscosity and elasticity in varying amounts. When this viscoelasticity is measured dynamically, there is a phase shift between the force applied per unit area (stress) and the deformation related to initial dimensions (strain) which occurs in response. The tensile stress σ and the

deformation (strain) ε (or τ and γ for sheared viscous materials) are related via the elasticity modulus E as follows:

$$\sigma = E \varepsilon$$

Generally the measurements are represented as a complex modulus of elasticity E^* to insure an accurate expression as described in Figure 2-2: $E^* = E' + iE''$, where $i^2 = -1$; $|E^*| = \text{peak stress/peak strain}$.

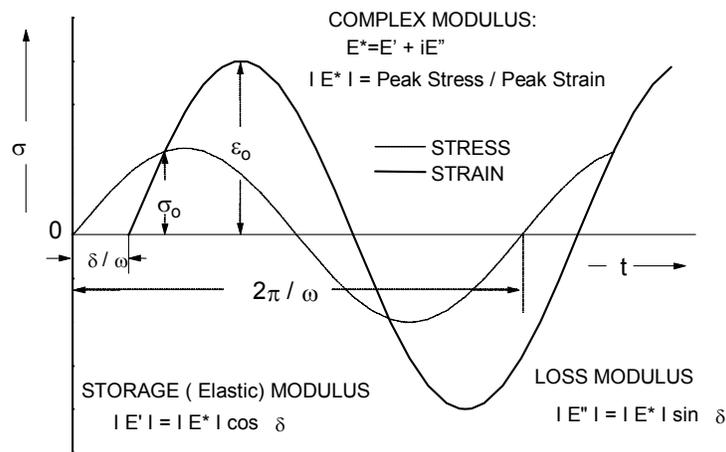


Figure 2-2 Illustration of the relationship between parameters of the dynamic mechanical analysis

In dynamic mechanical analysis, DMA, a sinusoidal strain or stress is applied to a sample and the response is monitored as a function of frequency. Polymers are not ideal energy elastic bodies; they are viscoelastic materials. In such cases the deformation (strain) lags behind the applied stress. For purely elastic materials, the phase angle will be zero, whereas for purely viscous materials, the phase angle will be 90° . Therefore the phase angle, taken as the tangent, is a parameter describing the viscoelasticity of a

material. The loss tangent is calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage modulus: $\tan \delta = E''/E'$, because $E'' = E' \sin \delta$ and $E' = E' \cos \delta$.

The magnitude of the phase angle for shearing a purely elastic material or a purely viscous material is depicted in Figure 2-3.

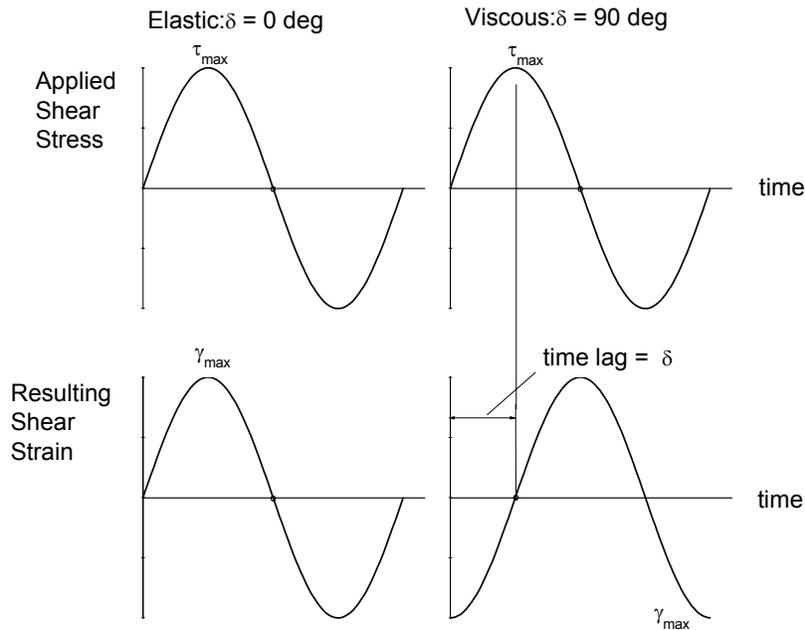


Figure 2-3 Illustration of the phase angle of a purely elastic material and a purely viscous material

2.4.4 Differential Scanning Calorimetry Analysis (DSC)

Being one of the most important thermal analysis methods, differential scanning calorimetry (DSC) is used to characterize materials by studying a wide range of thermal transitions in their system. More often than not DSC is used to determine melting and crystallization temperatures and thermodynamic parameters associated with these changes.

DSC measures the temperatures and heat flows associated with phase transitions in substances as a function of time and temperature. Such measurements provide important information about physical and chemical changes that involve endothermic or exothermic effects, or heat capacity changes.

In the power compensated DSC instrument used in this research, the temperatures of a sample and an inert reference material are controlled independently using two separate, identical furnaces. The temperatures of the sample and the inert reference are made identical by varying the power input of the furnaces. The instrument measures the energy needed to approaching zero temperature difference between the sample and the reference material. The heat capacity changes in the sample relative to the reference is measured by the energy required to complete the above job, as the two specimens are within the identical temperature system that changed at a controlled rate.

Since $T_{\text{sample}} = T_{\text{reference}}$, $\Delta H = k(\Delta W)$, Where ΔH is the heat capacity change, k is a constant, and ΔW is the change in energy needed to keep T_{sample} equal to $T_{\text{reference}}$. DSC is primarily used to characterize polymers and other organic materials, but it is also applicable for testing some inorganic materials. Table 2-5 listed the main measurements made by DSC (Bhadeshia, 2002).

Table 2-5 Main measurements made by DSC

Glass transition measurements	Oxidative stability
Degree of crystallinity	Specific heat measurement
Melting point	Purity measurement
Reaction kinetics	Quality control of raw materials

2.4.5 Thermogravimetry Analysis (TGA)

Being one of the oldest thermal analytical procedures used for the study of polymeric systems, the thermogravimetry analysis is a technique of evaluating the thermal decomposition kinetics of materials by monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a function of temperature (Description, 2003). Not all thermal events result in a change of the sample mass: melting, crystallization, and glass transition do not exhibit a mass change; whereas desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition do. TGA is best known for its ability to provide information on the bulk composition of compounds. The usefulness of TGA for analyzing complex systems is greatly enhanced by the ability to record simultaneously the first derivative of the weight loss, that is, the derivative of the thermogravimetric curve.

2.5 Conclusion

In recent decades, most research globally wide were concerned with the different methods of incorporating natural fibers, such as hemp, flax, kenaf or bagasse into various types of polymer compositions, in order to modify their properties and to decrease their costs. The application of bast natural fibers such as kenaf and bagasse in forming of nonwoven composites were focused on the binding of the natural fibers with different kinds of petroleum-derived synthetic adhesives that were not easily biodegradable. The commonly used method of processing was the blending of thermo moldable synthetic fibers with cellulosic fiber components, followed by thermo bonding of the composite. The synthetic fiber used as a fiber component not only increased tensile strength and the flexural rigidity of the final product, but also helped to bond the natural fibers together

and aided to mold the nonwoven composites to the desired shape. This is a very important processing factor in manufacturing boards and side panels for the automotive industry. However, there is a negative effect of incorporating synthetic fibers in composite nonwovens: if heated close to the softening temperature of the synthetic fibers, the nonwoven product will deform. Therefore, the present study investigated the possibility of replacing the synthetic bonding material in the nonwoven composites by cellulose from solution, in order not only to increase the biodegradability of the material, but also to avoid the deformation of final products. The cellulose solution may also contain cellulose acetate as a plasticizing agent, aiming to increase the flexibility of the composites. These new biobased composites will have an enhanced mechanical strength, a better acoustic performance, will result in a reduced material weight at a lower production cost, and will have an improved thermal stability of final products under extreme temperature changes.

Chapter 3 Materials and Methods

Seven types of nonwoven composite structures were studied as follows:

(1) - (3) Bagasse/Cotton (70/30) cellulose webs bonded with 0.5%, 2%, and 5% cotton derived lyocell solution.

(4) Kenaf/Cotton (70/30) cellulose webs bonded with 0.5% cotton derived lyocell solution.

(5) Bagasse/Cotton (70/30) cellulose webs bonded with 0.5% cotton derived lyocell solution containing 0.2% acetate, as a plasticizing component for bonding cellulose (lyocell) composite.

(6) Kenaf/Cotton (70/30) cellulose webs bonded with EBC (70/30 cellulose/EBC), obtained earlier at LSU (Chiparus, 2004).

(7) Bagasse/Cotton (70/30) cellulose webs bonded with EBC (70/30 cellulose/EBC), obtained earlier at LSU (Chiparus, 2004).

Following steps have been considered in the present study: the fiber web formation, the preparation of the biodegradable adhesive systems, the bonding of the nonwoven webs with adhesives to form the nonwoven composites, and the analysis of nonwoven composites.

3.1 Fibers Used to Form the Cellulose Web

3.1.1 Kenaf Fibers

Kenaf fibers used in this study were purchased from the Mississippi Company. The average fiber length was 2 inches and the fiber fineness was 9 tex.

3.1.2 Bagasse Fibers

Bagasse fibers were prepared as shown in the following (Chiparus, 2004). Selected crushed and squeezed cane stalks from a Louisiana sugar mill were boiled for one hour in a 2N NaOH solution (ratio: 1Kg cane/20 L NaOH solution). After washing thoroughly with water the delignified bagasse fibers were dried in an air-circulating Blue M Electric Company Oven at 135°C for 45 minutes. The cleaning process was carried out at USDA (United States Department of Agriculture) Southern Regional Research Center in New Orleans using a Cleaning McPhearson Machine with a loss of 82%.

3.1.3 Cotton Fibers

Cotton fibers were greige Maxxa type, provided by USDA Southern Regional Research Center. The average fiber length was 1.12 inches and the fiber fineness was 4.1 micronaire.

3.2 Fiber Web Formation

Carding and Needle-Punching were used to form the staple fiber web.

3.2.1 Carding

Carding is a process used to comb the individual fibers to be relatively parallel, and to make the different kinds of fibers blend uniformly. Cotton fibers were blended manually with kenaf or bagasse fibers in the desired ratio and fed twice into the LSU F015D Universal Laboratory Carding Machine shown in figure 3-1. Cotton fibers acted as an entangling material for the coarse kenaf or bagasse fibers; the mixed staple fibers were oriented and entangled to form a loose, continuous fiber web.



Figure 3-1 The LSU F015D Universal Laboratory Carding Machine

3.2.2 Needle-punching

Needle-punching is a process used to entangle fibers in the direction perpendicular to the web surface, making the fiber web much more compact with balanced absorbability. A needle-punching process was employed for the web bonding using a Morisson Benkshire needle-punching machine with the speed of 5.4 feet/min and 228 strokes/min, correspondingly. In this research, the needle-punching had another function, that is, to punch lots of tiny holes through the cellulose web, thus allowing the lyocell solution to penetrate the web easier. Each sample was needle-punched two times, faced up and down.

3.3 Preparation of Cotton Derived Lyocell Solution as the Web Adhesive

Cellulose solution used as the web adhesive in this research was prepared by dissolving scrapped recycled cotton fabric into NMMO solvent. The amount of cotton added has to be measured accurately so that the cellulose content in solution is closely controlled. For the preparation of the 0.5% and 2% cotton/NMMO solutions, the weighed cotton was mixed with a 50% NMMO solution in water. For the preparing of (0.5%

cotton, 0.2% acetate)/NMMO solution, scrapped acetate fabric was weighed and added together with the scrapped cotton. A small amount (0.1% by weight) of N-propyl gallate (NPG), an inhibitor preventing cellulose degradation, was added to the system in each case.

Cellulose dissolves in the NMMO-water system only when the molecular ratio NMMO:water is unitary, i.e., when the monohydrate $\text{NMMO}\cdot\text{H}_2\text{O}$ is formed. The NMMO concentration in monohydrate is 86.7%. At this concentration the NMMO solution is solid at room temperature and melts to a viscous liquid at 72° C. On the contrary, the 50% NMMO solution in water is a liquid at ambient temperature but does not have the power to dissolve cellulose. Therefore, after mixing cellulose fibers (i.e., cotton) with 50% NMMO solution, which was partially absorbed by cotton fibers, it was necessary to reduce the water content of the system until it reached ~13-14%, viz., the water content of the monohydrate ($\text{NMMO}\cdot\text{H}_2\text{O}$). The excess water was removed by evaporation at a temperature that was 20-25°C higher than the melting point of the monohydrate (72°C).

The evaporation of water from the mixture was carried out in a rotary evaporator (shown in Figure 3-2). The evaporator was operated at a low pressure (0.2-0.3 Torr), provided by a water-suction pump, to let the water evaporate at a relatively low temperature (about 95°C). This is because the NMMO solvent will undergo an exothermic degradation process if overheated. The temperature was carefully controlled to stay below 100°C, because at $T > 100^\circ\text{C}$ the NMMO will slowly oxidize the cellulose. This oxidation reaction will reduce the degree of polymerization of the cellulose chains. In addition, as shown in Figure 3-3, a small portion of the NMMO solvent will degrade to

other amines, generating colored compounds. The degradation will be strongly catalyzed by transition metals such as copper and iron, so that the NPG stabilizer acted both as an antioxidant and a chelation agent. As indicated above, the water was distilled until the original 50% NMMO solution concentrated to a 87% NMMO solution. At this point, the N-Methyl Morpholine N-Oxide monohydrate, that is, NMMO·H₂O was formed. The cotton fiber easily dissolved at this concentration. The final product was an amber-colored viscous cellulose solution, resembling honey both from the point of view of the color and viscosity.

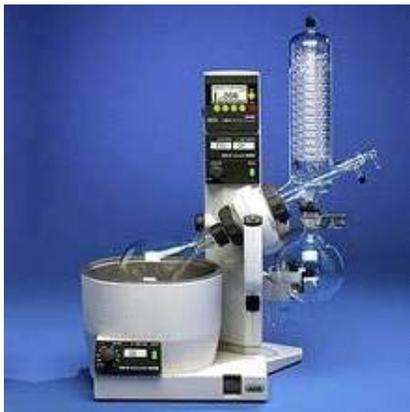


Figure 3-2 The rotary evaporator used to prepare 0.5% and 2% cellulose solutions

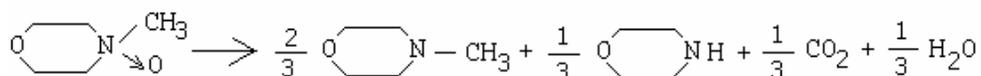


Figure 3-3 Decomposition of NMMO

The cellulose solutions having the concentration higher than 3% are very viscous and have a very low fluidity. Therefore it is practically impossible to dissolve the cotton scraps thoroughly inside the rotavapor. Besides, even if the cellulose solution was properly prepared, it will be very hard to remove the solution from the rotavapor flask.

Consequently, for the preparation of the 5% cotton/NMMO solution, a gear-type instrument was used, viz., the HAAKE Rheocord Torque Rheometer shown in Figure 3-4. The first step was to prepare the monohydrate $\text{NMMO}\cdot\text{H}_2\text{O}$ from 50% NMMO solution. The necessary amounts of monohydrate were obtained by distillation of the excess water as indicated above. The monohydrate still in the liquid state ($T > 72^\circ$) was sealed in polyethylene bags and let to crystallize in a dessicator where it was stored until the use. Then, subsequently the required amounts of scrapped cotton and solid $\text{NMMO}\cdot\text{H}_2\text{O}$ were weighed and added together into the Rheometer. The limitation of this procedure was the amount of cotton/NMMO solution (50g) which could be prepared at each time.

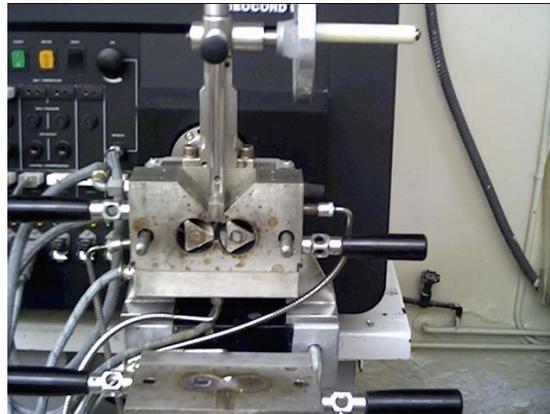
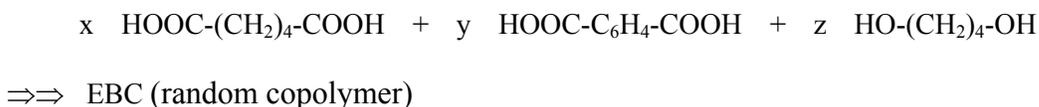


Figure 3-4 HAAKE Rheocord Torque Rheometer used to prepare 5% cellulose solution

3.4 Biodegradable Synthetic Polyester Used as a Web Adhesive

The synthetic polymer used as an adhesive for bonding the cellulosic webs (Chiparus, 2004) was the Eastman poly(tetramethylene adipate-co-terephthalate), also referred in the following as Eastar BioCopolymer (EBC). It is a biodegradable random copolyester obtained from adipic acid, terephthalic acid and butanediol:



The melt-blown polyester nonwoven fabric (57 g/m^2) was obtained from EBC pellets at the TANDEC (Textiles and Nonwovens Development Center) unit from the University of Tennessee, Knoxville, TN.

3.5 Thermal Bonding of Fiber Web Using Adhesives

3.5.1 Thermal Bonding of Fiber Webs Using Cellulose Solutions

The nonwoven composites bonded with cellulose solutions were formed using the “solution coating” method, viz., assembling of fiber web layers and lyocell solution in a “bread and butter” sandwich style, where the web was the “bread” and the cellulose solution (lyocell adhesive) was the “butter”, followed by pressing the fibrous webs and the adhesive “sandwich” into a flexible sheet. The preparation steps are described below:

First, the hot cotton/NMMO \cdot H₂O solution (i.e., lyocell solution) was poured inside several sealed top polyethylene bags and the bags were flattened to form thin layers. The lyocell solution layers were allowed to cool down and turned into solid layers at room temperature. The tops of the plastic bags were tightly sealed because NMMO \cdot H₂O is very hygroscopic.

Second, the needle punched kenaf/cotton or bagasse/cotton cellulose webs were cut into $8 \times 8 \text{ inch}^2$ pieces and heated in an oven set at 95°C . Subsequently, the solid lyocell solution layers (“the butter”) were removed from the plastic bags and inserted immediately between the layers of cellulose webs (the “bread”). If there were 4 layers of cellulose webs, 3 pieces of solid lyocell solution were used. The multi-layer sandwiched

material was then kept inside the oven at 95°C until all of the solid lyocell solution layers melted.

Third, the "multi-layer sandwich" was removed from the oven and put in between the heated plates of the Vantage Press shown in Figure 3-5. The press was operated at 100°C and 80 tons of pressure for 10 minutes. The width between the heated plates was controlled by two pieces of 1/8 inch spacer. After that, the power of the machine was turned off, and the temperature and the pressure were allowed to decrease slowly. The "multi-layer sandwich" was kept pressed inside the machine for a total of 8 hours, letting the adhesive to thoroughly penetrate the webs.

Fourth, the pressed "multi-layer sandwich" was removed from the Vantage Press and soaked inside a basin of warm water. The solvent NMM·H₂O slowly diffused out of the "sandwich" and dissolved into the water. The sandwiched sample (i.e., the composite nonwoven sample) was then manually pressed under water until no yellowish color came out. The polymeric chains of cellulose from lyocell solutions precipitated inside the webs at the contact with water, acting as a "glue" sticking together the composing natural fibers. The NMMO solvent that was washed out could be recycled.

Fifth, the thoroughly washed "all cellulose multi-layer sandwich" (which was different from the "multi-layer sandwich" from the step three because the NMMO solvent had been washed away) was inserted again between the heated plates of the Vantage Press and keep there at 100°C and 80 tons for 5 minutes. Subsequently the pressure was turned "off", and the heating was maintained "on" until the multi-layer composite nonwoven was completely dried. The formation of the composite nonwoven by thermal bonding the fiber webs with cellulose solution is schematically presented in Figure 3-6.



Figure 3-5 Vantage Press (Model 200H-24-BCPX)

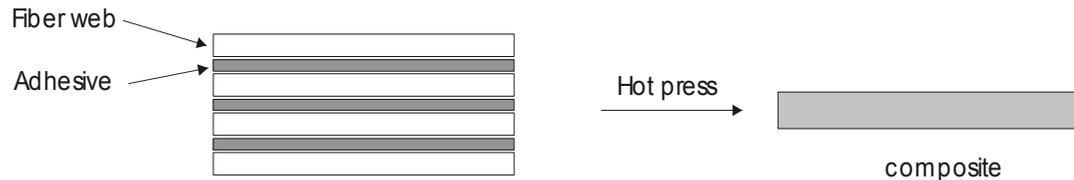


Figure 3-6 Formation of the composite nonwoven by thermal bonding of fiber webs with cellulose solution acting as an adhesive

3.5.2 Thermal Bonding of Fiber Webs with EBC

Bagasse/cotton (70/30) or kenaf/cotton (70/30) cellulosic webs were bonded with biodegradable synthetic polyester (70/30 cellulose/EBC) as described in the dissertation of Chiparus (2004). The thermal-bonding was conducted in a Carver Laboratory Press provided with heated plates. The thermally-bonding temperature was set at 150°C (EBC melted at this temperature) and the heating time was one minute. The thickness of the thermally-bonded nonwoven was set to 1/8 inch. The pressure applied was 8.62 Pa (12,500 psi). Due to the limitation of the plate dimensions, the pressed samples measured 5 in x 6 in.

3.6 Testing Procedures

3.6.1 Tensile Analysis

The ultimate tensile strength of nonwoven composites was determined according to ASTM D5035-95 using an INSTRON tester Model 4301 provided with a 5 KN load cell. The INSTRON software of Series IX Automated Materials Testing System with an interface type 4200 was used for recording of data. Sample sizes were 1 in x 3 in. The Pressley clamps were mounted in specially built grips for the tensile test, the grip distance was set at 2 inches and the specimen gauge length was 1 inch. Before testing, the samples had been conditioned at 20°C and 65% relative humidity for 24 hours. The crosshead speed was set at 0.5 in/min. The samples were mounted between the Pressley clamps and pulled apart until breaking. Recorded tensile properties include: displacement at maximum load, load, stress, strain, maximum percent strain, and modulus. At least three samples were analyzed for each type of nonwoven structure, and the mean and the standard deviation were determined.

3.6.2 Thermal Conductivity and Thermal Transmission

Thermal conductivity and thermal transmittance tests were performed using a thermal conductivity meter (FOX 200, LaserComp Corporation) according to ASTM D1518- 85 standard procedure. Measurement of thermal conductivity and transmittance of poorly conductive materials is based on the simultaneous measurement of ΔT across the sample and of the heat flux through the sample. The thickness of the sample was determined according to the standard procedure ASTM D1777-85. Each sample (8 in x 8 in) was conditioned at 20°C and 65 % RH for at least 24 hours and then was placed between two plates, referred as “cold” [$T_{cp} = 21.0^{\circ}\text{C}$ (69.9°F)] and “hot” [$T_{hp} = 36.6^{\circ}\text{C}$

(97.9°F)] plate, respectively. The average of three measurements for each sample was used to calculate the mean values of the thermal conductivity and thermal transmittance for each nonwoven specimen. Figure 3-7 illustrates the thermal conductivity and thermal transmission measurements.

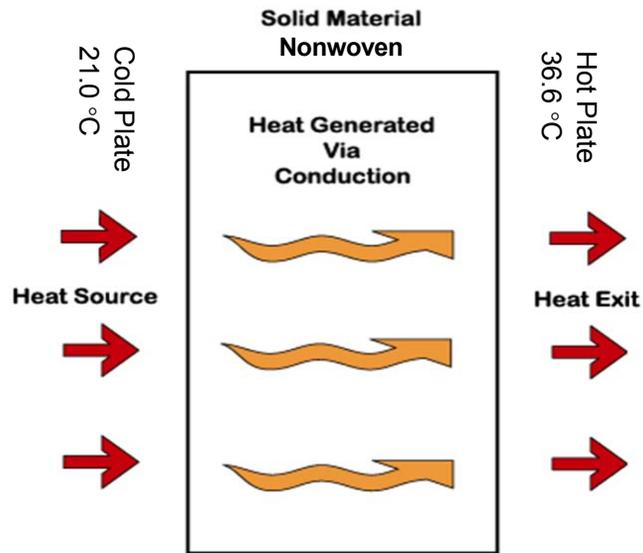


Figure 3-7 Thermal conductivity and thermal transmission

3.6.3 Dynamo-Mechanical Analysis (DMA)

Dynamo-mechanical analysis is a tool to investigate viscoelasticity of materials. Dynamo-mechanical analysis of the composite nonwovens prepared in the present investigation was performed in bending mode for rigid samples using a Seiko Dynamo-Mechanical Spectrometer DMS 110, and in stretching mode for soft samples using Seiko DMS 200. A large temperature range (-100°C to 200°C) and a train of frequencies (0.1 Hz, 1 Hz, 10 Hz and 100 Hz) were used.

3.6.4 Differential Scanning Calorimetry Analysis (DSC)

Differential scanning calorimetry analysis of the selected sample was conducted using a thermal analysis instrument: Modulated DSC 2920 from TA Instruments Inc. with a heating rate of 5°C/min in the flow nitrogen of 40 ml/min. The size of the sample was around 7 mg.

3.6.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the composite nonwoven and its components was carried out both in air and inert atmosphere (nitrogen) with a heating rate of 5°C/min using a thermal analysis instrument: Hi-Resolution TGA-2950 from TA Instruments Inc. The size of the sample was around 7 mg.

Chapter 4 Results and Discussion

Tensile analysis, thermal conductivity, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA) were conducted on selected nonwoven sample(s).

4.1 Tensile Analysis

Table 4-1 presents the mechanical properties of selected nonwoven samples. When all- cellulosic composite nonwovens were compared, the breaking strength and the elastic modulus were higher for the kenaf/cotton sample than that of the corresponding bagasse/cotton nonwoven. The kenaf/cotton samples were also less strained than the bagasse/cotton nonwovens. Unexpectedly, mechanical properties of the bagasse/cotton nonwoven prepared with 2% cellulose solution were inferior to that of the nonwoven made with 0.5% cellulose solution. Possible explanation: non-uniformity of the sample due to the high viscosity of the applied cellulose solution. As expected, however, the highest values were recorded for the kenaf/cotton samples bonded with biopolyester.

Table 4-1 Mechanical properties of nonwoven samples

Nonwoven	Stress at Max. Load (psi)	Strain at Max Load (in/in)	Modulus (psi)
Bagasse/cotton/ 2% cellulose	669	0.22	4,223
Bagasse/cotton/ 0.5% cellulose	2,410	0.09	91,030
Kenaf/cotton/ 0.5% cellulose	2,911	0.07	131,636
Kenaf/cotton/BioPolyester (Chiparus, 2004)	7,554	0.16	257,518

4.2 Thermal Conductivity and Thermal Transmittance

Data of thermal conductivity and thermal transmittance had been collected for bagasse/cotton nonwoven samples stabilized with 0.5% and 5% cotton lyocell solution. The results were presented in Figures 4-1 to Figure 4-3. Thermal conductivity, expressed as normalized data, was somewhat higher for the more densely fabricated nonwoven, containing more non-fibrous cellulose from lyocell solution (Figure 4-2).

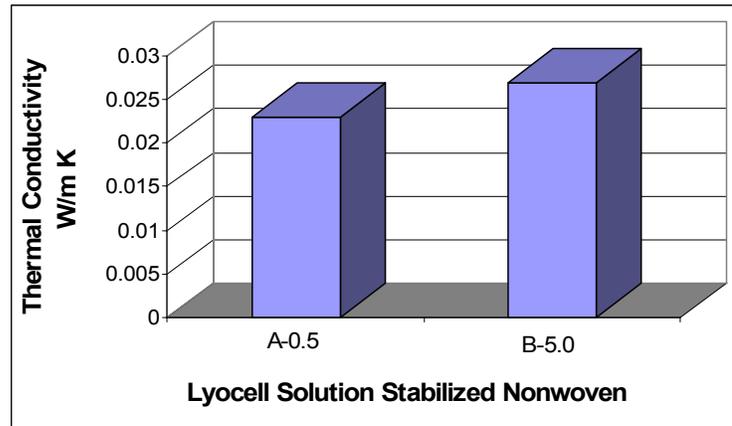


Figure 4-1 Thermal conductivity of all-cellulosic cotton/bagasse nonwoven composites stabilized with 0.5% (A) and 5% (B) cotton derived lyocell solution

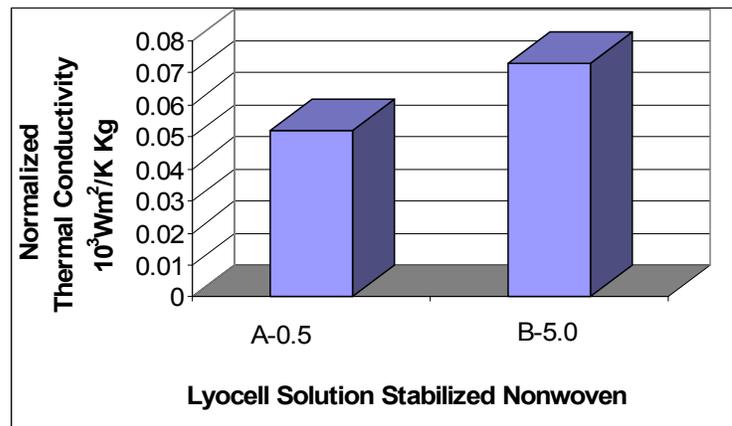


Figure 4-2 Normalized thermal conductivity of cotton/bagasse nonwoven composites stabilized with 0.5% (A) and 5% (B) cotton derived lyocell solution

On the contrary, the thermal transmittance was related to the thickness of the sample, being higher for samples stabilized with a less concentrated lyocell solution (Figure 4-3).

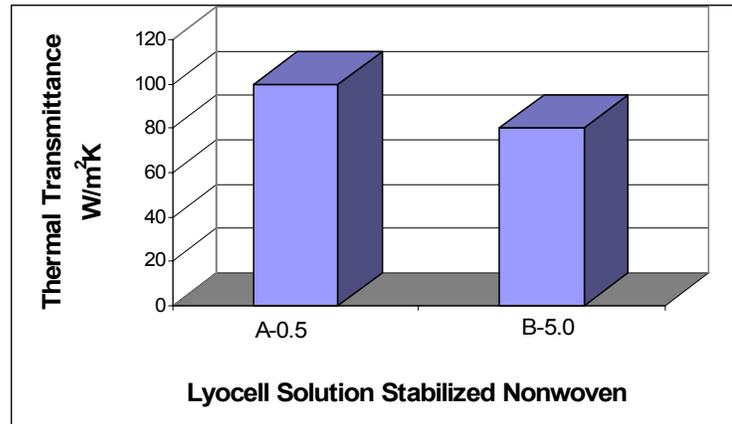


Figure 4-3 Thermal transmittance of cotton/bagasse nonwoven composites stabilized with 0.5% (A) and 5% (B) cotton derived lyocell solution

However, when compared with similar composite nonwovens stabilized with EBC, the lyocell containing cotton/bagasse were much better thermal insulators (Table 4-2). They had a much lower bulk density and a fraction of thermal conductivity and heat

Table 4-2 Comparison between thermal conductivity data of cotton/bagasse composite nonwovens stabilized with lyocell or EBC

Cotton/bagasse nonwoven	d Bulk Density Kg/10 ³ m ³	λ Thermal Conductivity W/mK	λ/d Normalized Thermal Conductivity 10 ³ Wm ² /KKg	U Heat Transmission W/m ² K
Stabilized with 0.5% lyocell	0.442	0.023	0.052	100
Stabilized with 5% lyocell	0.370	0.027	0.073	80
Stabilized with EBC (6 layers) (Negulescu, <i>et al</i> , 2002)	0.792	0.076	0.096	258

transmission characteristics of EBC stabilized counterparts. Despite of the much lower density, the normalized thermal conductivity (λ/d) was still 0.5-0.75 of that of the EBC composite nonwovens.

4.3 Dynamo-Mechanical Analysis (DMA)

4.3.1 Composite Nonwovens Bonded With Cellulose From Solution

The parameters of interest were the components of the complex modulus of elasticity, E^* (including the storage modulus E' , and the loss modulus E'') and their inverse ratio (E''/E'). E' quantifies the elastic component and E'' reflects the viscous character of the sample. The E''/E' ratio (or $\tan\delta$) is very sensitive to any structural change in the sample. If there are no significant changes in the sample, the elastic modulus and its components will decrease while heating (the sample will soften gradually).

However, in the case of all-cellulosic nonwoven samples containing only kenaf and cotton or bagasse and cotton fibers bonded with cellulose (lyocell), the cellulosic components were plasticized by water and heating drove off the water. The result: stiffening of the sample, as reflected by the increase of the elastic modulus components, viz., the storage modulus, E' (Figure 4-4 and Figure 4-5) and the loss modulus, E'' as well (Figure 4-6 and Figure 4-7). The modulus components were also dependent upon the frequency, with the peak temperatures registered at the lowest frequency used (0.1Hz).

When all-cellulosic composite nonwovens were compared, the elastic moduli E' (Figure 4-8) and E'' (Figure 4-9) were higher for the kenaf/cotton sample than that of the corresponding bagasse nonwoven. The trend (i.e., the shape of curves) was the same, and the difference was not too large, with the ratio of maximum values as $E'_{\text{kenaf}} \approx 1.6E'_{\text{bagasse}}$,

and $E''_{\text{kenaf}} \approx 1.3E''_{\text{bagasse}}$. This observation suggests perhaps a better bonding of supplier kenaf fibers as compared with the coarser bagasse fibers.

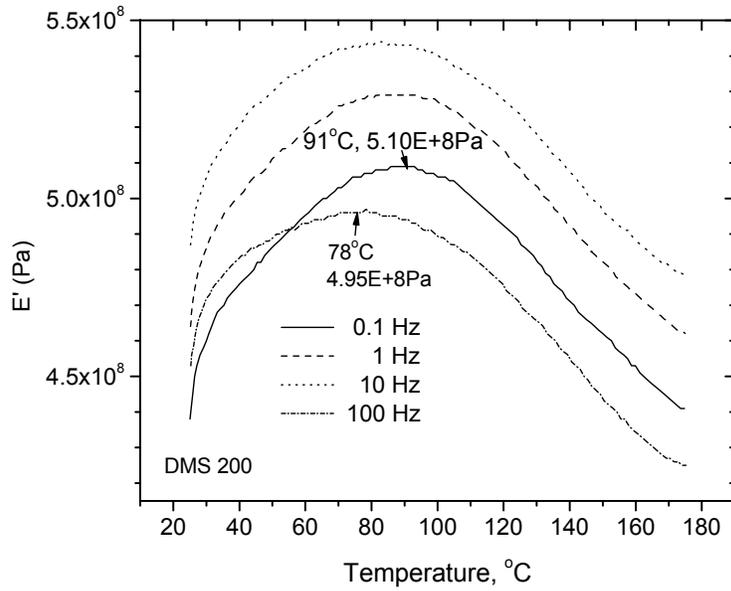


Figure 4-4 Dependence upon temperature of the storage modulus of elasticity E' of kenaf/cotton nonwoven bonded with 0.5% cellulose solution

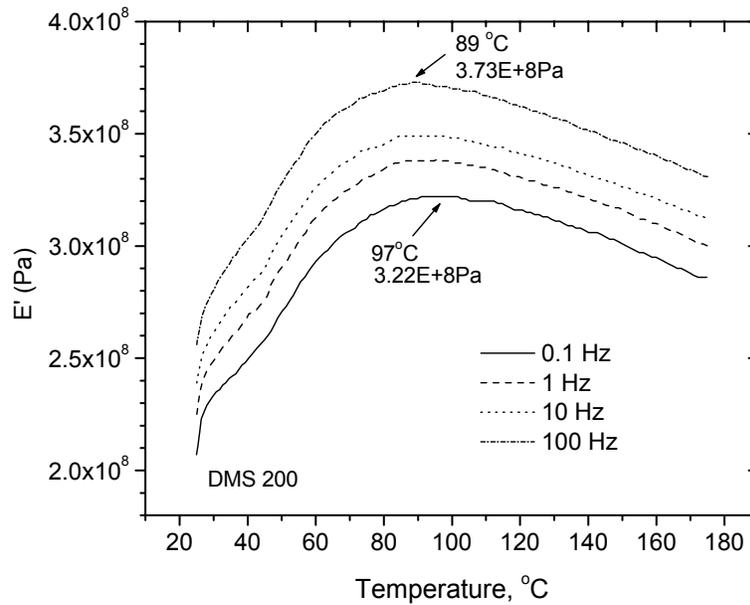


Figure 4-5 Dependence upon temperature of the storage modulus of elasticity E' of bagasse/cotton nonwoven bonded with 0.5% cellulose solution

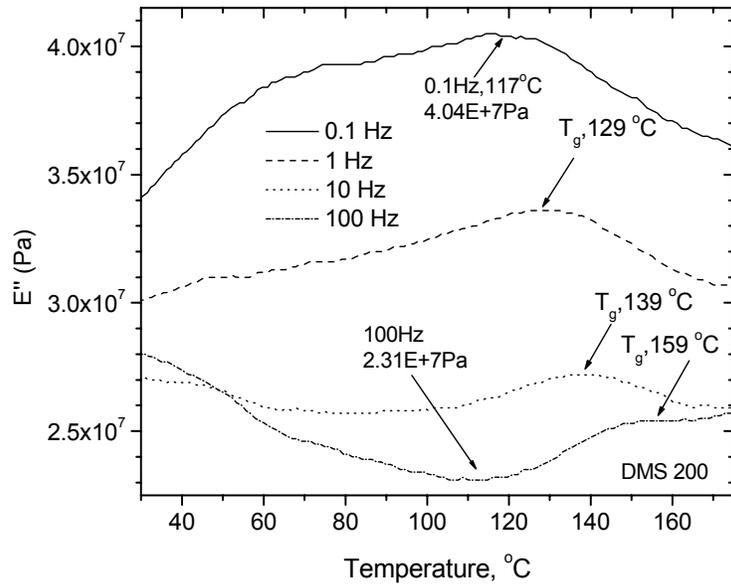


Figure 4-6 Dependence upon temperature of the loss modulus of elasticity E'' of kenaf/cotton nonwoven bonded with 0.5% cellulose solution

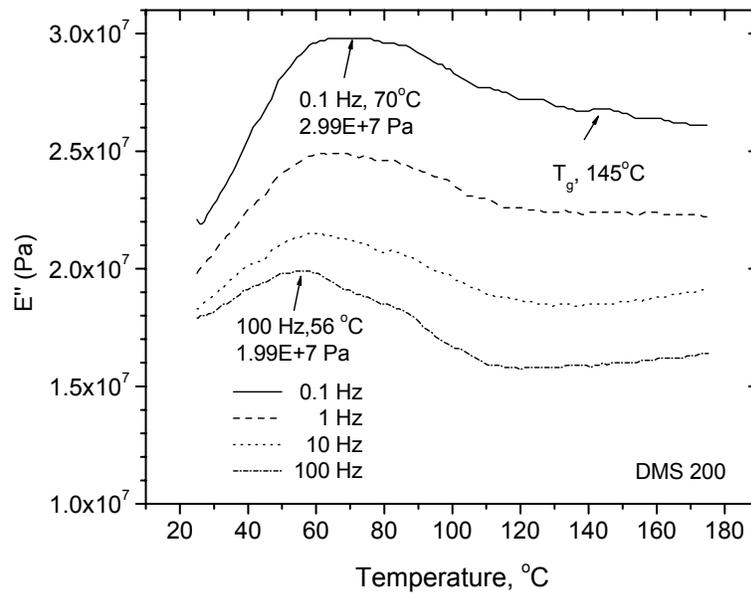


Figure 4-7 Dependence upon temperature of the loss modulus of elasticity E'' of bagasse/cotton nonwoven bonded with 0.5% cellulose solution

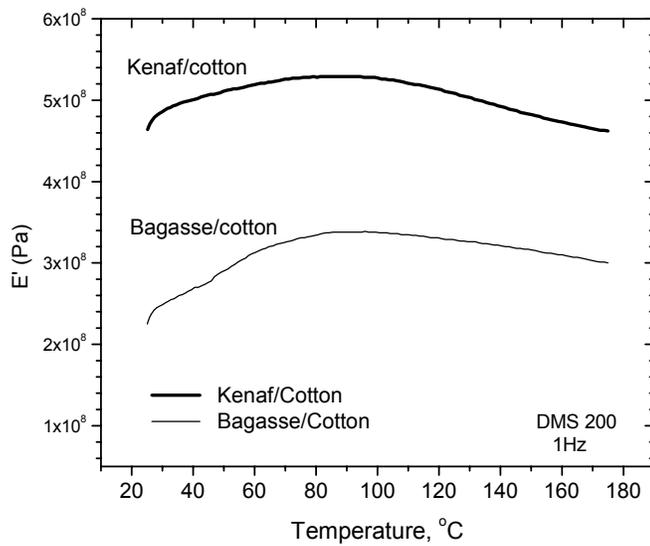


Figure 4-8 Dependence upon temperature of E' of bagasse/cotton & kenaf/cotton composite nonwovens bonded with 0.5% cellulose solution

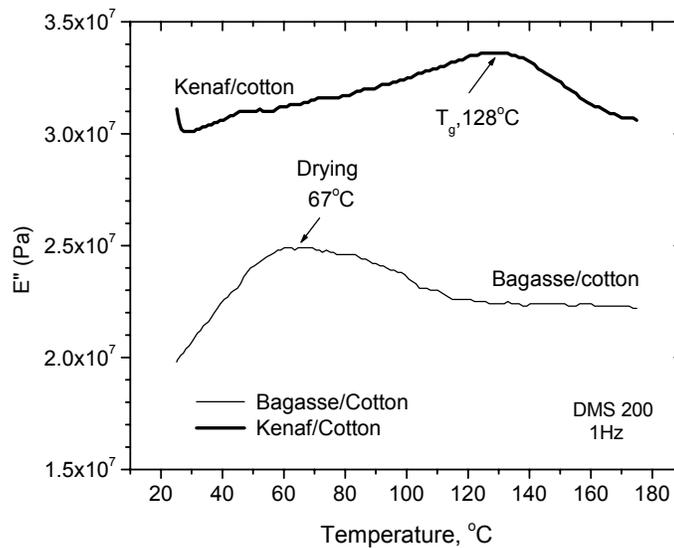


Figure 4-9 Dependence upon temperature of E'' of bagasse/cotton & kenaf/cotton composite nonwovens bonded with 0.5% cellulose solution

The E''/E' ratio ($\tan\delta$) reflected the glass transition of cellulosic chains, observed after 100°C in dried kenaf/cotton and bagasse/cotton nonwoven composites, with the T_g clearly shown by the kenaf component (Figure 4-10), while for the bagasse-based

nonwoven the tangent δ reflected mainly the drying (Figure 4-11). Data for $\tan\delta$ at 1 Hz of kenaf/cotton and bagasse/cotton nonwovens bonded with 0.5% cellulose solution are compared in Figure 4-12. Because $E'_{\text{kenaf}} : E'_{\text{bagasse}} > E''_{\text{kenaf}} : E''_{\text{bagasse}}$, the tangent for bagasse is higher than that of kenaf nonwovens. This translates in a less elastic behavior of bagasse composites, viz., they can be permanently deformed at a smaller load than that necessary to deform the kenaf counterpart. At the same time, the strength of the easier deformable lyocell-stabilized bagasse nonwovens should be inferior to all-cellulosic kenaf nonwoven of similar composition, as confirmed by data presented in Table 4-2 for 0.5% lyocell concentration.

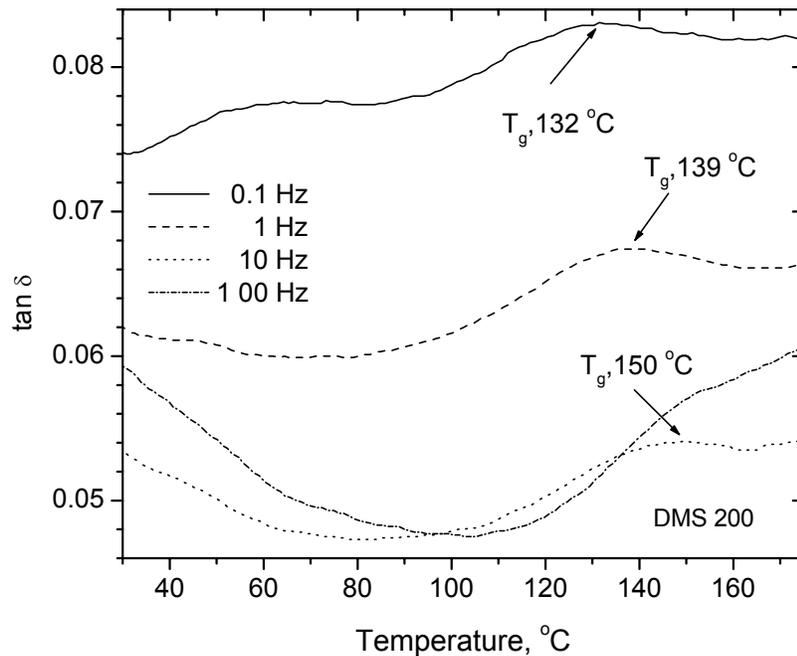


Figure 4-10 Dependence upon temperature of the E''/E' ratio ($\tan\delta$) of kenaf/cotton nonwovens bonded with 0.5% cellulose solution

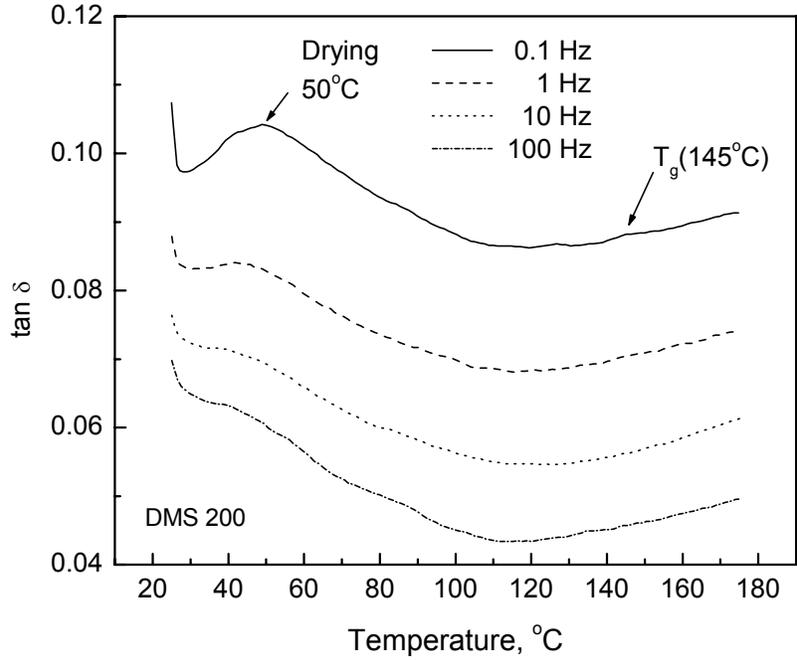


Figure 4-11 Dependence upon temperature of $\tan\delta$ of bagasse/cotton nonwovens bonded with 0.5% cellulose solution

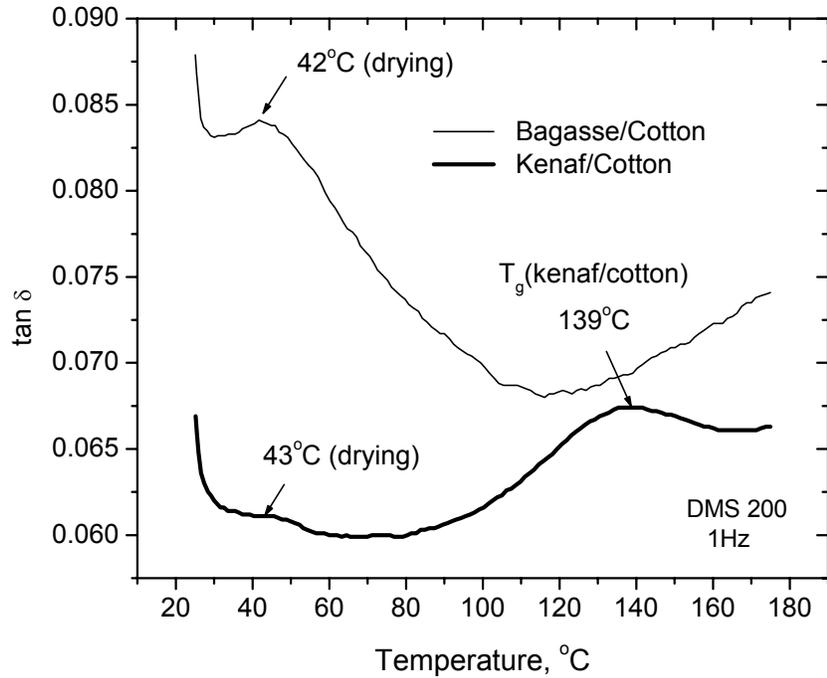


Figure 4-12 Dependence upon temperature of $\tan\delta$ of bagasse/cotton & kenaf/cotton composite nonwovens bonded with 0.5% cellulose solution

4.3.2 Composite Nonwovens Bonded with Synthetic EBC Polyester

As stated before, if there are no significant changes in the sample, the elastic modulus and its components will decrease while heating (the sample will soften gradually). This was seen only in the nonwoven composites bonded with synthetic EBC polyester (Figure 4-13) where the polymer dictated the elastic character of the whole sample (Chiparus, 2004).

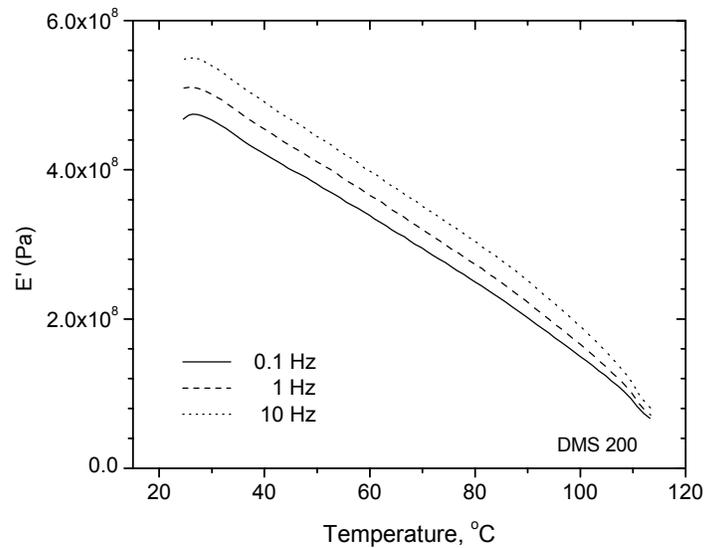


Figure 4-13 Dependence upon temperature of the storage modulus of elasticity E' of the kenaf/cotton nonwoven bonded with synthetic EBC polyester (Chiparus, 2004)

4.4 Cellulose Acetate Plasticization

4.4.1 Differential Scanning Calorimetry Analysis (DSC)

Lyocell solutions containing 0.2% acetate in addition to 0.5% cotton cellulose were used to stabilize and plasticize a cotton/bagasse nonwoven composite. The plasticizing effect was reflected by the low glass transition of acetate seen in DSC traces

of nonwoven samples (~ 40°C, Figure 4-14), as compared with high T_g data of cellulosic components recorded in DMA investigations (145°C, Figure 4-7).

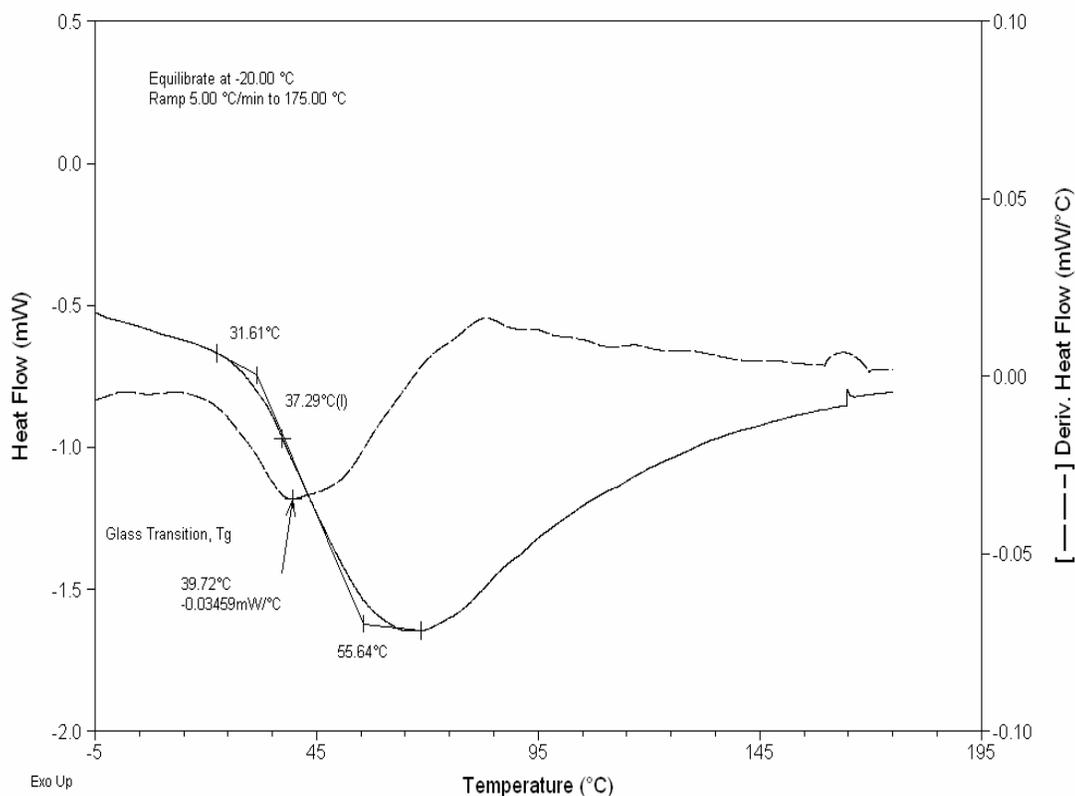


Figure 4-14 DSC traces of bagasse/cotton nonwoven stabilized with 0.5% lyocell solution containing 0.2% cellulose acetate. Heating rate: 5°C/min.

4.4.2 Thermogravimetry Analysis (TGA)

TG curves from this analysis provide information on changes in the mass of a sample during heating or cooling process. The DTG curve, i.e., the first derivative of the sample mass change as a function of temperature, gives the rate of the mass change. As the temperature increase, the sample might experience a mass gain due to oxidation, but

more often than not the TG curve shows a weight loss indicative of drying at $T \leq 100^\circ\text{C}$ or of thermal decomposition at $T > 250^\circ\text{C}$. The maximum rate of the weight change is recorded as a peak in the DTG curve.

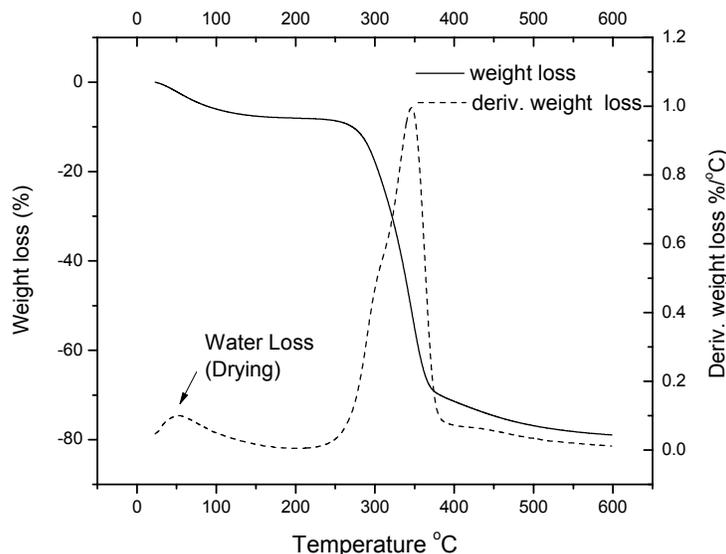


Figure 4-15 TG and DTG curves for composite cotton/bagasse nonwoven plasticized with cellulose acetate. Inert atmosphere (nitrogen). Heating rate: $5^\circ\text{C}/\text{min}$.

Figure 4-15 shows the gravimetric loss and its first derivative recorded during thermal analysis of the composite cotton/bagasse nonwoven plasticized with cellulose acetate. The weight loss of the composite nonwoven depicted by the TG curve is a monotonous decreasing function of temperature. The changes in the mass could be divided into three distinct regions. In the first region, starting from room temperature up to 250°C , the weight loss is due to water vaporization (drying). The weight change was not significant and the composite was thermally stable. In the second rather narrow region, from 250 to 370°C , the composite nonwoven experienced a great weight loss because of the thermal decomposition. About 60% of the sample decomposed into volatiles. In the third region in the temperature range of 370 to 600°C , the composite

remnant continued to decompose slowly with 10% of the weight loss. A series of maxima related to vaporization of water or to nonwoven decomposition were noticed in the corresponding DTG curve. The first peak, seen at about 50 °C, indicated the water loss from the sample due to vaporization. The second peak hidden as a shoulder at about 300 °C, and the third, large peak at about 350 °C indicated the thermal decomposition of cellulosic species at increasing temperature.

The mass loss profile for composite materials is usually the sum of the individual profiles of each component under the same experimental conditions. As shown in Figure 4-16, the acetate sample had a lower water content and a better thermal stability than the cotton/bagasse composite nonwoven containing cellulose acetate. Compared to the weight loss of 7.5 % for cotton/bagasse composite, the weight loss of acetate fiber was only 3.3% at 150 °C. It was noticed also that the cotton/bagasse composite nonwoven decomposed earlier than acetate fibers (the temperature for a 10% weight loss for cotton/bagasse composite nonwoven and for cellulose acetate was 271°C and 288 °C, respectively).

It may also be noticed from Figure 4-17 that the rate of the weight loss of cotton/bagasse composite nonwoven due to thermal degradation in the second stage was lower than that of the pure acetate fiber. Compared to a single DTG peak for cellulose acetate, the DTG curve of the cotton/bagasse composite nonwoven exhibited a peak at a slightly lower temperature and a peak hidden in the shoulder region shown as a peak in the deconvolution presented in Figure 4-18, which were caused by the combination of thermal decompositions of cotton, bagasse, and cellulose acetate. Thus, by adding a just

small amount of cellulose acetate in the cotton/bagasse composite, the thermal stability of the cotton/bagasse/acetate composite nonwoven could be improved.

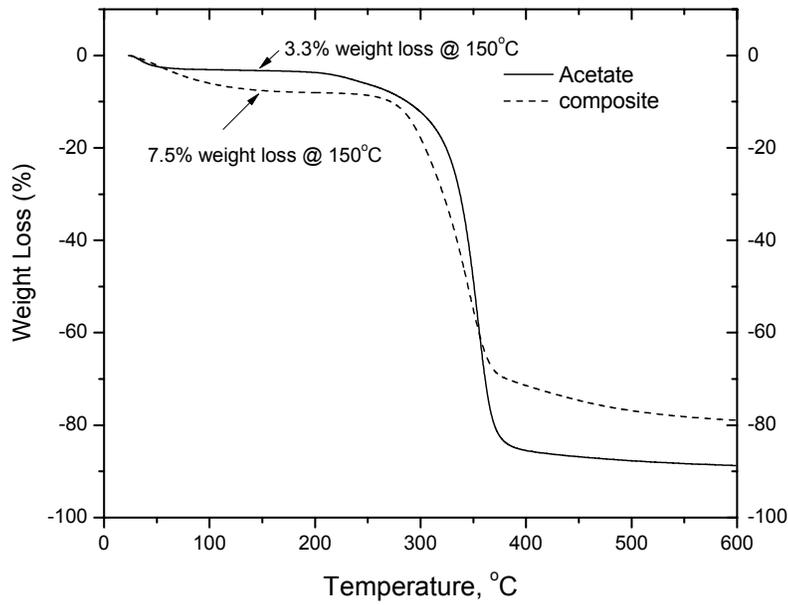


Figure 4-16 Comparison between TG curves of cellulose acetate fibers and of cotton/bagasse nonwoven composite containing cellulose acetate

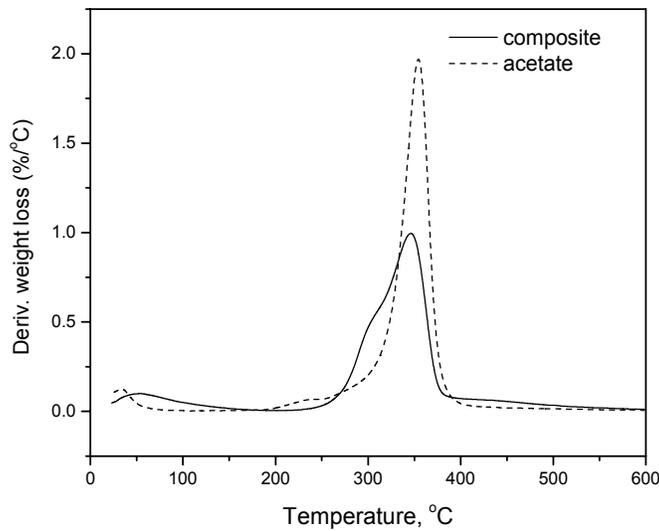


Figure 4-17 Comparison between DTG curves of cellulose acetate fibers and cotton/bagasse composite nonwoven containing cellulose acetate

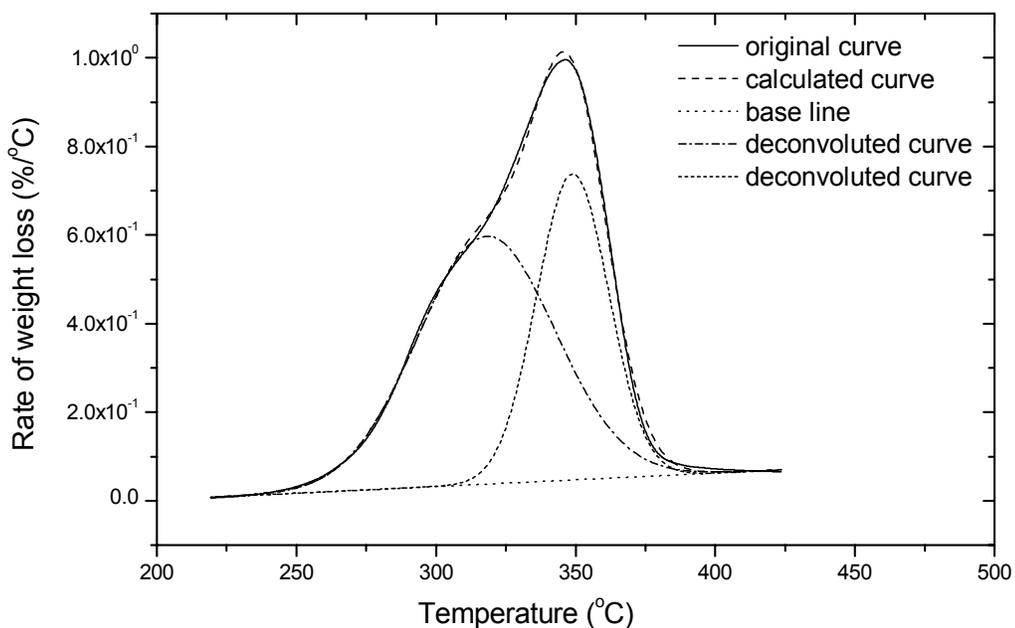


Figure 4-18 Deconvolution the main DTG peak from thermal analysis of the cotton/bagasse composite nonwoven containing cellulose acetate

As mentioned earlier, the profile of thermograms (DTG) for composite materials could represent a combination of the individual profile of each component. Overlapping of individual profiles such as that of DTG maxima could result in a representation with shoulder(s), which could be deconvoluted in separate peak maxima. As shown in Figure 4-18 and Figure 4-19, the original DTG curve for acetate nonwoven was deconvoluted into two separated curves (each curve with its own peak). The calculated curve, which was the sum of the two separated curves, agreed very well with the original DTG trace. The ratio of area of deconvoluted peaks can be used to calculate the actual composition of the material.

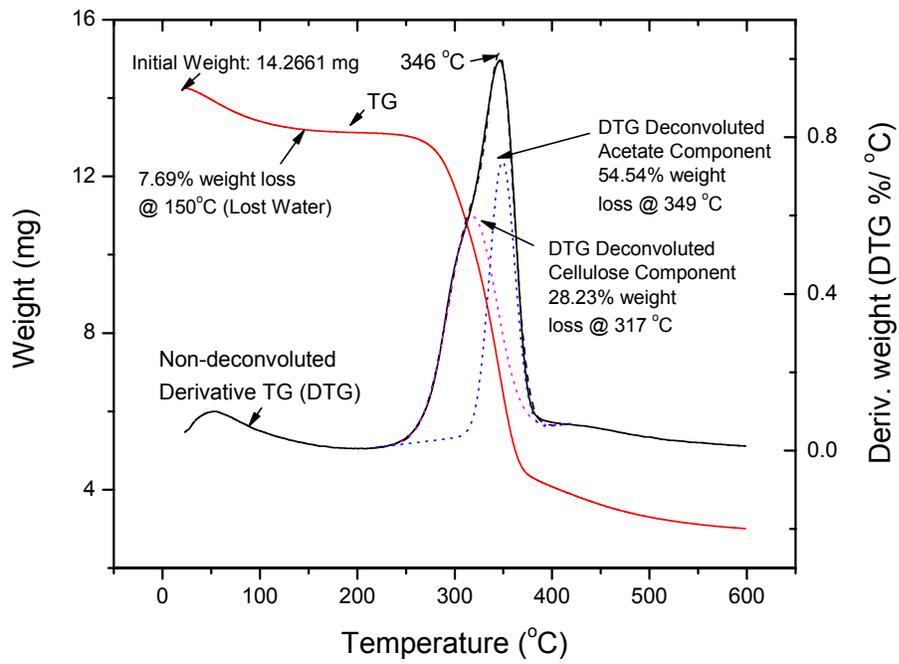


Figure 4-19 Thermal analysis of cellulose acetate plasticized cotton/bagasse composite nonwoven

Chapter 5 Summary and Conclusions

5.1 Biodegradability of All-Cellulosic Biobased Composite Nonwovens

The time-frame for a thorough investigation of biodegradability of all-cellulosic biobased composite nonwovens prepared in the present study was too short. At the same time, the driving force for such an investigation was practically inexistent because all composing materials were natural fibers (biodegradable) and lyocell (biodegradable cellulose). There is no reason to suppose that just by putting the fiber components in a physical contact by carding and punching in order to assemble the webs and subsequently to stabilize the webs in a composite nonwoven using cotton derived lyocell the biodegradability characteristics of the resulted system will be affected.

5.2 Economic Considerations

Even if the cost of obtaining the type of composite nonwovens described in the present work was not in the scope of the study, the following should be mentioned regarding the economic feasibility for their preparation:

- a) Bagasse is a raw material resulted as a byproduct of a well established industry in this country (i.e., sugar), with the purchasing cost practically covering only that of the transportation from the source.
- b) Kenaf is an industrial bast fiber producing plant the cultivation and the use of which became a reality and is encouraged in this country.
- c) Cotton fibers used for the preparation of webs are at the end of the quality of commercial cotton fibers or might originate from recyclable textile of very low cost (covering the cost of collection and transportation).

- d) NMMO is an industrial product with a rather high cost as compared to that of fibers, but the expenses related to it may be substantially lowered by recovering and recycling (technology already in use in US for preparation of lyocell fibers).

The determining costs to be considered relate, however, to delignification of bagasse and kenaf fibers (sodium hydroxide, water, energy) and water and energy involved in the final steps of pressing, washing out the solvent and drying.

5.3 Conclusions

- a) The novelty of this work is the preparation of all-cellulosic composite nonwoven materials using only natural fibers (cotton, bagasse and kenaf).
- b) It was shown that synthetic polymers can be substituted for the stabilization of nonwovens by a solution of cellulose that was prepared from recyclable cotton textiles.
- c) The all-cellulosic composite nonwovens were obtained by hot pressing the webs and films of cellulose solutions in a “bread and butter” type of sandwich, with multiple “bread” and “butter” layers, similarly to the preparation of cellulosic nonwoven stabilized with synthetic polymers.
- d) All-cellulosic composite nonwovens were biobased because all nonwoven components were of a biological origin (only natural fibers have been used throughout their entire preparation).

- e) The physical characteristics of all-cellulosic composite nonwovens were comparable to that of biodegradable composite nonwovens prepared earlier at LSU from natural fibers and a biodegradable synthetic polyester.
- f) The biodegradability of all-cellulosic composite nonwovens will be a characteristic related to their bio-based origin. The economics of the all-cellulosic composite nonwovens will be dictated by the economics of delignification of annually renewable fibers, of bagasse in particular.

5.4 Future Investigations

The present study could be continued as follow:

- a) Determine the real time-frame for biodegradability in a compost medium of all-cellulosic nonwovens prepared from natural fibers and lyocell solutions.
- b) Enlarge the spectrum of utilization of all-cellulosic nonwovens prepared from natural fibers and lyocell by introduction on cellulose chains of acid (i.e., carboxymethyl groups) or basic (i.e., aminogroups) functionalities.
- c) Nonwovens containing carboxymetil groups can be reacted with urea and other nitrogen-rich compounds to render the nonwoven a fertilizing material with excellent characteristics to be applied as geotextiles mats.
- d) Nonwoven containing amino groups can be used as ion exchangers for arresting metallic ions and other cationic residuals from wastewaters.
- e) Replace the lyocell gluing solution with other biobased polymers, such as plant-derived polyesters.

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