# THERMAL ANALYSIS OF FIRE RETARDED BIOBASED COMPOSITE NONWOVENS: THERMAL ANALYSIS OF

## NONWOVENS AND COMPONENTS Ioan I. Negulescu Xiaoqun Zhang Louisiana State University AgCenter Baton Rouge, LA Dharnidhar V. Parikh USDA Southern Regional Research Center New Orleans, LA

### <u>Abstract</u>

Composite nonwoven materials have been prepared from biobased materials only, viz., natural fibers (cotton and other natural fibers) and plant derived polyhydroxyalkanoates as reinforcing component. Fire retarding finishing has been performed using halogen-free compositions that contained only phosphorus, nitrogen and boron as retarding elements. Thermal analysis was focused on degradation of nonwovens and their components both in air and inert atmosphere (nitrogen) to complete decomposition. A correlation has been made between the rate of thermal degradation and fire retardation as indicated by the oxygen index. Modulated thermogravimetric analysis (MTGA) has been used for determination of kinetic parameters (Setting decomposition temperature,  $T_{dec}$ , and activation energy, Ea) of a series of fire retarded cotton and rayon fibers and fabrics.

#### **Introduction**

Fibers derived from annual plants, alone or together with low quality greige cotton fibers have a high potential in the manufacturing of composite nonwovens that are quite promising marketing materials, especially in building and automobile insulation markets [1-5].

The extent of nonwoven applications increased dramatically in the last decades. More often than not the polymers used for binding cellulosic fibers in nonwoven materials are oil-derived synthetic thermoplastics (e.g., polypropylene) or thermosets (e.g., epoxy) [6, 7].

Until recently, little consideration was given to the disposability of these plastics. In particular, the single-use applications have become a tremendous environmental and ecological problem. However, the time came to recognize bioderived fibers and polymers as partners and/or replacements of synthetic equivalents [8]. Very promising from this point of view are the plant derived polyesters, better known as *polyhydroxyalkanoates* (PHAs). They are a family of biodegradable thermoplastic polyester polymers, originally produced naturally by a limited number of bacteria as part of their energy storage mechanisms [9, 10]. Most of the PHAs identified to date are linear head-to-tail polyesters composed of 3-hydroxy fatty acid monomers [11]. The majority of the research to date dealing with production and degradation of PHAs has focused on polyhydroxybutyrate, PHB [12]. These bioplastics are currently obtained by engineering genetically *Escheria Coli* assisted fermentation of plant-derived sugars (glucose). PHAs are completely biodegradable and are carbon dioxide neutral within the context of a well- designed "cradle to grave" management plan, which allows for life cycle assessments [9]. However, due to their high crystallinity, PHA polymers are brittle. Plasticization, i.e., the use of small molecular compounds that can disrupt the crystallization process after blending with polymers in the molten state [13], is necessary when PHA-containing flexible materials are produced.

Physical and mechanical characteristics of natural fibers will also influence the final product. Bagasse and greige cotton fibers have been considered in the present investigation alongside with thermoplastic biobased polyester to be employed for manufacturing of composite nonwovens. The preparation of nonwovens, their flame retardation, as well as the most significant thermal properties of nonwovens and their components will be presented and discussed in the following.

# **Objectives**

This work presents the achievements of a series of studies in progress. The objectives of these studies are:

- To prepare biodegradable, flame-retarded nonwoven materials containing at least 50% cellulosic fibers reinforced with biobased polymers.
- To analyze their thermal resistance/degradation and ability to burn in an oxygen enriched atmosphere
- To determine kinetic parameters of thermal decomposition of FR nonwovens and of their components

# Materials and Methods

The composite nonwovens were obtained in different ways according to the fire retarding composition. Details are given in the following.

*Delignification of the bagasse fiber bundles*: Bagasse from a Louisiana sugar mill was boiled in 2.5% Na<sub>2</sub>CO<sub>3</sub> solution for 1.5 hours, washed with water and ground.

The ground fibers were then dried in a circulation oven at 100°C and conditioned at room conditions (23°C and 50% relative humidity). These operations have been carried out at the LSU AgCenter Audubon Sugar Institute (ASI).

*Plant-Derived Polyester*: The polyhydroxyalkanoate was a gift sample from a US Company. It was a powder-like poly(hydroxy butyrate) of high molecular weight ( $Mw\sim10^5$  Daltons) with a melting temperature of 172°C (by differential scanning calorimetry, heating rate: 5C/min). Besides binding the bagasse fibers, PHA was used also for hydrophobicization of surfaces of fire retarded (FR) nonwovens as shown in the following.

*Plasticizer*: Tributyl citrate (TBC) ester was prepared as described in a recent publication [13] from citric acid (Fisher Scientific) and butyl alcohol (Mallinckrodt, Paris, KY) by Fisher esterification with a cation exchange resin, AG 50W-X4, 100-200 mesh, hydrogen form (Bio-Rad, Sunnyvale, CA) as a catalyst.

*Plasticized PHA*: The polymer and the plasticizer were weighted, pre-mixed and blended in a HAAKE torque rheometer at 60 rpm above the melting temperature of PHA ( $T_{max}=180^{\circ}C$ ) in order to attain a workable viscosity of the PHA melt. The stop criterion for blending was the stabilization of the torque value after feeding the components.

*Preparation the flame retarding solutions.* Fire retarding compositions used for the treatment of bagasse composites are shown in Tables 1 and 2.

Table 1. Composition of the Non-Durable Flame Retarding Solution (NDFR).

Component	Parts	Content (%)
Borax	7	16.1
Boric Acid	3	6.9
Ammonium	5	10.3
Phosphate		
Water	29	66.7

Table 2. Composition of the Durable Flame Retarding Solution (DFR).

Component	Content (g/L)	
Organic Phosphorous Compound	350	
Fabric Softener	40	
Phosphoric Acid (80%)	25	
Melamine Formaldehyde	30	
Triton X-100	2.0	
Water	To 1,000 mL	

The components of the NDFR solution have been purchased from Aldrich and used as received. The components of DFR solutions have been provided by USDA ARS Southern Regional Research Center from New Orleans, LA.

#### Fabrication Steps of Flame Retarded Nonwovens:

- •The bagasse or bagasse/cotton fibers bundles were soaked with NDFR solution, squeezed on a padding machine to a wet pick up of 100-120% and dried in a circulation oven at 110°C.
- •The FR dried fibers were then wetted and blended with PHA powder (10-20% PHA based on dried FR bagasse fibers).
- •The blend was evenly distributed in a container made of aluminum film and pressed at 360°F into a nonwoven (the thickness of the nonwoven was controlled by spacers).
- •The NDFR nonwoven was coated with a thin film of PHA by immersion in chloroform solution followed by solvent evaporation. The film made the composite water proof by covering with a PHA film.

*Determination of the Oxygen Index*: The oxygen index (OI) was determined according to the standard method ASTM D2863-00 "Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (Oxygen Index)".

*Other Cellulosic Fibers & Fabrics analyzed by modulated thermal analysis for determination of kinetic parameters of thermal decomposition:* 

- SRRC Greige Cotton.
- SRRC FR#1 treated greige cotton. FR #1 includes DMDHEU, diammonium phosphate, urea, TritonX-100, polyethylene emulsion, MgCl26H2O and citric acid.
- SRRC FR#2 [FR(A)] treated greige cotton A. FR (A) is a modified FR containing diammonium phosphate, urea, TritonX-100 and citric acid.
- SRRC modified FR (A) treated terry towel.
- SRRC commercial FR(B) treated greige cotton.
- SRRC commercial FR (B) treated terry towel.
- Commercial Rayon staple fibers.
- FR rayon (a commercial flame retarded rayon permanently FR treated in the fiber forming process.

# **Results and Discussion**

# **Determination of the Oxygen Index of FR Nonwovens**

The pick-up of the FR agent by bagasse fibers and its content in the final composition of the bagasse nonwoven have been determined gravimetrically after conditioning the materials (fibers, final composite nonwovens) at 23°C and 50% RH. The uniformity of the distribution of NDFR and DFR compositions inside the fibers was checked by scanning electron microscopy (SEM) of nonwoven cross-sections. No powder-type structures were visible on the surface or between the fibers). The uniformity of the distribution of NDFR was checked also by polarized light microscopy. While no powder-like structure (crystals) were visible, the anisotropy of microcrystals of the FR agent absorbed by fibers became evident in polarized light.

The fire retarding efficiency was tested according to MVSS 302 methodology for testing materials for automotive interiors. All FR samples prepared in this work passed this test. High oxygen index numbers, over 40, have been obtained for all FR compositions (Table 3). However, the oxygen index of non-treated bagasse, PHA and of their combination as a hot-pressed nonwoven was close to atmospheric composition. Very high oxygen indices obtained for all FR samples will allow the reduction of the FR agent in the final nonwoven composition to a more acceptable value of 35%. A balance between the amount of the bagasse and that of the FR agent and reinforcing polymer can be negotiated in favor of the physical properties and the cost of the final fire retarded nonwoven compositions (both PHA and FR agents are more expensive than cellulosic fibers).

	Bagasse	Bonding	Density	Oxygen Index
Sample	(%)	Polymer	$(g/cm^3)$	(%)
_		(%)		
NDFR2 13.3%	76.0	10.6 PHA	0.58	>50
DFR 26%	64.0	10.0 PVA	0.80	41
Pure Bagasse	100.0	0.0 Polymer	0.53	24
Nonwoven				
Pure PHA Film	0.0	100.0 PHA	1.25	20
Bagasse/PHA	68.0	32 PHA	0.69	21
Nonwoven				

Table 3. Oxygen Index of FR nonwovens and of reference bagasse and bagasse/PHA materials.

Te oxygen index of bagasse nonwoven composite samples prepared with plasticized PHA is presented in Table 4. All compositions passed the minimum accepted value OI = 35. The highest index (OI = 37) was observed for the sample containing 21% PHA plasticized with 15% TBC.

Table 4. Oxygen Index of FR bagasse nonwovens mechanically stabilized with plasticized PHA containing 15% TBC

Sample	Oxygen Index	Bagasse	NDFR2	Plasticized PHA	Density (g/cm <sup>3</sup> )
1	35	36.8%	29.9%	33.3%	1.06
2	37	39.0%	31.6%	21.0%	1.06
3	35	39.5%	31.9%	28.4%	0.98

#### **Thermogravimetric Analysis of FR Nonwovens**

Thermogravimetric analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.

TGA allows the determination of material composition and the prediction of material stability to elevated temperatures. However, the question arises: inert  $(N_2)$  or reactive (air) thermal degradation atmosphere? The atmosphere plays an important role in the thermal degradation process, particularly at higher temperatures at which the material can ignite. Therefore, it is imperative to analyze FR materials always in AIR and compare data with that collected for thermal degradation in inert atmosphere (Figure 1).

#### Thermal Degradation in Air of FR Nonwovens

Thermogravimetric analysis in air of bagasse nonwovens prepared in this work indicated that decoposition of FR samples left behind a large amount of residue (30-40%) at 600°C. While PHA underwent a sudden volatilization above 250°C, pure bagasse decomposed at a slower pace and the FR nonwovens containing both bagasse fibers and polyester (PHA) registered only a ~20% loss after 300°C. It seems that it is the formation of the residue which protects the FR samples for a live burning in air and enables them to exhibit large OI indices [14]. Interestingly, the amount of residue was almost the same (~40%) both for nonwoven samples treated with NDFR and DFR (Figure 1).



Figure 1. Thermal degradation in air of flame retarded bagasse nonwoven samples.

#### **Thermogravimetric Analysis of FR Cotton and Rayon Fibers and Fabrics**

*TGA Kinetics*. Simple kinetic information has been obtained with the constant heating rate method developed by Flynn and Wall late in sixties [15, 16].

$$d\alpha/dt = Z \exp(-Ea/RT)(1-\alpha)^{t}$$

where:  $\alpha$  = fraction of decomposition t = time (seconds) Z = pre-exponential factor (1/seconds) Ea = activation energy (J/mole) R = gas constant (8.314 J/mole K) n = reaction order (dimensionless) In order to determine Ea, Flynn and Wall rearranged this equation to get the following equation [16]:

$$Ea = (-R/b) d(\ln\beta)/d(T^{-1})$$

where:

b = constant assuming n=1  $\beta$  = heating rate (°C/minute) T = temperature of weight loss (°C) A plot of (1n $\beta$ ) versus (1/T) is constructed. The slope of this straight line plot is then used to calculate activation energy (Ea), and the pre-exponential factor (Z).

*Modulated Thermogravimetric Analysis, MTGA* [17, 18]. This technique, which was developed by TA Instruments (MTGA<sup>TM</sup>), superimposes a sinusoidal temperature modulation on the traditional underlying heating profile. This sinusoidal temperature program produces a change in the rate of weight loss. The use of discrete Fourier transformation allows kinetic parameters to be calculated on a continuous basis.



Figure 2.Early stages for thermal decomposition of greige cotton in AIR using the MTGA program

For the example shown in Figure 2 the following MTGA program has been used operating a TA Instruments TGA 2950 thermobalance:

- 1. High Resolution Sensitivity 1
- 2. Modulate +/-5°C every 200 sec
- 3. Select gas (Air or N2)
- 4. Ramp 2.00°C/min Res 4 to 600°C

While both cotton and rayon are considered to be almost pure cellulose, their thermal decomposition in inert atmosphere  $(N_2)$  differs both from the point of view of weight loss vs. temperature behavior (TG), as well as from that of the weight loss rate (DTG) and Ea. It seems that the rayon is more stable as it has a higher setting temperature, but at 600C it is already 87% decomposed as opposed to cotton which still has some 30% charred residue.

Comparing the thermal decomposition of greige cotton treated with FR A with that of the pure FR it was obvious that the FR cotton was not a simple blend of the two components (i.e., cotton fibers and FR A) as both TGA and DTG traces of the FR A greige cotton do not exhibit the characteristics of the flame retardant A as if it was the case of a physical mixture. Interestingly enough, the nature of the atmosphere (air or nitrogen) in the thermal degradation process of FR rayon did not affect the weight loss amount (TG) and the Ea which were practically identical (Table 5). Only above 300C, when almost 60% of the materials volatilized, there is a clear difference both between the shapes of TG traces and, of course, between the residual amounts at 600C.

MTG kinetic parameters for all FR Cotton and Rayon Fibers and Fabrics are collected in Table 5. The activation energy data correlate very well with the Ea  $\approx$  195.5 kJ/mol determined by Mamleev et al. [19] for analysis of cellulose thermal decomposition in reactive atmosphere (synthetic air). It has been observed thermal degradation in air of greige cotton and of FR A treated terry towel fabric did not follow the same trends., particularly when the shapes of DTG curves were compared. However, despite of the difference, the T<sub>dec</sub> and Ea of FR A greige cotton and FR terry towel are similar (Table 5). Similarities were found also between thermal degradation of FR B treated greige cotton and fabric samples. As expected, differences were recorded when the thermal degradation atmosphere

was switched from reactive (air) to non-reactive (nitrogen), cases in which, save for the residual content, the  $T_{dec}$  and Ea also changed. Changes for FR samples should be attributed also to the FR nature as the two fire retardants A and B behave quite differently (Table 5).

Atmosphere	Sample	Setting T <sub>dec</sub> °C	Ea kJ/mol	Residue % weight
AIR	Greige Cotton	242	206	8.2
N <sub>2</sub>	Greige Cotton	249	213	30.4
AIR	FR # 1 Greige Cotton	209	195	9.7
N <sub>2</sub>	FR # 1 Greige Cotton	217	203	33.7
AIR	FR (A) Greige Cotton	209	192	1.2
$N_2$	FR (A)Greige Cotton	224	188	36.2
AIR	FR (A) Terry Towel	204	194	5.67
N <sub>2</sub>	FR (A) Terry Towel	209	187	34.8
AIR	FR (B) Greige Cotton	239	184	12.8
AIR	FR (B) Terry Towel	251	182	10.1
N <sub>2</sub>	Rayon Staple Fibers	249	213	30.4
AIR	FR Rayon Staple Fibers	237	133	5.3
N <sub>2</sub>	FR Rayon Staple fibers	217	203	33.7
AIR	FR A	128	231	11.4
AIR	FR B	152	106	30.9

Table 5. MTG kinetic parameters for FR Cotton and Rayon Fibers and Fabrics

# **Preliminary Conclusions and Future Work**

- Very efficient FR formulations have been used for the treatment of bagasse fibers.
- Thermogravimetric Analysis, particularly MTGA, is a versatile tool for characterization of FR textile materials. However, the MTG kinetic data should be correlated with other characteristics of FR materials, such as the FR composition, FR content, OI, etc
- Future work will be concentrated on these correlations

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