Chapter 3

EXPERIMENTAL

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3.1 Materials Description

3.1.1 Cellulose acetate butyrate (CAB)

Cellulose acetate butyrate (plastized) was obtained from Eastman Kodak, Kingsport, Tennessee, as TENITE Butyrate formula 285, a thermoplastic polymer. The manufacturer did not provide information on the type of plasticizer used or the acetyl and butyryl contents of the material (proprietary information). The physical properties, however, are listed in Table 3.1.

Cellulose acetate butyrate, a mixed cellulose ester plastic, is normally prepared by esterifying acetylation grade cotton linters with a mixture of acetic acid, butyric acid, and butyric anhydride using sulfuric acid catalyst. There are several grades of the ester that can be produced using this method depending on the ratio of acetyl to butyryl groups in the fully esterified mixed ester. This ratio can be varied by varying the concentration of the corresponding derivatizing anhydrides in the esterification mixture. The mixed ester has the following chemical structure:

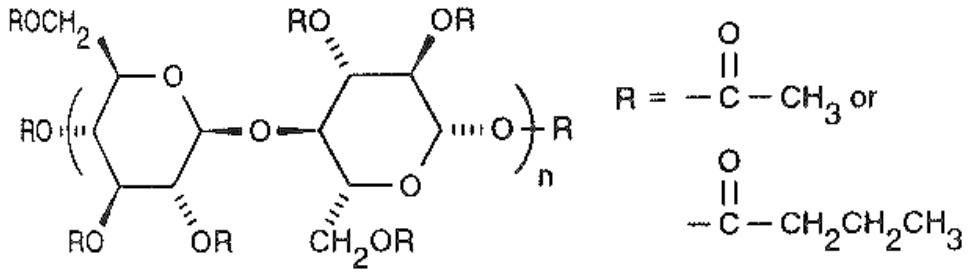


Table 3.1 Physical properties of TENITE Butyrate formula 285.

Property	Unit	ASTM Method	Value
Tensile stress @ yield (50 mm/min.)	MPa	D638	40.7
Tensile stress @ break (50 mm/min.)	MPa	D638	51.0
Elongation at break (50 mm/min.)	%	D638	55
Flexural modulus of elasticity (1.27 mm/min.)	MPa	D790	1,724
Flexural yield strength (1.27 mm/min.)	MPa	D790	57.2
Vicat softening temperature (Conditioned 4 h @ 70 ^{o} C)	^{o}C	D1525	115
Specific gravity		D792	1.20

Unless noted otherwise, all tests are run @ 23 ^{o}C and 50 % relative humidity.

3.1.2 Cellulose fibers

Four types of cellulose fibers were used in this work; water-washed steam exploded fiber (WEF), alkali extracted steam exploded fiber (AEF), acetylated steam exploded fiber (surface modified) (AAEF), and commercial oat filler (COF). The fibers were obtained by steam exploding Yellow Poplar wood chips at a severity (log R_o parameter) of 4.23, which was performed on a Stake Technology steam explosion machine at the Pilot/Demonstration Laboratory of the Thomas M. Brooks Forest Products Center located at Virginia Tech (Figure 3.1 and 3.2). The steam explosion severity (R_o), which combines the parameters of retention time, t, and reaction temperature, T, is defined as

$$R_o = \int_o^t \exp\left[(T_1 - T_o) / 14.75 \right] dt$$

where

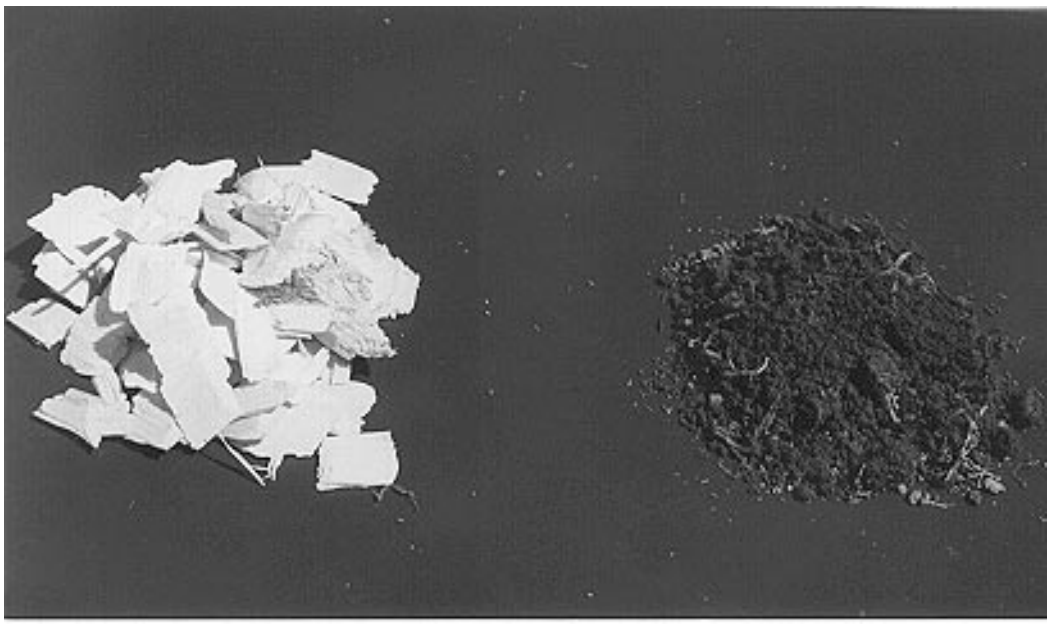
R_o = steam explosion severity factor

T_1 = reaction temperature, ^oC

T_o = base temperature, ^oC

t = retention time

The process was then followed by fiber fractionation (Figure 3.3), which included washing with water at 50 ^oC and extracting with 20 % aqueous alkali at an 8:1 liquor-to-fiber ratio at 70 ^oC. Both water-washed and alkali extracted steam exploded fibers used in this study were obtained from this process. Acetylated steam exploded fibers (surface



Wood chips Steam exploded fibers

Figure 3.1 Starting materials and products after steam explosion.

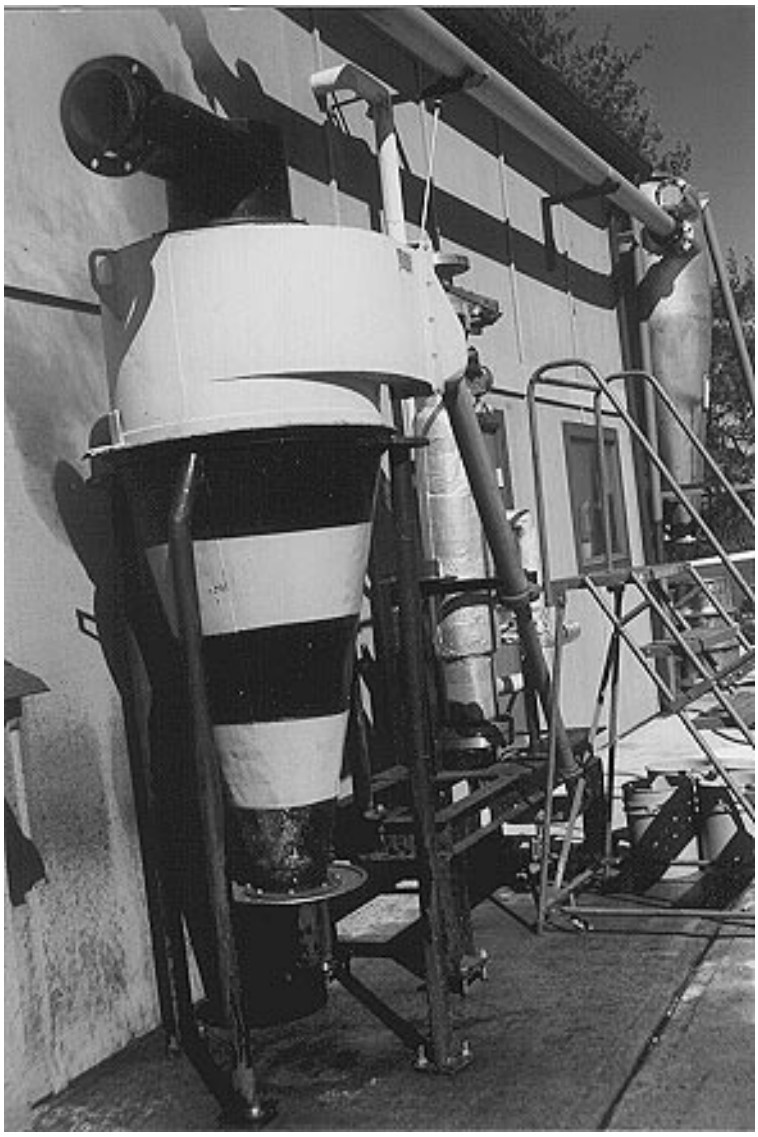


Figure 3.2 Steam explosion machine (batch gun) at the Pilot/Demonstration Laboratory of the Thomas M. Brooks Forest Products Center located at Virginia Tech.

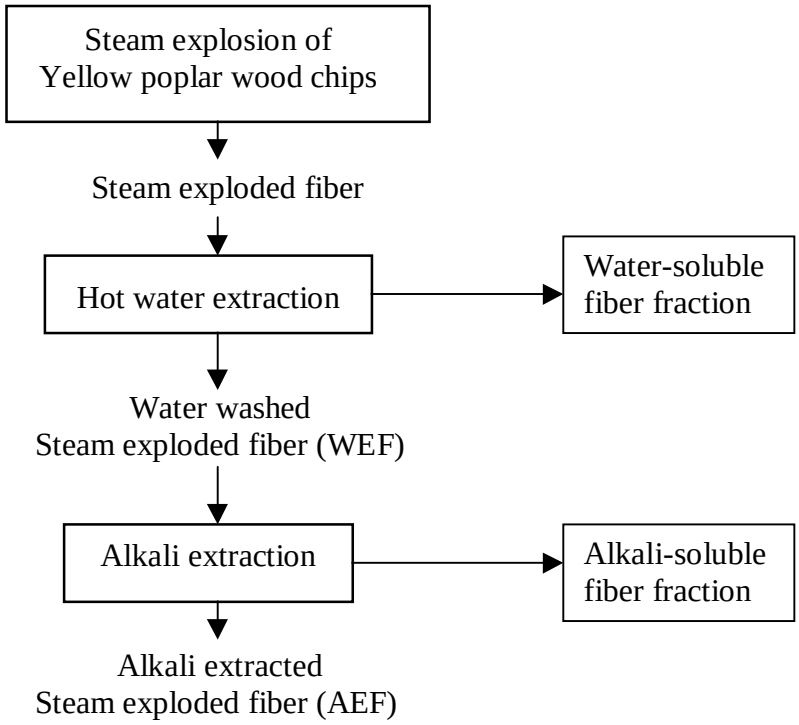


Figure 3.3 Fractionation process of steam exploded fibers.

modified) were prepared by esterifying the alkali extracted steam exploded fibers with a mixture of acetic acid and acetic anhydride. The reaction was carried out in a PARR reactor at 150 ^{o}C for 6 hrs, which typically produces a weight gain of 15-20 % by weight (experimental value). Although the fibers were treated differently after steam explosion, the fiber geometry was assumed to be unchanged. Commercial oat filler was obtained from Dr. Ramani Narayan of Michigan State University. All the fibers, i.e., WEF, AEF, AAEF, and COF were then characterized in terms of their fiber length, color, and also their thermal stability (Table 3.2). Steam explosion, fiber fractionation, acetylation as well as determination of thermal stability were carried out by Dr. Rajesh. K. Jain, Research Associate, Dep. Wood Science and Forest Products, Virginia Tech.

Table 3.2 Fiber characteristics

Fiber type	Fiber length[1] (mm)	Color	Pretreatment before compounding	Thermal stability [2] (^{o}C)
WEF	1.2 – 1.3	dark brown	water-washed (Hemicellulose is removed)	250
AEF	1.2 – 1.3	light brown	alkali-extracted (Lignin is removed)	270
AAEF	1.2 – 1.4	light brown	alkali-extracted followed by acetylation	280
COF	0.3 – 0.4	light yellow	none	245

[1] Determined by cellulose fiber suspending in distilled water and stirring overnight using a magnetic stir plate to separate the fibers. A drop of the suspension was then placed on a glass slide and observed through an optical microscope. The fibers (except COF) were found to show a wide distribution of fiber lengths. The lengths of approximately 20-30 fibers that appeared to be among the longest fibers were determined using a computer equipped with an image analysis package. The average fiber length for each fiber type was reported.

[2] Thermal stability was assessed by subjecting the fibers to a rise in temperature of 10 ^{o}C per minute from room temperature to 150 ^{o}C in an air atmosphere. This was followed by a gradual rise of 2 ^{o}C per minute from 150 to 400 ^{o}C. An arbitrary weight loss figure of 2 % of the weight recorded at 120 ^{o}C was chosen to define thermal stability. The value reported is the temperature threshold at which the moisture-free fiber has lost 2% of its weight.

3.2 Sample Preparation

3.2.1 Compounding

In order to assist fiber dispersion, cellulose fibers were fiberized in a double-bladed kitchen blender for 8 seconds. The fiberized cellulose fibers and the pelletized cellulose acetate butyrate (CAB) were dried at 60 ^{o}C under vacuum for 24 h to eliminate moisture content and stored in a desiccator prior to compounding.

A total of 34 samples with two replicates for each formulation were melt-compounded using a Haake Rheomix 900 kneader (Figures 3.4 and 3.5). The fiber content was varied from 10 to 40 % by weight. A mixing temperature of 204 ^{o} C, a mixing time of 20 minutes, and a rotor speed of 60 rpm were employed to compound the samples. These conditions were chosen as approximately optimal on the basis of several pre-trials (see section 4.1). Sample identification and compounding conditions are listed in Table 3.3. A high mixing temperature as well as a long mixing time was used to facilitate mixing between the fibers and the matrix. Possible risks of these processing conditions involve depolymerization of the matrix by heat as well fiber breakage by shear forces.

The compounding process was performed in the following order. First, CAB pellets were added inside the mixing chamber through sequential feeding within the first three minutes. Once the polymer had melted (which took about 2 min), the fibers were added in the subsequent three-minute time period. The compounding then was continued

Table 3.3 Sample identification and compounding conditions.

Sample	Fiber content (% by weight)	Mixing time (min.)	Mixing temperature (^{o}C)[1]
CAB		20	204
CAB/WEF	10	20	204
	20	20	204
	30	20	204
	40	20	204
CAB/AEF	10	20	204
	20	20	204
	30	20	204
	40	20	204
CAB/AAEF	10	20	204
	20	20	204
	30	20	204
	40	20	204
CAB/COF	10	20	204
	20	20	204
	30	20	204
	40	20	204

[1] Corresponds to actual temperature as recorded; set temperature was 195 ^{o}C.

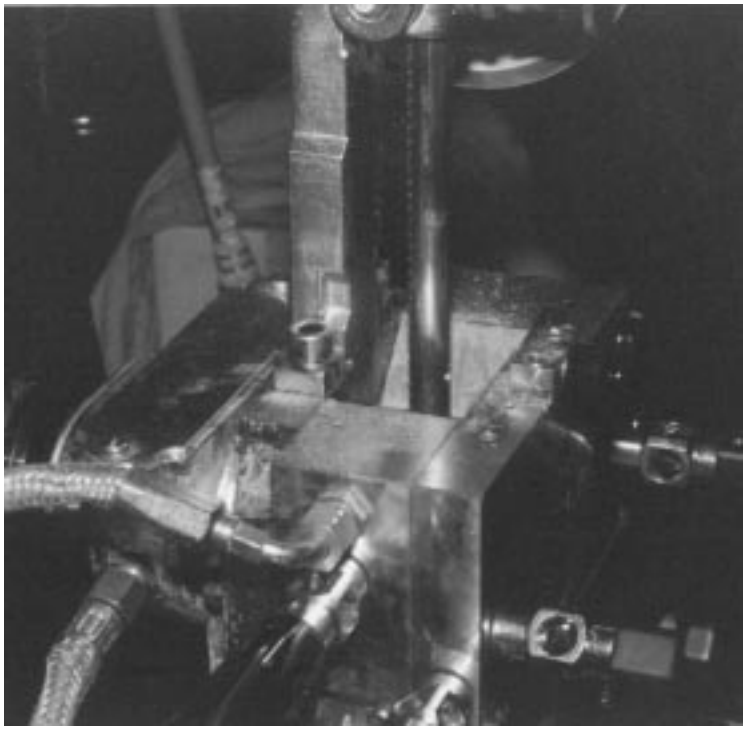


Figure 3.4 Mixing chamber.

Figure 3.5 Haake Rheomix 900.

for another 12 minutes. The thermoplastic fiber mixture was recovered and stored in a desiccator for subsequent compression molding experiments.

The variation of mixing torque was measured over mixing time. This data was continuously recorded by the built-in computer program during compounding and the corresponding dynamic torque at the end of processing was reported.

3.2.2 Compression molding

The melt compounded mixtures obtained from the kneader were compression molded in a Carver hot press into sheets with the dimensions of 100 x 100 x 2.5 mm, at 195 ^{o} C. The mold was first preheated for 1 minute. The compounded material was then placed in the mold and heated for 10 minutes under a constant pressure of 0.50-0.75 metric tons, followed by cooling at room temperature for 15 minutes.

3.3 Process and Product Characterization

3.3.1 Minimat tensile testing

The mechanical properties of the composites were determined on a Polymer Laboratories Minimat Materials Tester equipped with 1000 N load cell following procedures from ASTM D638. The test specimens (dogbone-shaped) were cut from compression molded sheets using a die punch cutter with a gauge length of approximately 7.5 mm and a width and thickness of approximately 2.75 mm and 2.20 mm respectively. All the specimens were kept in a desiccator prior to testing to avoid moisture absorption. The tests were then conducted at room temperature ($23 \pm 2\ ^{o}$ C) with a strain rate of 0.125 mm/min. From the stress-strain curves, the modulus of elasticity (E), the maximum tensile stress (σ) and the elongation at break (ε) were determined. At least 5 specimens were tested for each set of samples and the mean values as well as the standard deviations were calculated.

3.3.2 Scanning electron microscopy (SEM)

The tensile fracture surfaces of the composite samples were examined at 500 and 2000 magnification using an AMRAY 180D (diffusion pump system) scanning electron microscope operated at 15 kV. The fractured tensile specimens were mounted on an aluminium mount. To avoid electron charging effects, the specimens were coated at the bottom by Ladd Silver conducting paint and were then sputtered with gold in a Denton

vacuum DV 515 evaporator. A total of approximately 50 micrographs (25 micrographs for each magnification) were obtained for each test sample prepared.

3.3.3 Image analysis

The quality of fiber dispersion within the composites was studied quantitatively using a Zeiss microscope equipped with a Metamorph Image Analysis System. Test specimens of 40 μm thickness were used in this work, and these were cut using a sliding microtome. The specimens were then mounted on glass microscope slides and examined under the microscope with the same amount of light. Approximately 60 – 70 images were analyzed for each specimen and the quality of fiber dispersion of the images was quantified by measuring their 'standard deviation of gray level'.