

## New Broom Fiber (*Spartium junceum* L.) Derivatives: Preparation and Characterization

ROBERTA CASSANO,<sup>\*,†</sup> SONIA TROMBINO,<sup>†</sup> ERMELINDA BLOISE,<sup>†</sup>  
RITA MUZZALUPO,<sup>†</sup> FRANCESCA IEMMA,<sup>†</sup> GIUSEPPE CHIDICHIMO,<sup>§</sup> AND  
NEVIO PICCI<sup>†</sup>

Departments of Pharmaceutical Sciences and Chemistry, University of Calabria, Rende (CS), Italy

In the past decade interest in biopolymers has increased. Attempts were made to prepare new composite systems from biopolymers by binding different synthetic polymers to a biopolymer backbone. This paper reports the synthesis and characterization of derivatized broom fibers to prepare composites with either degradability or fireproofing properties. Synthetic strategies are described for the introduction of polymerizable functional groups or fluorine atoms on the glucose of cellulose chains of broom. The fibers containing polymerizable groups were copolymerized with dimethylacrylamide and styrene and, after that, investigated by optical polarizing microscopy (OPM) and scanning electron microscopy analysis (SEM). The materials containing fluorine were submitted to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for the purpose of verifying the fireproofing. Such derivatized biomaterials could be successfully used for applications in agriculture and in the packaging area.

**KEYWORDS:** Broom fibers; functionalization; fluorine; agriculture; packaging; polymer

### INTRODUCTION

Over the past decade, polymer composites reinforced with natural fibers have received ever-increasing attention, from both academic and industry points of view. The main advantages that they have are low cost and high specific mechanical properties that allow their usage as a good, renewable alternatives to the most common synthetic reinforcement, such as glass fibers, which are not biodegradable (1–3). There is a wide variety of different natural fibers applicable as reinforcement or fillers. Cotton, jute, and flax are the vegetable fibers most commonly used to reinforce polymers such as polystyrene (4, 5), polyesters (6), polyolefins (7, 8), and epoxy resins (9, 10) due to their availability and properties. Broom is a further important fiber with numerous advantages, abundantly available, and biodegradable; because it is made of cellulose, on combustion, broom fibers do not generate toxic gases and are able to produce materials by combination with plastic mixtures. These fibers, known as vermenes, show extraordinary traction resistance and flexibility. Broom fiber and generally vegetable fiber composites provide improved specific or synergistic characteristics not obtainable by any of the original components alone and can be highly cost-effective materials for a number of applications such as those for the food industry. Besides the advantages mentioned above, the fiber composites possess also some disadvantages

such as their poor compatibility with a hydrophobic polymer matrix, the high affinity of natural fibers toward water, and their relatively poor thermal stability. This leads to the formation of weak interfaces that result in poor mechanical properties of the composites.

For such reason the idea to link halogenated or polymerizable molecules to broom fibers by covalent bond (**Figure 1**) to produce poorly flammable materials and to improve fiber strength and fiber/matrix adhesion in fiber composites was conceived (11). These systems could be applied in agriculture and in the packaging area. In this paper, we report the synthesis and characterization of broom fiber derivatives obtained by esterification with molecules containing fire retardant or polymerizable groups. Trifluoroacetic acid and heptafluorobutyric acid were used as efficient flame retardants in substitution of ozone-depleting and toxic substances containing chlorine and bromine (12). To obtain renewable plastic fibers, they were initially reacted with acryloyl chloride, 4-vinylbenzyl chloride, and 4-vinylbenzoyl chloride. Oxidized broom fibers were successfully used to prepare an amide-linked polymerizable conjugate with 4-aminomethyl styrene chlorohydrate. The obtained materials were characterized by Fourier transform infrared (FT-IR) spectroscopy; the degree of substitution (DS) of ester, ether, and amide derivatives was determined by titration. Moreover, the fireproofing of materials containing fluorine was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurement. The broom fibers derivatized with polymerizable groups were copolymerized with dimethylacrylamide and styrene, both in equimolecular amounts or with

\* Corresponding author (telephone +39 984493296; fax +39 984493163; e-mail roberta.cassano@unical.it).

<sup>†</sup> Department of Pharmaceutical Sciences.

<sup>§</sup> Department of Chemistry.

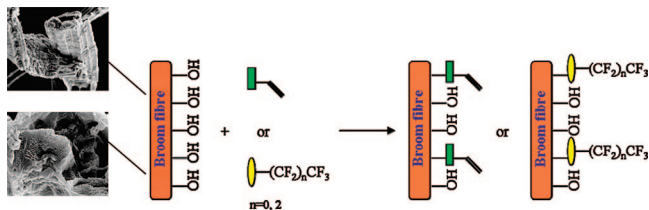


Figure 1. Schematic illustration of fiber derivatization.

the comonomers in large excess to obtain fibers covered from one polymeric girdle. These latter, inserted as support fibers in polymeric materials, would furnish strong interfaces and then composites with a much greater resistance than those realized with nontreated fibers. The unreacted, derivatized, and polymerized broom fibers were submitted to morphological analysis using high-resolution optical and scanning electron microscopes.

## MATERIALS AND METHODS

**Chemicals and Materials.** Natural cellulose fibers from broom (*Spartium junceum* L.) were supplied by Prof. G. Salerno (Department of Chemistry, University of Calabria, Italy). *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), lithium chloride (LiCl), dicyclohexylcarbodiimide (DCC), thionyl chloride ( $\text{SOCl}_2$ ), pyridine (Py), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium hydroxide (NaOH), acryloyl chloride ( $\text{CH}_2=\text{CHCOCl}$ ), trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ; TFA), trifluoroacetic anhydride [ $(\text{CF}_3\text{CO})_2\text{O}$ ; TFAA], heptafluorobutyric acid ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{COOH}$ ), heptafluorobutyric anhydride ( $(\text{CF}_3\text{CF}_2\text{CF}_2\text{CO})_2\text{O}$ ), 4-vinylbenzyl chloride ( $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{Cl}$ ), vinylbenzoic acid, dimethylacrylamide (DMAA), styrene, azobisisobutyronitrile (AIBN), potassium phthalimide, hydrazine monohydrate, hydrochloric acid, phosphoric acid, calcium acetate, phenolphthalein, and sodium nitrite were supplied by Sigma Chemical Co. (St. Louis, MO). Ethanol and diethyl ether were obtained from Fluka Chemika-Biochemika (Buchs, Switzerland) and Carlo Erba Reagents (Milan, Italy). Water, trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ), and acetonitrile (ACN) were of HPLC grade and obtained from Fluka Chemika-Biochemika.

**Measurements.** FT-IR spectra were measured on a Jasco 4200 using KBr disks. UV-vis spectra were performed by a V-530 JASCO spectrophotometer. HPLC analysis was performed with a Jasco BIP-I pump and a Jasco UVDEC-100-V detector set at 247 nm. A C18 Supelcosil LC-18 material, 3  $\mu\text{m}$  particle size, in a 4.6  $\times$  150 mm cartridge format (Supelco, Bellefonte, PA) column with linear gradient 0% B–100% B in 10 min (A, 0.1%  $\text{CF}_3\text{COOH}$  in  $\text{H}_2\text{O}$ ; B, 0.1%  $\text{CF}_3\text{COOH}$  in ACN, 1 mL/min) was employed. The measurement of transition temperatures was carried out using DSC-NETZSCH 200 by heating 0.8 mg of sample at 5  $^\circ\text{C min}^{-1}$ , operated under nitrogen. Scanning electron microscopy (SEM) photographs of the materials before and after polymerization were obtained with a JEOL JSMT 300 A; the surface of the samples was made conductive by deposition of a gold layer on the samples in a vacuum chamber. The polymerized materials were also studied with an Olympus FV1000-IX81 polarizing optical microscope. Thermogravimetric analysis of halogenated broom fibers was performed in air using a Perkin-Elmer Pyris 1 TGA.

**Fiber Chemical Modification.** Broom fibers were pretreated to obtain delignified materials (13). In particular, the broom fibers were reacted with aqueous alkali (about 10% NaOH) for 10 min (under reflux) and filtered to obtain the complete separation of fibrous substances from the marrow. The delignified materials were washed, until neutrality, with distilled water and then autoclaved with pressurizing air (40 bar of total pressure) for 3 h to 120  $^\circ\text{C}$ .

Pretreated broom fibers were subjected to the heterogeneous reactions shown in Scheme 1 after drying overnight at 80  $^\circ\text{C}$  under reduced pressure until a constant weight.

**Synthesis of Trifluoroacetate Broom Fibers (2).** TFA (40 mL) was added to 1.0 g of pretreated broom fibers, and the mixture was kept for 20 min at room temperature. Then 20 mL of TFAA was added and the mixture was stirred at room temperature for 4 h. The resulting

material was filtered off, washed with diethyl ether (300 mL), and dried at room temperature for 20 h under vacuum. The crude product contains traces of TFA and diethyl ether. These impurities can be removed by heating the product to 150  $^\circ\text{C}$  for 40 min under vacuum (14). FT-IR analysis confirmed ester linkage of trifluoroacetic derivative 2. Yield = 1.4 g.

**Synthesis of Heptafluorobutyrate Broom Fibers (3).** This derivative was prepared according to the same procedure as in the previous section employing 0.9 g of pretreated broom fibers, 20 mL of heptafluorobutyric acid ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{COOH}$ ), 10 mL of heptafluorobutyric anhydride ( $(\text{CF}_3\text{CF}_2\text{CF}_2\text{CO})_2\text{O}$ ), and 200 mL of diethyl ether. FT-IR analysis confirmed ester linkage of heptafluorobutyric derivative 3. Yield = 0.49 g.

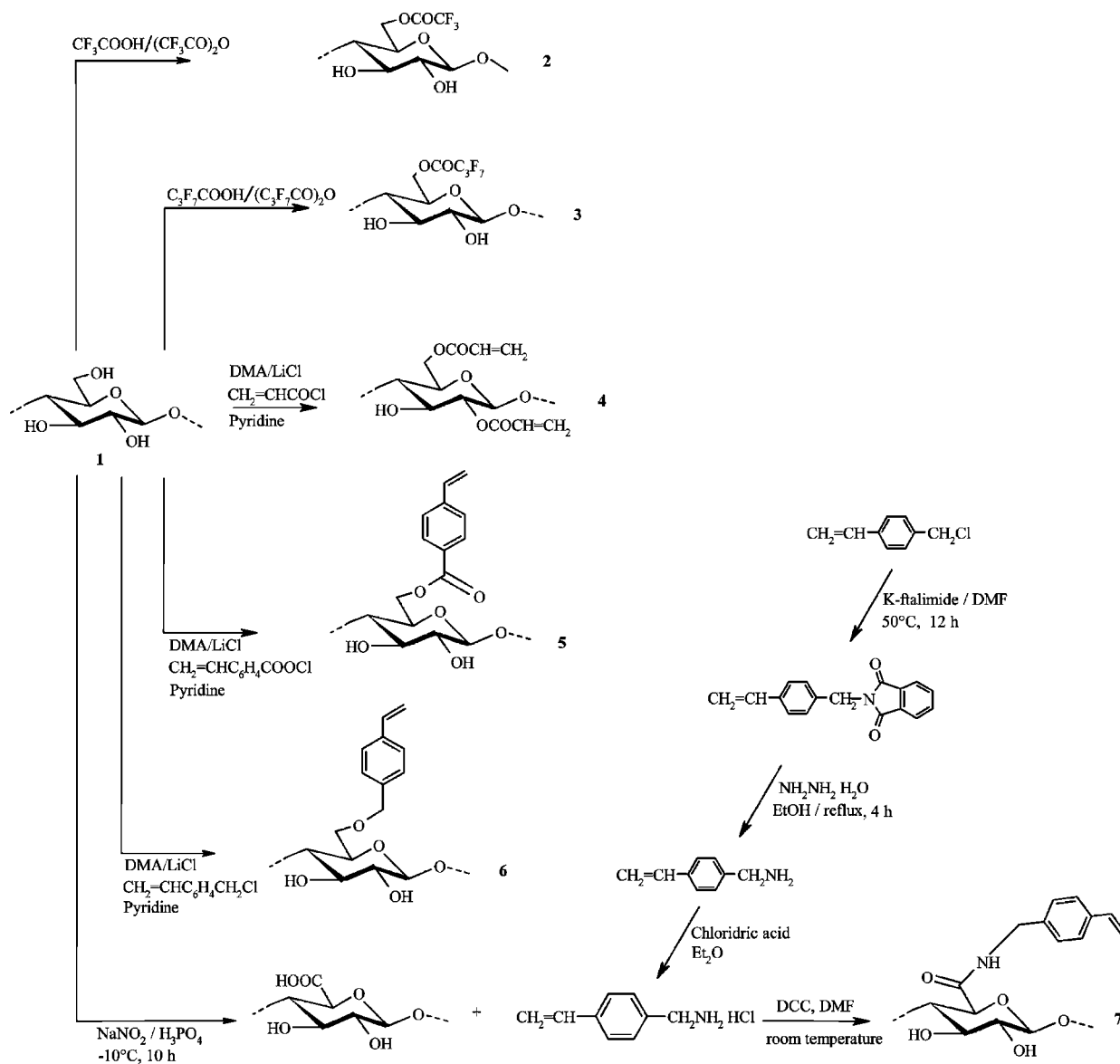
**Synthesis of Acrylate Broom Fibers (4).** To a heterogeneous system of 1.1 g of pretreated broom fibers in 50 mL of DMA and 3.3 g of LiCl in a three-necked flask equipped with a stirrer was added under inert atmosphere a mixture of 10 mL (0.124 mol) of dried pyridine and 20 mL of DMA (15). Acryloyl chloride (5 mL, 0.061 mol) was added within 30 min. The stirring was continued at room temperature. Then the heterogeneous reaction mixture was initially left to stand overnight and stirred for a further 6 h at 30  $^\circ\text{C}$ . After that, it was filtered off, washed with 200 mL of methanol, suspended in 96% (w/w) ethanol, and carefully dispersed. After filtration and washing with ethanol (four times with approximately 25 mL of ethanol), the material was dried at 50  $^\circ\text{C}$  under vacuum. FT-IR analysis confirmed ester linkage of acrylic derivative 4. Yield = 1.4 g.

**Synthesis of Vinylbenzoate Broom Fibers (5).** Thionyl chloride (14.6 mL) was added to 10.8 g (0.072 mol) of 4-vinylbenzoic acid, and the mixture was stirred for 2 h at 40  $^\circ\text{C}$ . The residual  $\text{SOCl}_2$  content was removed by distillation under vacuum, and after that, 6.2 g of vinylbenzoyl chloride was collected at 81  $^\circ\text{C}/2$  torr. The latter (5.8 g, 0.03 mol) was added, within 30 min, to a solution of pretreated broom fibers (0.8 g) in 36 mL of DMA, 2.4 g of LiCl, and 7 mL of dry pyridine. Then the heterogeneous system was left to stand overnight and stirred for a further 6 h at 30  $^\circ\text{C}$ . After the addition of methanol (200 mL), filtration, suspension in ethanol (150 mL), and final filtration, the sample was dried at 50  $^\circ\text{C}$  under vacuum. FT-IR analysis confirmed ester linkage of acrylic derivative 5. Yield = 0.9 g.

**Synthesis of Vinylbenzyl Ether Broom Fiber Derivative (6).** Pretreated broom fibers (1.1 g) were suspended in 50 mL of DMA and 3.3 g of LiCl. After the addition of 10 mL (0.124 mol) of dried pyridine and 20 mL of DMA, 8.5 mL of 4-vinylbenzyl chloride (9.2 g, 0.060 mol) was added slowly during 10 min. The mixture was stirred for 70 h at 25  $^\circ\text{C}$  and for 6 h at 30  $^\circ\text{C}$ . After cooling at room temperature, the resulting material was amended with methanol (200 mL), filtered off, and washed many times with ethanol (200 mL). The product was dried at 50  $^\circ\text{C}$  under vacuum. FT-IR analysis confirmed ether linkage of derivative 6. Yield = 0.8 g.

**Synthesis of Oxidized Broom Fiber–Aminomethyl Styrene Conjugate (7).** Appropriate amounts of oxidized broom fibers (0.8 g, equivalent to 2.3 mmol/g of COOH), DCC (1.6 g,  $8 \times 10^{-3}$  mol), and AMS (16) (1.2 g,  $7 \times 10^{-3}$  mol) were placed in 60 mL of DMF and stirred at room temperature. The concentration of free AMS was periodically monitored by HPLC. The reaction supernatant (250  $\mu\text{L}$ ) was withdrawn, appropriately diluted with the HPLC mobile phase, and then analyzed. The reaction was stopped when the amount of AMS in the reaction medium no longer declined. The reaction mixture was then filtered, and the material obtained was thoroughly washed with methanol (150 mL) and dried at 50  $^\circ\text{C}$  in a vacuum desiccator. FT-IR analysis confirmed ester linkage of amidic derivative 7. Yield = 0.9 g of pure product.

**Determination of the Carboxyl Group Content of Cellulose Samples by Methylene Blue Sorption.** A weighted fiber sample was suspended in 25 mL of aqueous methylene blue chloride solution (300 mg/L) and 25 mL of borate buffer of pH 8.5 for 1 h at 20  $^\circ\text{C}$  in a 100 mL flask and then filtered. Ten milliliters of the filtrate was transferred to a 100 mL calibrated flask. Then 10 mL of 0.1 N HCl and subsequently water, up to 100 mL, were added. Then the methylene blue content of the liquid was determined photometrically, employing

**Scheme 1.** Various Routes to Regioselectively Functionalized Pretreated Broom Fiber Esters and Ether with Different Moieties

a calibration plot, and from the result the total amount of free, nonsorbed, methylene blue is calculated. The carboxyl group content of the sample is obtained according to

$$\text{mmol of COOH/g of oven-dry sample} = [(7.5 - A) \times 0.00313]/E \quad (1)$$

where  $A$  is the total amount of free methylene blue (mg) and  $E$  is the weight of oven-dry sample (g) (17, 18).

**Quantitative Analysis of Ester Groups.** A sample of 50 mg of ester derivative was dispersed in 5 mL of 0.25 M ethanolic sodium hydroxide solution under reflux for 17 h. The dosing in return of the excess of soda was realized by titration with 0.1 N HCl (first equivalent point). The moles of chloride acid used between the first and second equivalence correspond to the moles of free esters. The degree of substitution (DS) was determined by

$$\text{DS} = \frac{\text{MM}_{\text{glucose unit}}}{(g_{\text{sample}}/n_{\text{free ester}}) - (\text{MM}_{\text{free ester}} - \text{MM}_{\text{H}_2\text{O}})} \quad (2)$$

where  $n_{\text{free ester}}$  is equal to  $(V_2^{\circ\text{ep}} - V_1^{\circ\text{ep}}) \times [\text{HCl}]$ ,  $\text{MM}_{\text{glucose unit}}$  is the molecular mass of the glucose unit,  $g_{\text{sample}}$  is the weight of the sample,  $n_{\text{free ester}}$  is the moles of free ester,  $\text{MM}_{\text{free ester}}$  is the molecular mass of free ester, and  $\text{MM}_{\text{H}_2\text{O}}$  is the molecular mass of water.

**Determination of Vinylbenzyl and Aminomethyl Styrene Content of Derivatives 6 and 7.** The classical method to obtain information on the vinyl group of 6 and 7 is the number iodine determinations (19).

$$\text{iodine no.} = \frac{(\text{blank titers} - \text{sample titer, mL})(0.01269)(100)}{\text{sample wt (g)}} \quad (3)$$

An iodine monochloride (Wij's reagent) reagent is reacted with the double bonds, and the excess reagent (as iodine) is titrated with sodium thiosulfate solution. More exactly, 0.3 g of 6 was mixed with 20 mL of Wij's solution and 10 mL of carbon tetrachloride/glacial acetic acid 3:7. It is then left in the dark for 30 min. Next, 15 mL of 10% potassium iodide solution and 10 cm<sup>3</sup> of deionized water are added. This is then titrated against 0.1 M sodium thiosulfate(VI) solution and five drops of 1% starch paste solution. One milliliter of 0.1 M sodium thiosulfate solution is equal to 0.01269 g of iodine. The difference between a control titration and the titration with the fat present multiplied by this factor gives the mass of iodine absorbed by the broom fiber derivatives 6 and 7.

**Copolymerization of Broom Fibers.** The grafting of derivative 4, with structopendant unsaturated ester moieties, was carried out in DMF employing AIBN as initiator and DMAA or styrene as comonomer (20). The materials copolymerized with DMAA were washed first with

**Table 1.** Experimental Conditions of the Copolymerization Reactions

| derivative <b>4</b> (g) | comonomer DMAA (g) | comonomer styrene (g) | initiator AIBN (g) | solvent DMF (mL) | washing solvents      |                                        |              |
|-------------------------|--------------------|-----------------------|--------------------|------------------|-----------------------|----------------------------------------|--------------|
|                         |                    |                       |                    |                  | H <sub>2</sub> O (mL) | washing solvents <i>n</i> -hexane (mL) | acetone (mL) |
| 1.0                     | 0.46               |                       | 0.01               | 25.0             | 3·20                  |                                        | 3·20         |
| 0.57                    | 9.62               |                       | 0.30               | 25.0             | 3·300                 |                                        | 3·300        |
| 0.50                    |                    | 0.5                   | 0.01               | 25.0             |                       | 3·20                                   | 3·20         |
| 0.51                    |                    | 7.13                  | 0.22               | 25.0             |                       | 3·300                                  | 3·300        |

water and after with acetone. On the contrary, those copolymerized with styrene were washed initially with *n*-hexane and subsequently with acetone. The experimental conditions of the copolymerization reactions are reported in **Table 1**. Further studies to prepare copolymers of the materials **5–7** are in progress.

## RESULTS

**Synthesis of Broom Fiber Derivatives 2–7.** Halogenated or polymerizable materials (**2–6**) were realized from pretreated broom fibers using trifluoroacetic and heptafluorobutyric acids or acryloyl chloride, vinylbenzoyl chloride, 4-vinylbenzyl chloride. Moreover, the conjugate **7** was prepared after initial oxidation of broom fibers and subsequent reaction with aminomethyl styrene chloridate. The formation of broom cellulose esters of organic acids was conducted along the routes of esterification of alcoholic hydroxy groups, well-known from low molecular organic chemistry: the chloride of the organic acid in question or the anhydride with the corresponding acid was employed as the agent to obtain an appreciable degree of esterification. Halogenated esters of broom cellulose (**2**, **3**) with substituted monocarboxylic aliphatic acids were prepared by reaction with a mixture of CF<sub>3</sub>COOH and (CF<sub>3</sub>CO)<sub>2</sub>O or CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>COOH and (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CO)<sub>2</sub>O. Partial recovery of derivative **3** was ascribed to the remarkable fragmentation of fibers after treatment with CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>COOH and (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CO)<sub>2</sub>O. Acrylate and vinylbenzoate esters (**4**, **5**) were prepared with acryloyl- or vinylbenzoyl chloride as the agent in the presence of pyridine in DMA/LiCl as the medium (21). Cellulose etherification was performed with the broom fibers suspended in an aprotic system such as DMA/LiCl to obtain **6**. The synthesis pathway consists in the reaction of fibers with 4-vinylbenzyl chloride in the presence of pyridine as base (22). Finally, the oxidized broom fiber–aminomethyl styrene conjugate **7** was prepared through reaction of 6-carboxy fiber derivatives with 4-aminomethylstyrene chloridate using *N,N'*-dicyclohexylcarbodiimide as a condensation agent and *N,N*-dimethylformamide as solvent. The 6-carboxy broom fiber derivative was synthesized in accordance with a procedure found in the literature (23), and the determination of carboxyl group content was realized by methylene blue sorption (17). Its FT-IR spectra showed considerable changes in comparison with the spectra of starting fibers and an oxidized sample. The formation of all broom fiber derivatives was confirmed by FT-IR spectroscopy. Their yields are 1.4 g for trifluoroacetate broom fibers, 0.49 g for heptafluorobutyric derivative, 1.4 g for acrylic ester, 0.9 g for vinylbenzoate broom fibers, 0.8 g for vinylbenzyl ether broom fiber derivative, and 0.9 g for oxidized broom fiber–aminomethyl styrene conjugate.

**Carboxylic Group Content of Broom Fiber Derivatives 2–5 (DS).** Complete or partial esterification of the hydroxy groups is among the principal reaction routes to the cellulose derivatives carrying covalently bound substituents. A complete functionalization of all the hydroxy groups of cellulose is more an exception than a rule, and most of the products are

**Table 2.** Degree of Substitution Values of Compounds **2–5**

| compound | substitution degree |
|----------|---------------------|
| <b>2</b> | 0.82                |
| <b>3</b> | 0.37                |
| <b>4</b> | 1.70                |
| <b>5</b> | 0.71                |

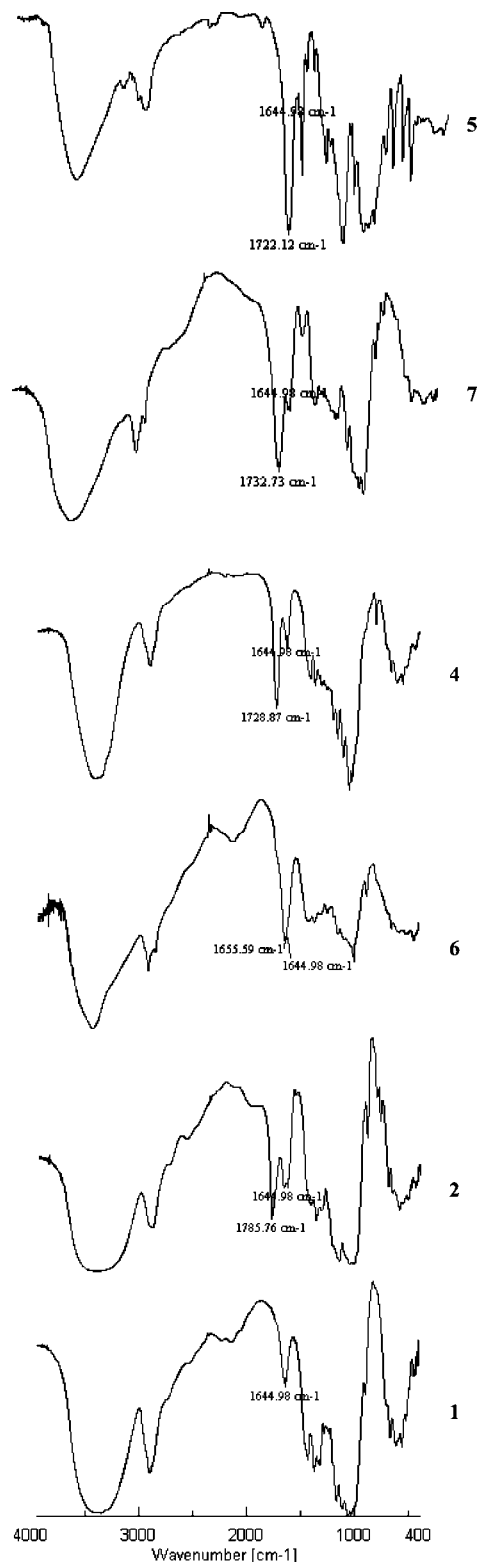
cellulose compounds still containing a fairly large number of free hydroxy groups. Thus, information on the extent of reaction and on distribution of the substituents is of great importance. The extent of reaction is usually characterized by the DS, denoting the average number of hydroxy groups modified per AGU, and thus covering the range from 0 to 3. With regard to the DS values of samples **2–5**, determined by titration and calculated by eq 1, they were 0.82 and 0.37 for trifluoroacetate (**2**) and heptafluorobutyrate (**3**) esters, respectively, 1.70 for acrylate derivative (**4**), and finally of 0.71 for vinylbenzoate derivative (**5**) (**Table 2**).

**Vinylbenzyl and Aminomethyl Styrene Content of Derivatives 6 and 7.** Samples **6** and **7** were independently reacted with an excess of iodine monochloride solution (Wij's reagent) under controlled conditions. Halogens add quantitatively to the vinyl group. Unreacted halogens were determined by titration with thiosulfate. The iodine number, defined as the grams of halogen, expressed as iodine, was 17 (corresponding to 0.65 mmol/g) for derivative **6** and 26 (equivalent to 0.98 mmol/g) for derivative **7**.

**FT-IR Investigations.** FT-IR spectroscopy was used to obtain qualitative information about the broom fibers after derivatization. The FT-IR spectra of unreacted broom fibers (**1**) and derivatives **2–7** are compared in **Figure 2**. As reported, the band at 1644 cm<sup>-1</sup> (spectrum a) typical of unreacted broom fibers is visible in the spectra of all derivatives. Additionally, spectrum b of **2** shows the characteristic peak of carboxylic group of ester at 1786 cm<sup>-1</sup>. The spectrum of derivative **3**, not shown, is analogous to spectrum b. The peaks at 1729 and 1722 cm<sup>-1</sup> in spectra d and f are due to C=O stretching vibration belonging to the carboxylic groups of the esters **4** and **5**. Note the stretching vibration of vinyl group (C=C) with the ether **6** at 1655 cm<sup>-1</sup> in spectrum c. The peak at about 1732 cm<sup>-1</sup> in spectrum e is due to C=O (amide) stretching vibration of the amide **7**. In spectra e, f, and c the peaks between 3000 and 3100 cm<sup>-1</sup> are assigned to C–H (aromatic) stretching vibration due to the phenyl group of compounds **5–7**.

**High-Resolution Optical Microscopy and Scanning Electron Microscopy (SEM).** The surface roughness characterization was initially effected through investigation with high-resolution optical microscope (**Figure 3**). Morphological analysis of the fiber was also carried out using SEM, which is the most widely used of the surface analytical techniques. SEM represents an invaluable tool for studying surface topography and failure analysis. The technique, which enables qualitative three-dimensional (3-D) imaging of surface features, clearly illustrated, as did the optical microscopy, that the untreated broom fiber





**Figure 2.** FT-IR spectra of broom fibers: unreacted (1); trifluoroacetate (2); vinylbenzyl ether (6); acrylated (4); oxidized broom fiber-aminomethyl styrene conjugate (7) vinylbenzoate (5).

surface (**Figure 4a**) was not more homogeneous than that exhibited by materials copolymerized with a stoichiometric amount of DMAA (**Figure 4b**) and copolymerized with an excess of DMAA (**Figure 4c**). All derivatives are shown to be fibrous and to have a smoother surface compared with that of untreated fibers. The broom fibers containing acrylic groups furnished, after copolymerization with dimethylacrylamide, a



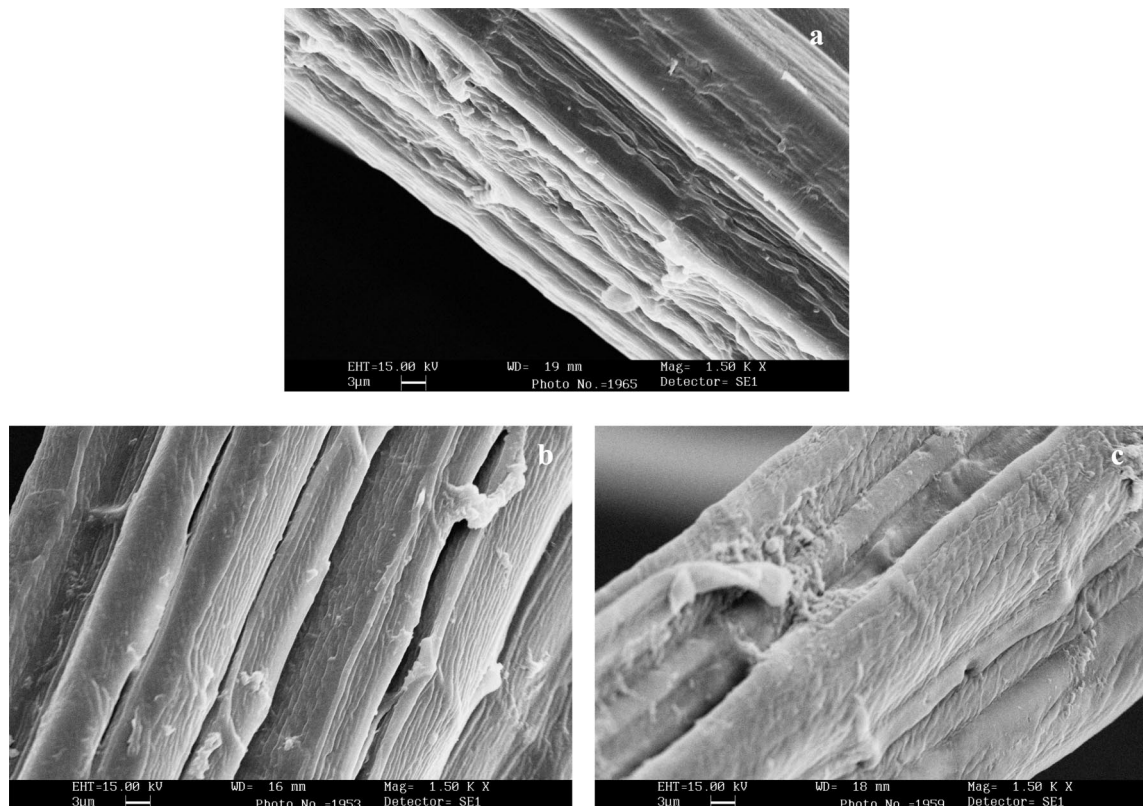
**Figure 3.** Optical micrographs of acrylated broom fibers copolymerized with (a) a stoichiometric amount of DMAA and (b) an excess of DMAA.

material that maintains unchanged its fibrous nature but show that it is covered by a polymeric layer to the same fiber. The material functionalized with styrenic groups, copolymerized with an equimolecular amount or excess of styrene, furnished fibrous materials covered with a varying thickness layer of styrenic polymer. The thickness of the polymeric layer is obviously a function of the excess of comonomer used. Photomicrographs of the surface of copolymerized fibers show what has been, until now, suggested.

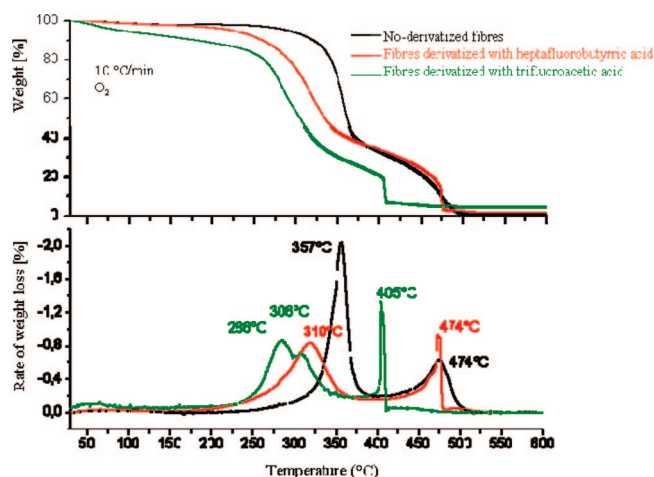
**TGA.** In a TGA mass loss versus increasing temperature of a sample is recorded. The TGA was performed on heating from 30 to 600 °C 5 mg samples at 10 °C/min under oxygen flow (30 mL/min). Experiments were repeated twice. These operating conditions allowed us to study the thermo-oxidative degradation of broom fibers modified with fireproofing compounds such as trifluoroacetic and heptafluorobutyric acids. **Figure 5** reports the weight loss curves (top) and the corresponding weight loss rates (bottom). Thermo-oxidative degradation of underivatized fibers takes place in two steps. The first step of volatilization (between 225 and 400 °C with a maximum rate of decomposition  $v_{\max \text{ dec}}$  at 357 °C) left a carbonaceous residue of about 40 wt % of the initial mass, whereas in the second step (between 410 and 520,  $v_{\max \text{ dec}}$  at 474 °C) the residue is fully volatilized. The poly fluoro acid treatment modifies the thermo-oxidative behavior of broom fibers with respect to those not derivatized. Similarly to what was observed for the neat fibers, heptafluorobutyric acid derivatized fiber **3** thermo-oxidative weight loss takes place in two well-separated steps; however, the first step of weight loss is shifted to lower temperature (from  $v_{\max \text{ dec}} = 357$  °C to  $v_{\max \text{ dec}} = 319$  °C), whereas the second step takes place abruptly, as evidenced by the sharpened weight loss rate curve (**Figure 5**, bottom). The trifluoroacetic acid derivatized fiber (**2**) has three steps of weight loss: the first two, partially overlapped, from 225 to 370 °C with  $v_{\max \text{ dec}}$  at 286 and 306 °C, the third one from 380 to 420 °C with  $v_{\max \text{ dec}}$  at 405 °C. The release of halogen derivatives, which is a fundamental step of the flame-retardant mechanism of halides (24), may explain the reduced thermal stability of derivatized fibers, evidenced by the shift to lower temperature of the first weight loss steps. The last weight loss steps, at 474 °C for **3** and at 405 °C for **2**, respectively, may be due to a rapid collapse of a protective (carbonaceous) layer formed during the earlier thermo-oxidative degradation steps of the chemically modified fibers, followed by an abruptly oxidation of the organic residue. To fully understand the chemical degradation mechanism that led to the observed thermo-oxidative behaviors, a more focused study is needed.

## DISCUSSION

Broom fiber derivatives with a variety of DS values were successfully prepared by introducing polymerizable or polyha-

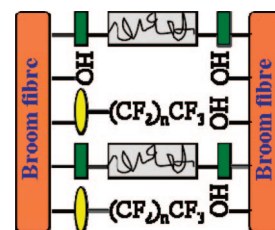


**Figure 4.** Photomicrographs of broom fibres: (a) unreacted; (b) copolymerized with a stoichiometric amount of DMAA; (c) copolymerized with an excess of DMAA.



**Figure 5.** Thermogravimetry (a) and derivative (b) curves of broom fibers and of fibers functionalized with trifluoroacetic and heptafluorobutyric acids.

logenated residues in pretreated material. The formation of all broom fiber derivatives was confirmed by FT-IR spectroscopy. Fluorinated material thermal stability was evaluated by TGA. The results suggested that the presence of the fluorine atoms changes the thermal decomposition behavior of broom fibers. The decreased ignition of broom fibers modified with TFA in comparison with heptafluorobutyrate derivative is mostly attributed to the different DS. Relative to the broom fibers derivatized with polymerizable groups, the choice to use acrylamidic or styrenic monomers for their covering has been dictated by the necessity to have on the surface a hydrophilic or lipophilic polymeric layer, covalently linked to the fiber. This should allow the fibers so modified to be used as filler in composite polymeric material that should present a much greater



**Figure 6.** Schematic illustration of polymerized halogenated fibers.

resistance to those realized with nontreated fibers. In the future, derivatives containing fluorine atoms will be submitted to treatment with compounds containing polymerizable groups to obtain halogenated, poorly flammable, polymerizable materials (**Figure 6**). These materials, entirely obtained by renewable sources, could be used in agriculture, in the realization of cordage or for packings of natural products, or to replace aluminum-based containers (25, 26) used in food packaging. In fact, the National Institute of Nutrition (NIN), which is part of the Indian Council of Medical Research, has concluded that the intake of aluminum compounds from many sources is on the rise and producing detrimental effects on human health. Particularly, the aluminum may contribute significantly to the development of Alzheimer's disease and other nervous disorders (27).

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## LITERATURE CITED

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