UTILIZATION OF FIBERS OBTAINED BY PEROXYFORMIC ACID PROCESSING OF BROOM AS REINFORCING AGENTS FOR BIOCOMPOSITES

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Broom (*Cytisus scoparius*) samples were processed in media containing formic acid and hydrogen peroxide (MILOX process) to obtain cellulose-enriched solids. The chemical processing of broom samples was assessed by means of a centered, second order factorial design of experiments. Empirical models derived from the experimental data gave a close interpretation of the experimental patterns, and enabled the selection of operational conditions for achieving extensive delignification and hemicellulose removal, while minimizing the dissolution of cellulose. Broom samples processed under the selected conditions were employed to reinforce PLA composites, which were characterized mechanically and by DSC, SEM, and water absorption experiments.

Keywords: Cytisus scoparius; Broom; MILOX; PLA; Biocomposite; Injection moulding

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INTRODUCTION

The utilization of oil-based chemicals for the synthesis of commodity polymers, as well as the environmental concerns generated by their disposal, are challenges to the polymer industry. In recent years, a great effort has been made for obtaining biodegradable materials from renewable sources, which could contribute to the solution for waste-disposal problems and reduce net greenhouse gas generation (Jerez et al. 2007; Kakuta et al. 2009; Philip et al. 2007; Willians and Hillmyer 2008; Yang et al. 2010). Although costs have been reduced considerably, these polymers are still more expensive than oil-derived commodity plastics, and new advances in such fields as separation and purification, polymerization, or genetic engineering are being considered (Datta and Henry 2006; Philip et al. 2007; Siracusa et al. 2008; Willians and Hillmyer 2008). The higher oil prices in the last years have led to increases in the price of conventional plastics. Although bioplastics are not derived from fossil fuels, such fuels often supply the energy needed in manufacturing, and alternative energy sources should be considered (Vink et al. 2003). In 2006 NaturWorks increased the price of PLA, changing the trend of decreasing price for bioplastics (Bohlmann 2007). On the other hand, environmental concerns and legislative incentives, particularly in the European Union (EU) and the

United States (US), tend to promote the use of biodegradable plastics. Bioplastic producers are expected to compete on price with conventional producers by 2015.

Properties of biodegradable polymers can be modified and improved by formulation of composites based on the utilization of lignocellulose-based reinforcing agents, which can reduce the overall costs without affecting biodegradability (Iovino et al. 2008; Kim et al. 2006). A number of studies have considered the reinforcement of polymers with fibers obtained from cellulosic substrates (such as stems, leaves, coir, or wood) modified by chemical and/or physical treatments (Li et al. 2007). Cunha et al. (2006) reported on the utilization of spent cellulose fibers recovered from a kraft pulping industry as reinforcing agents for PLA-based composites. Graupner (2008) employed kraft lignin as a natural adhesion promoter in cotton-PLA composites, achieving improvements of increased tensile strength and Young's modulus.

The kraft process is the world's leading technology for chemical pulp production, but 1000 metric tons of pulp per day has been cited as the minimum plant capacity to reach profitable operation, owing to the large investment required. Alternative technologies based on the utilization of organic solvents (organosolv pulping) offer comparative advantages for small-size plants (Hergert 1998).

On the other hand, both legal restrictions and social awareness foster the development of these technologies owing their environmental impact. A variety of organosolvents have been tested, but two main groups can be cited: organic acids (notably formic acid and acetic acid) and alcohols. Both types of technologies can achieve extensive delignification, leading to easily bleached pulps.

Among organosolvents, formic acid shows interesting features as an agent for lignocellulose fractionation, including its ability to reach an extensive delignification with simultaneous hemicellulose hydrolysis at good pulp yield. Several approaches dealing with the fractionation of lignocellulosic substrates in formic acid media have been reported, including operation in aqueous formic acid, acid-catalysed aqueous formic acid, and formic acid-peroxyformic acid mixtures in aqueous media (Ligero et al. 2008; Mire et al. 2005; Sundquist and Poppius-Levlin 1998; Villaverde et al. 2010). Among them, the latter technology (known as MILOX process) exhibits a better selectivity, since delignification is accompanied with lesser weight losses (Ligero et al. 2008)

The MILOX process (nomenclature derived from "MILieu pure OXidative pulping") is based on the action of a carboxylic acid (mainly formic acid) and the corresponding peroxyacid. Formic acid acts as a solvent for lignin and extractives, and breaks down the hemicellulose chains, whereas peroxyformic acid causes oxidative depolymerization of lignin, renders it more hydrophilic, and enhances its solubility. The MILOX process has been applied to softwoods (Obrocea and Cimpoesu 1998; Sundquist and Poppius-Levlin 1998), hardwoods (Abad et al. 2000, 2001; Dapía et al. 2000; Da Silva et al. 1998), and non-wood materials (Da Silva et al. 1998; Jahan et al. 2007; Ligero 2008; Villaverde et al. 2010). Typically, this process is made up of three sequential stages. In the first one, the lignocellulosic raw material is reacted in a medium containing water, formic acid, and hydrogen peroxide. Peroxyformic acid is generated in situ through an equilibrium reaction between formic acid and hydrogen peroxide, and electrophilic HO^+ ions are formed (De Filippis et al. 2009). The HO^+ ions react with lignin through ring hydroxylation, oxidative ring opening, substitution of side-chains, cleavage of beta-aryl ether bonds, and epoxidation. The second stage is performed in the same reaction medium used in the previous step, but the temperature is raised and held for a given period of time. In this stage delignification takes place mainly through the hydrolysis of beta-aryl ethers. The harsher conditions used in this step may result in increased cellulose losses. In the third stage, the delignified solid phase from the previous treatments is reacted again with formic acid and hydrogen peroxide. This procedure can be modified by omitting some of the three stages, depending on the material treated (Sundquist and Poppius-Levlin 1998)

A pilot plant using MILOX technology was constructed at Chempolis Ltd. in Oulu, Finland, treating grass or wood as raw materials. The energy consumed in liquor evaporation for solvent recovery was found to be an important production cost, and added-value can be obtained for subproducts (lignin and sugars in liquors) (Sundquist and Poppius-Levlin 1998). Perttunen et al. (2001) used the liquors as fermentation media for lactic acid production, the monomer used in PLA synthesis. Using reed as a raw material, fermentation of liquors after concentration and detoxification enabled the production of 33 g lactic acid L^{-1} and 17 g acetic acid L^{-1}.

The increasing demand for products from the production of pulp and paper, biofuels, or bioplastics have focused efforts on the search for alternative raw materials that can be used alternatively or complementarily to wood. *Cytisus scoparius*, a perennial, leguminous shrub native to western and central Europe, has become an ecologically damaging, invasive species. In Galicia (NW Spain), *Cytisus scoparius* is one of the three main shrub species, which are spreading over a surface of around 800 000 ha (Núñez et al. 2004). Broom fibers (*Spartium junceum*) were analysed for their mechanical properties (Angelini et al. 2000) and used as reinforcement in polypropylene composites, studying the influence of a surface treatment with stearic acid (Nekkaa et al. 2006).

One of the most important commercial biodegradable thermoplastic polymers is polylactic acid (PLA) (Siracusa et al. 2008; Datta and Henry 2006). Recently Naturworks LLC, the major world producer of PLA, has doubled the production capacity of its PLA plant in Blair, Nebraska, USA, reaching 140,000 metric tons/year. PLA presents satisfactory mechanical properties, favourable melting point (around 160-180 ºC, below the temperatures at which natural fibers start to degrade), versatility (with many applications in various industrial fields), and suitability for melt processing, namely by injection molding (Kakuta et al. 2009). However, the tenacity of PLA is limited, and reinforcement by a suitable material could result in improved mechanical properties and dimensional stability.

The objective of this work is to assess the ability of formic–peroxyformic system processing for reaching an extensive delignification of *Cytisus scoparius*, measuring the effects caused by modification of the most influential operational variables by empirical modelling based on the Response Surface Methodology. The SCAN viscosity of processed solids was included among the measured effects in order to assess the cellulose depolymerization caused by treatments. Raw and delignified *Cytisus scoparius* samples were assayed as reinforcing agents for PLA-based composites obtained by injection molding, and their mechanical properties (tensile strength, impact strength and Young's modulus) were tested. Additionally, composites were characterized for technological (water uptake), thermal (DSC), and structural (SEM) properties.

MATERIALS AND METHODS

Raw Material

Cytisus scoparius samples were collected in the outskirts of Ourense (northwest of Spain), air dried, chipped, milled to pass 1 mm screen, homogenized in a single lot to avoid compositional differences among aliquots, and stored in polypropylene bags until use.

Commercially available polylactic acid (PLA 3051, supplied by Naturworks as a granulate) was employed as a polymeric matrix. This product had the following properties: density, 1.25 g/cm^3; melting temperature, 150-155 ºC; glass transition temperature, 60.0 ºC; and melt flow index (at 210 ºC and 21.2 N), 30.3 g/10 min.

Analytical Characterization of Raw Material and Processed Solids

Analytical assays were performed according to the following methods: moisture, ISO 638:1978; ash content, ISO 776; SCAN viscosity, SCAN C15:62, after chlorine delignification; ethanol extractives, as per Browning (1967), quantitative acid hydrolysis, TAPPI T 13m; Klason lignin, by gravimetric determination of the residue from the TAPPI T 13m assay; acid soluble lignin, spectrophotometrically by TAPPI UM 250; cellulose (as glucan), xylan, other polysaccharides, formyl and acetyl groups, by HPLC determination of the glucose, xylose, other sugars, formic and acetic acid contained in hydrolyzates from the quantitative acid hydrolysis. Raw material hydrolyzates, after neutralization with barium hydroxide, were analyzed using an Aminex HPX-87P column (BioRad) with deionized water as the mobile phase (flow rate 0.6 mL/min). The monosaccharides present in the media (glucose, xylose, and arabinose) were individually resolved in chromatograms. Additional HPLC analyses were carried out in an Agilent 1200 series chromatograph fitted with a refractive index detector (temperature, 50 ºC), using an ION-300 column (Transgenomic, Inc), and 0.0003 M H_2SO_4 as mobile phase (flow rate, 0.6 mL/min), for quantification of acetic and formic acids, furfural, and hydroxymethylfurfural.

Milox Pulping

The desired amounts of *Cytisus scoparius* samples, water, and formic acid were introduced in 500 cm^3 stirred glass reactors with temperature control, and heated to the target temperature (70 ºC). Once the system reached isothermal conditions, hydrogen peroxide (33% w/v) was added at the appropriate proportion, and the first stage was considered to begin (zero time). After 1 hour the temperature was increased and the system was kept under reflux. The second stage was considered to begin when the liquors in the reactor reached the normal boiling temperature. Exhausted solids from the reaction media were withdrawn, filtered, and washed (first with hot 80% formic acid and then with water until achieving neutral pH). Samples for determination of viscosity were resuspended in distilled water and defibered for 30 s at 5000 r.p.m. (Ultraturrax T-50 device, IKA Labortechnik, Germany) before analytical processing.

Experimental Design and Statistical Analysis

Table 1 shows the operational conditions selected for experiments 1 to 15, which corresponded to an incomplete centered, second-order, factorial design with minimum dead volume. Statistical designs have been widely employed for assessing complex problems, owing to their ability to give quantitative interrelationships between operational and experimental variables with a reasonable number of experimental tests. In particular, Surface Response Methodology has proved to be a useful tool for assessing MILOX pulping (Ligero et al. 2008; Abad et al. 2000, 2001). The empirical models derived from experimental data enable the evaluation of the dependent variables as the sum of the contributions of the independent, dimensionless variables through first order, interaction, and second-order terms, according to the generalized expression,

$$y_j = \mathrm{b}_{0j} + \Sigma_i \mathrm{b}_{ij} x_i + \Sigma_i \Sigma_k \mathrm{b}_{ikj} x_i x_k \qquad (1)$$

where y_j stands for the dependent variable considered; x_i or x_k (i or k: 1 to n, k≥i) are the independent variables; and $\mathrm{b}_{0j}....\mathrm{b}_{ikj}$ are regression coefficients calculated from experimental data by multiple regression (usually by least-squares method). In this study, the fixed variables were: liquor-to-solid ratio (g liquor/g solid = 12), temperature of the first stage (T_1 = 70 ºC), reaction time of the first stage (t_1=60 min), and temperature of the second reaction stage (T_2, normal boiling temperature). The independent variables were: formic acid concentration (*FAC*), reaction time of the second stage (t_2), and hydrogen peroxide concentration (*HPC*). The variation ranges selected for the independent variables were based on literature data and on the results of previous experiments (data not shown). The measured responses (dependent variables) were: pulp yield (*PY*), residual Klason lignin (*KL*), variables related to the chemical composition of pulps, and SCAN viscosity. This information is summarized in Table 1.

Table 1. Fixed, Independent, and Dependent Variables Considered in the Experimental Design

Type of variable	Variable	Nomenclature	Value	Units
Fixed	Liquor-to-solid ratio	*LSR*	12	g liquor / g solid[1]
	Temp. of the 1st stage	T_1	70	ºC
	Time of the 1st stage	t_1	60	min
	Temp. of the 2nd stage	T_2	NBT[2]	ºC
Independent	Time. of the 2st stage	t_2	30-120	min
	Hydrogen peroxide conc.	*HPC*	1-5	g/100 g wood[1]
	Formic acid conc.	*FAC*	72-98	weight % of liquid
Dependent	Cellulose content	y_1		g cellulose /100g solid[1]
	Xylan content	y_2		g xylan/100g solid[1]
	Formyl groups content	y_3		g formyl groups/ 100g solid[1]
	Klason Lignin content (KL)	y_4		g Klason lignin/100g solid[1]
	Pulp yield (PY)	y_5		g treated solid/100g solid[1]
	SCAN viscosity	y_6		(mL/g)

[1] Oven-dry basis [2] Normal boiling temperature

Table 2 shows the operational conditions considered in experiments 1 through 15 in terms of dimensional variables (see Table 1) and in terms of dimensionless, normalized experimental variables (x_1: dimensionless time of the 2nd stage; x_2: dimensionless hydrogen peroxide concentration; x_3: dimensionless formic acid concentration). These dimensionless variables, with variation ranges (-1,1), are related to the experimental ones by means of the following equations,

$$x_1 = 2\,(t_{2i}-t_{2med})/(t_{2max}-t_{2min}) \tag{2}$$

$$x_2 = 2\,(HPC_i-HPC_{med})/(HPC_{max}-HPC_{min}) \tag{3}$$

$$x_3 = 2\,(FAC_i-FAC_{med})/(FAC_{max}-FAC_{min}) \tag{4}$$

where t_2, HPC, and FAC are the independent variables defined in Table 1, the subscript i refers to the number of the experiment considered, and the subscripts med, max, and min refer to the central point, upper limit, and lower limit of the variable's variation range, respectively.

Table 2. Operational Conditions Considered in Experiments 1 to 15 Expressed in Terms of the Dimensional and Dimensionless Independent Variables

	Dimensional, independent variables			Dimensionless, normalized, independent variables		
Experiment	t_2 (min)	*HPC* (%)	*FAC* (%)	x_1	x_2	x_3
1	120	5	85	1	1	0
2	120	1	85	1	-1	0
3	30	1	85	-1	-1	0
4	30	5	85	-1	1	0
5	75	3	85	0	0	0
6	75	3	85	0	0	0
7	75	3	85	0	0	0
8	120	3	72	1	0	-1
9	75	1	72	0	-1	-1
10	30	3	72	-1	0	-1
11	75	5	72	0	1	-1
12	120	3	98	1	0	1
13	75	5	98	0	1	1
14	75	1	98	0	-1	1
15	30	3	98	-1	0	1

Formulation and Testing of the Composite Materials

Composites were made up of PLA (as a polymeric matrix) and raw or processed *Cytisus scoparius* samples. Previously to processing, the fibers were dried overnight at 90ºC. PLA was stored in a vacuum drying unit (Piovan DPM 615) for 4 hours at 80 ºC, as recommended by the supplier. During processing, both fibers and PLA were subjected to minimal room exposure. Based on previous experiments (data not shown) the reinforcement to PLA mass ratio employed in this work was 1:4 g/g.

ISO 527 tensile and impact specimens (Model 1A, with 80 mm length in the narrow parallel-sided section and a constant rectangular cross-section of 10 x 4 mm^2) were obtained using an integrated compounding and injection moulding machine (twin screw extruder, with a screw diameter of 35 mm, L/D ratio of 18, and injection unit of 2300 kN clamping force). The operational conditions used in composite processing were: extrusion temperature, 170 ºC; injection temperature, 170 ºC; mold temperature, 25 ºC; extrusion speed, 70 r.p.m.; injection speed, 10 mm s^{-1}; holding pressure, 20 bar; and cooling time, 20 s.

Ten specimens from each experiment were tested in a Shimadzu Autograph AG-X testing machine with 50 kN load cell, at a crosshead speed of 2 mm min^{-1}. Ten impact specimens (ISO 179, Type 1A) were tested in a Ceast-Resil Impactor (15 J energy) at 23 ºC and 55% relative humidity. The following mechanical properties were measured: Tensile strength (σ_t), stiffness (E); strain at break (ε); and impact strength (I_s).

Tensile specimens were used to study the water absorption. Samples were immersed in distilled water at room temperature and the percentage of weight change was determined once the equilibrium value was reached. After immersion in distilled water, specimens were removed at different times, wiped with tissue paper to remove excess water, and weighed to determine the percentage of weight gain (w_t).

DSC Thermograms. Crystallinity Determination

The thermal behavior of neat PLA and composites was assessed by Differential Scanning Calorimetry (DSC) in a Setaram Setsys Evolution 16 system, using nitrogen as purge gas. The samples were heated at 10 ºC min^{-1} to reach 200 ºC, eliminating any previous history, cooled at the same rate to reach 30 ºC, and reheated to 200 ºC at 10 ºC min^{-1}. Calibrations of temperature and enthalpy energy scales were carried out using a pure indium standard. Glass transition (T_g), crystallization, and melting temperatures (T_m) as well as enthalpy values were determined. The same instrument provided TGA data upon heating up to 800 ºC.

Crystallinity (Xc) was calculated as the ratio between ΔH (enthalpy corresponding to crystallization prior to melting subtracted from enthalpy of melting of the sample) and ΔH_{100} (enthalpy corresponding to the melting of the 100% crystalline polymer), corrected to consider the mass fraction of PLA in the sample. In calculations, ΔH_{100} for PLA was assumed to be 93 J/g.

SEM Analysis

The fiber-matrix interface was studied by SEM images of selected zones of probe fracture surfaces. Samples were sputter coated with a thin gold layer, and images were obtained with a Philips XL 30 instrument.

RESULTS AND DISCUSSION

Raw Material Composition

The chemical composition of *Cytisus scoparius* samples, expressed as weight percent (oven dry basis) was as follows: ash, 0.78; ethanol extractives, 9.13; cellulose (as glucan), 40.9; xylan, 16.8; araban, 2.1; Klason lignin, 26.6; acetyl groups, 3.8; and acid soluble lignin was negligible. These values correspond to the averages of triplicate determinations. The SCAN viscosity of the raw material was 450 mL/g.

The cellulose content of samples was in the range reported for related species, as *Chamaecytisus proliferus* (Díaz et al. 2004) or *Spartium juncis* (Angelini et al. 2000), whereas the contents of extractives and lignin were slightly higher than those of related species and hardwoods, reaching similar values to those reported for softwoods. The ash content was comparatively low.

Milox Pulping

Table 3 lists the experimental results obtained for variables y_1 to y_6 (defined in Table 1) in experiments 1 to 15, whereas Table 4 shows the values of the regression coefficients calculated from experimental data for the models describing the behaviour of the main variables involved in pulping (cellulose content of pulp y_1, xylan content of pulp y_2, formyl groups content of pulp y_3, lignin content of pulp y_4, pulp yield y_5, and viscosity y_6), as well as their statistical significance on the basis of a t-test. The same Table includes the statistical parameters measuring the correlation and the statistical significance of the models. The high values of the Fischer´s F parameter confirmed the validity of the developed models.

Table 3. Experimental Results Obtained in Experiments 1 to 15 Expressed in Terms of the Dependent Variables y_1 to y_6

Experiment	y_1 Cellulose (%)*	y_2 Xylan (%)*	y_3 Formyl groups (%)*	y_4 Lignin (%)*	y_5 Pulp yield (%)*	y_6 Viscosity (mL/g)
1	82.5	5.3	6.1	7.7	42.1	566
2	79.9	5.5	6.2	9.4	44.5	546
3	72.5	7.5	6.2	10.7	49.0	597
4	73.5	7.5	6.1	9.8	46.4	576
5	79.8	7.4	6.4	7.5	44.0	594
6	79.4	7.5	6.3	7.7	44.7	569
7	80.0	7.2	6.4	7.8	43.9	579
8	79.5	8.3	4.6	10.2	43.8	599
9	71.3	9.6	4.7	13.6	48.2	604
10	66.1	11.5	4.4	14.7	50.7	622
11	76.3	9.2	4.7	10.0	45.5	631
12	76.2	4.9	9.4	7.9	44.6	549
13	76.2	5.1	9.3	7.9	43.5	595
14	72.6	5.2	9.5	9.4	45.0	606
15	69.5	7.1	9.0	10.4	49.3	598

* See Table 1 for definition

Cellulose content

The calculated dependence of the cellulose content of pulps (variable y_1) on the most influential operational variables (the reaction time of the second stage t_2 and the formic acid concentration *FAC,* this one by the quadratic term) is shown in Fig. 1. The highest cellulose content (82.5%) was obtained in experiment 1, which was performed in media containing 85 weight percent of formic acid at the highest values assayed for both reaction time of the second stage (t_2) and the hydrogen peroxide concentration (*HPC*). The maximum value predicted by the model for y_1 (83.7%) corresponded to the same operational conditions. Variable y_1 presented a limited variation range (from 79.8 to 83.7) in the *HPC* range studied (corresponding to 85.9 to 86.7 cellulose remaining in solid, being the maximum value obtained for *HPC*=3%). A preliminary analysis of experimental data confirmed that delignification was very selective, with low cellulose solubilization, as reported in the literature. The percents of cellulose recovery in the whole set of experiments, calculated from the experimental data of pulp yield and cellulose content of Milox pulping, were in the range 79.7 to 86.8%, with an average value of 84.3%. The model for this variable shows the same variation trends as that shown for cellulose content with *FAC* and t_2. These values are slightly lower than has been reported for hardwoods such as aspen (Abad 2000) or *Eucalyptus* (Abad 2001).

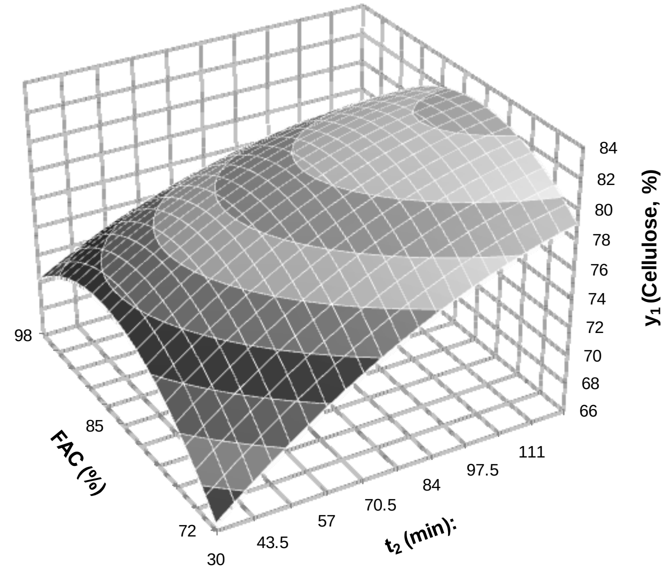

Fig. 1. Calculated dependence of the cellulose content of pulps (variable y_1) on the reaction time of the second stage (t_2) and on the formic acid concentration (*FAC*) for experiments performed at *HPC*= 3%

Xylan content

The xylan content of pulps (variable y_2) showed a marked dependence on t_2 and *FAC*. The model predictions (shown in Fig. 2) gave a close reproduction of the experimental results (see Table 3). Variable y_2 reached values of 5 to 6 weight percent of xylan under the severest conditions assayed. The percentages of xylan removal in treatments were in the range 65.5-87.0%, with an average value of 80.1%. These results proved the ability of the studied process to cause extensive xylan removal under conditions defined by high formic acid concentration and long treatment times. Under the experimental conditions of experiment 12 (corresponding to maximum values of t_2 and *FAC*), arabinan accounted for 0.28 weight percent of samples, with about 95% araban removal.

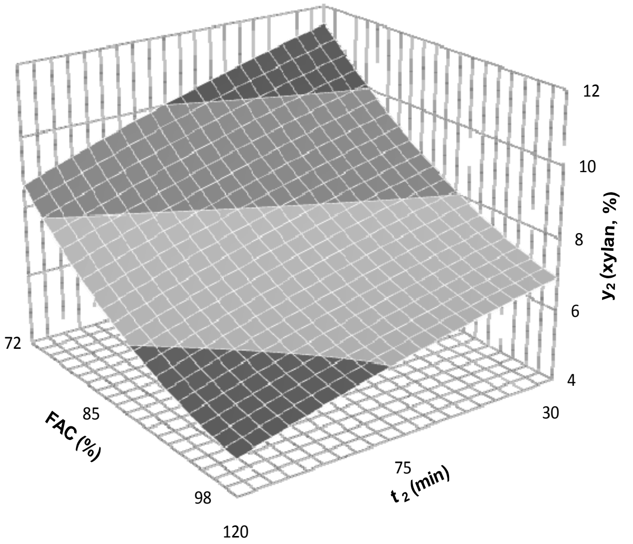

Fig. 2. Calculated dependence of the xylan content of pulps (variable y_2) on the reaction time of the second stage (t_2) and on the formic acid concentration (*FAC*) for experiments performed at *HPC*= 3%

Formyl groups

The content of formyl groups (variable y_3) was mainly affected by the formic acid concentration, as it can be inferred from the values of the coefficients shown in Table 4. This variable increased markedly with *FAC*, with variations of minor importance associated to t_2 and *HPC*. Within the studied variable range, the maximum contents of formyl groups (9.0-9.5%) corresponded to experiments 12-15, carried out at *FAC* = 98%. The acetyl groups content presents low values and variation range (from 0.3 to 1.3%), decreasing when t_2 or *FAC* increases. In the MILOX treatments an important deacetylation occurs (82-97% of original acetyl groups are removed) with the parallel incorporation of formyl groups.

Lignin content

The lignin content of pulps (variable y_4) was significantly affected by all of the independent variables. Figure 3 shows the calculated dependence of the lignin content of pulps on the most influential variables (t_2 and *FAC*). According to the signs and values of the coefficients in Table 4, the extent of delignification increased with the severity of the operational conditions. Considering the composition of the raw material and the models developed for both pulp yield and lignin content of pulps, the percentage of lignin removal reached in experiments can be easily calculated. More than 85% lignin removal was reached within a wide zone of the experimental domain. The lignin content of pulps varied in the range 7.6 to 14.7 weight percent, with an average value of 9.7%. Under harsh conditions, pulps with 7 to 8% lignin were obtained, corresponding to 72 to 88% lignin removal. These results proved the ability of treatments for extensive delignification.

Table 4. Regression Coefficients, Significance and Statistical Parameters Measuring the Correlation and Significance of Models Obtained for Variables y_1 to y_6

Parameter	y_1 Cellulose (%)	y_2 Xylan (%)	y_3 Formyl groups (%)	y_4 Lignin (%)	y_5 Pulp yield (%)	y_6 Viscosity (mL/g)
b_{0j}	79.8**	7.43**	6.41**	7.71**	44.2**	580.6**
b_{1j}	4.57**	-1.19**	0.0629	-1.28**	-2.55**	-16.7**
b_{2j}	1.54**	-0.0957	-0.0590	-0.968**	-1.15**	1.89
b_{3j}	0.168	-2.04**	2.34**	-1.60**	-0.718*	-13.7**
b_{12j}	0.389	-0.0374	0.0007	-0.198	0.054	10.4
b_{13j}	-1.68**	0.223	0.0483	0.493	0.537	-6.36
b_{23j}	-0.323	0.0571	-0.0779	0.505	0.325	-9.59
b_{11j}	-1.95**	-0.144	-0.192**	1.16**	1.43**	-13.2*
b_{22j}	-0.674	-0.782**	-0.0177	0.586	-0.123	3.85
b_{33j}	-4.94**	0.695**	0.696**	1.98**	1.45**	24.6**
*Significant coefficients at the 90% confidence level.						
**Significant coefficients at the 95% confidence level.						
R^2	0.9832	0.9930	0.9990	0.9615	0.9525	0.9310
F exp	33	79	575	13	11	7.5
Significance level	>99%	>99%	>99%	>99%	>99%	>98%

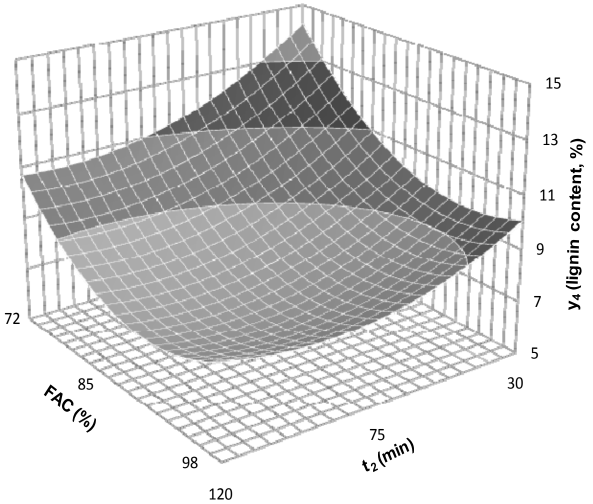

Fig. 3. Calculated dependence of the lignin content of pulps (variable y_4) on the reaction time of the second stage (t_2) and on the formic acid concentration (*FAC*) for experiments performed at *HPC*= 3%

Pulp yield

Several phenomena are responsible for the weight loss of the solid phase during treatments, including extractive removal, delignification, and hydrolysis of both hemicellulose and cellulose. Despite the limited variation range determined for pulp yield (variable y_5), the empirical model provided a good interpretation of the experimental data, and showed that the reaction time of the second stage (t_2) and the hydrogen peroxide concentration (*HPC*) were the most influential factors on y_5. The variation range and the general trends of the experimental results matched fairly with the model predictions. Pulp yield decreased mainly in the first 75 min of treatment, with minor variations being reached at longer treatment times. The lowest experimental pulp yield (42.1%) corresponded to experiment 1, which was performed at the highest values assayed for both reaction time of the second stage and hydrogen peroxide concentration.

SCAN viscosiy

The SCAN viscosity of treated solids is a variable of primary importance to quantify the depolymerization of cellulose caused by treatments, since the molecular weight distribution is a key factor for many final applications, particularly those limited by the strength of fibers. Viscosity of treated fibers presents higher values than the viscosity of original fibers. This can be explained by the selective removal of the hemicellulosic fraction. Further variations are related to cellulose hydrolysis during the Milox process. The model for viscosity showed major effects related to variations in the reaction time of the second stage (t_2) and in formic acid concentration. As expected, viscosities (in the experimental range 631-546 mL/g) decreased with the time of the second stage, with minor variation up to 75 min. In comparative terms, the viscosities reached in this work are slightly lower than the acceptable limits for unbleached pulps to be employed for dissolving pulp production (Dapía et al. 2000), but higher than the values reported for the Milox pulping of herbaceous plants like cardoon (Ligero et al. 2008)

Production of Biodegradable Composites Made up of PLA and Reinforcing Agents from *Cytisus scoparius*

MILOX pulping can be conceived as an environmentally friendly technology for biomass fractionation, owing to its ability to remove an important part of lignin and hemicelluloses, leading to a solid enriched in cellulose (which remains in the solid phase with little chemical alteration).

Based on the experimental trends discussed above for pulp yield, pulp composition, and SCAN viscosity, the operational conditions corresponding to the central point of the experimental design were selected to obtain the amount of MILOX fibers needed to assess its potential as a reinforcing agent for the manufacture of biodegradable composites. Considering the viscosity, their values represent an important decrease when time is higher than 75 min. If *FAC* is considered, it will be better to work with the lower value to obtain better viscosities, but this affects negatively in the cellulose content (that presents the highest value at *FAC*= 85%), and lignin and xylan removal. *HPC* presents a comparatively lower influence, favouring delignification mainly up to 3.5%, and maximum values for cellulose remaining in solid are obtained also at values close to 3%.

For comparative purposes, untreated *Cytisus scoparius* samples were also tested as reinforcing agents.

One of the crucial factors to be considered in composite formulation is the proportion of polymer matrix replacement by reinforcement agents. Usually, the strength increases with the reinforcement content up to a given threshold, which depends on the case studied. Even if percentages of replacement as high as 50% have been cited in the literature (Sriburi and Ogawa 2006), the usual maximum degree of replacement lies around 30% (Cunha et al. 2006; Huda et al. 2005). In our case, 20% of reinforcement was selected because higher percentages led to processability limitations.

Mechanical properties

Table 5 presents the experimental results obtained in the tensile tests. The moduli of composites made up of broom samples and MILOX-treated broom were 2.70 and 2.68 GPa respectively (increases of around 40% with respect to the neat PLA). The results show that the tensile strength of composites containing broom fiber and MILOX-treated broom composites presents similar values that correspond to a decrease around 16% with respect to non-reinforced samples. These results show that reinforcing agents were effective in terms of stiffness gain, and that the tensile strength decreased upon incorporation of reinforcements in the polymer matrix, which reduce the ability of the composites to transfer the applied stress. In general, the presence of reinforcing agents resulted in increased brittleness, with longer elongation for virgin PLA samples (4.63% as an average) than for composites, which presented similar values (2.7 to 2.9% strain at break).

According to the literature data reported for thermoplastic-cellulosic fiber composites obtained by injection moulding, generally the modulus is expected to increase significantly with respect to the unfilled polymer, whereas the tensile strength remain unaffected, and elongation is expected to be reduced significantly (Georgopoulos et al. 2005). In this study, these general trends have been confirmed experimentally for the behaviour of the modulus and elongation, but the tensile strength decreased in comparison to pure PLA. The decrease in tensile strength was smaller for MILOX-treated broom, the reinforcing agent with the highest cellulose content.

Impact strengths for composites were slightly higher than that of neat PLA, corresponding to increases of 16 and 5% for composites made up of broom samples and MILOX-treated broom, respectively.

Table 5. Mechanical Properties of Composites and Neat PLA Probes Measured by Tensile Test and Charpy Impact Test (mean values and standard deviations)

Composite	Tensile strength (MPa)	Young Modulus (GPa)	Strain at break (%)	Impact strength (J/m)
PLA	56.3 ± 0.9	1.91 ± 0.09	4.6 ± 0.3	12.3 ± 0.8
PLA +Broom	46.7 ± 1.2	2.70 ± 0.09	2.7 ± 0.2	14.2 ± 0.8
PLA +Milox Broom	47.5 ± 1.5	2.68 ± 0.03	2.9 ± 0.2	12.9 ± 1.5

DSC analysis

Figure 4 presents DSC data for PLA and composites made up of PLA and MILOX-processed broom. Both samples were characterized by a glass transition temperature (T_g), a crystallization zone, and a melting peak, which are typical for semi-crystalline polymers. In the first heating, neat PLA and Milox broom composite showed differences in the crystallization zone, occurring mainly at temperatures close to that of the glass transition temperature in neat PLA, (75-110 ºC), whereas the crystallization process occurred steadily up to melting in Milox broom composites. The values of T_g, T_m, enthalpy of pre-melt crystallization, ΔH_C, enthalpy of melting, ΔH_m, and crystallinity are listed in Table 6. In the second heating it can be noted that the thermal properties of the polymer were minimally influenced by the reinforcement, with similar values of T_g, pre-melt crystallization, and melting enthalpies, and close melting temperatures (152.5 ºC for neat PLA in comparison to 154.3 ºC for the composite). The peaks corresponding to pre-melt crystallization and melting had quite similar areas, indicating that the material had no crystallinity at the beginning of the second heating analysis, even considering the low cooling rate used in the previous stage.

TGA data showed that PLA began to disintegrate at 300 ºC, and that disintegration was practically complete at 380 ºC. In the case of composites containing MILOX-processed broom, around 90% disintegrated in the same manner, appearing as a second disintegration stage around 500 ºC.

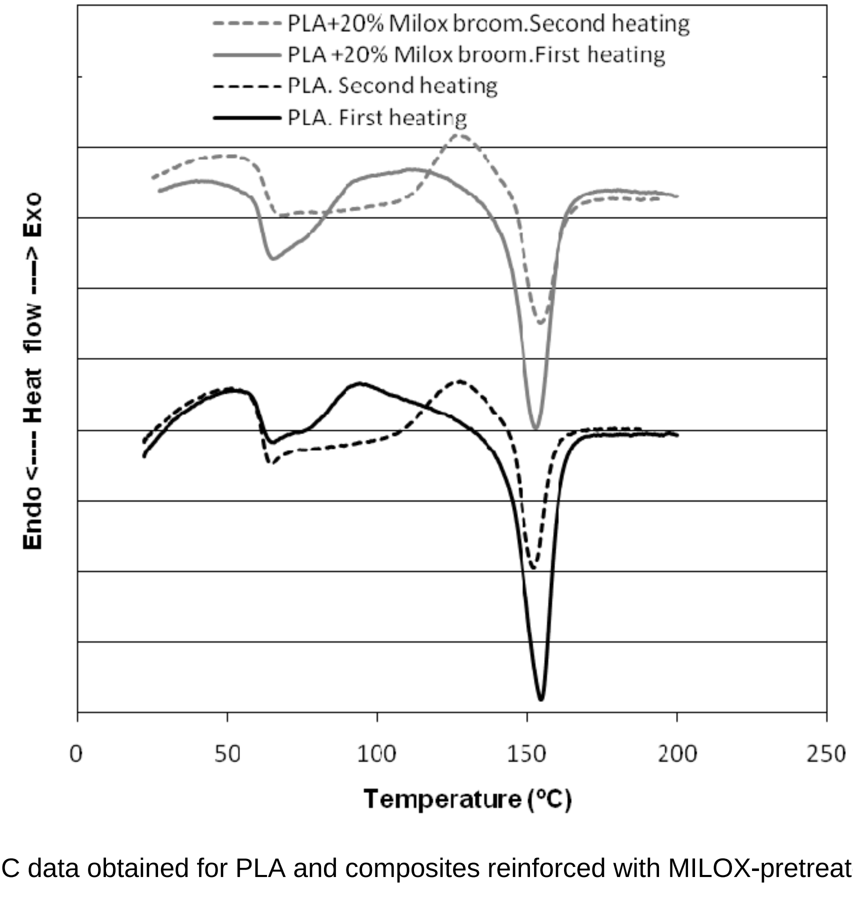

Fig. 4. DSC data obtained for PLA and composites reinforced with MILOX-pretreated *Cytisus scoparius*

Table 6. Thermal Properties Determined by DSC

Sample	Tg (ºC)	Tm (ºC)	ΔH_C (J/kg)	ΔH_m (J/kg)	Crystallinity (%)
PLA	60.3	154.4	14.8	27.6	13.8
PLA +Milox Broom	61.2	152.9	15.5	24.7	12.4

SEM analysis

The matrix–filler interface plays a critical role for ensuring that the properties of each component contribute optimally to the properties of the final product. The outcome is affected by a number of factors, including the nature of interfaces, the operational conditions (which may result in thermal degradation), and superficial chemical changes (which could affect the bulk properties adversely). In this work, the interfacial compatibility was assessed by SEM of the rupture surface of composites reinforced with unprocessed and MILOX-processed broom. Figure 5 shows the corresponding images. In the case of broom fibers a good impregnation of fibers is observed, and in some cases fibers were broken upon the tensile stress. Matrix presents cracks at some points. The lack of volatile components in the Milox fibers, together with the mild conditions employed in extrusion-injection processing, are factors that could contribute to a good compatibility between phases. In microphotographs the presence of holes can be observed; these were formed from pull-outs of fibers and damage of fibers, in relation with the lower mechanical properties determined with respect to unreinforced matrix.

Water absorption

One of the most important limitations of vegetable fibers for composite formulation is their dimensional instability due to moisture absorption. This phenomenon is mainly caused by the hydrogen bonding between water molecules and the hydroxyl groups present in the cellulose structure. A strong fiber/matrix interfacial adhesion can help to avoid the water penetration reducing the hygroscopicity, and, consequently, the worsening in the mechanical performance of materials. Figure 6 shows the time course of water uptake by neat PLA and composite probes. Neat PLA presented low water absorption, but the percentage of water absorption increased with the presence of reinforcement, as reinforcement increases the overall polarity. Composites made up of broom presented a high percentage of water absorption, about 8%. Swelling of composites containing broom fibers was visually observed, with a superficial roughness detectable by touch.

Composites containing MILOX-treated broom show lower percentage of retained water than untreated fiber composites, a fact possibly related to the presence of formyl groups, less hydrophylic than hydroxyl groups, and superficial lignin. Dimensional stability and flat surface were clearly observed.

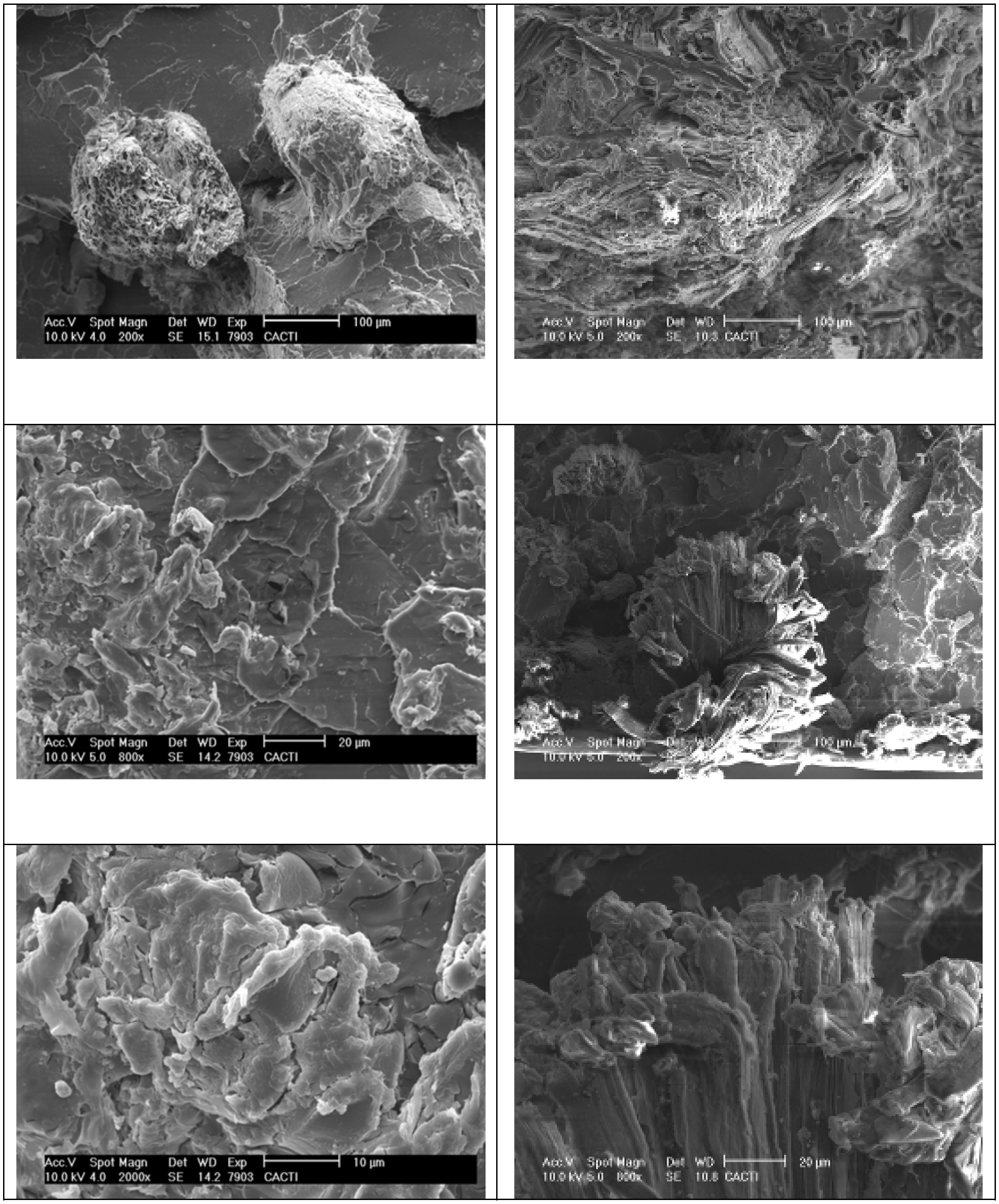

Fig. 5. SEM images of tensile fracture surfaces of PLA composites reinforced with broom (left) and Milox broom fibers (right)

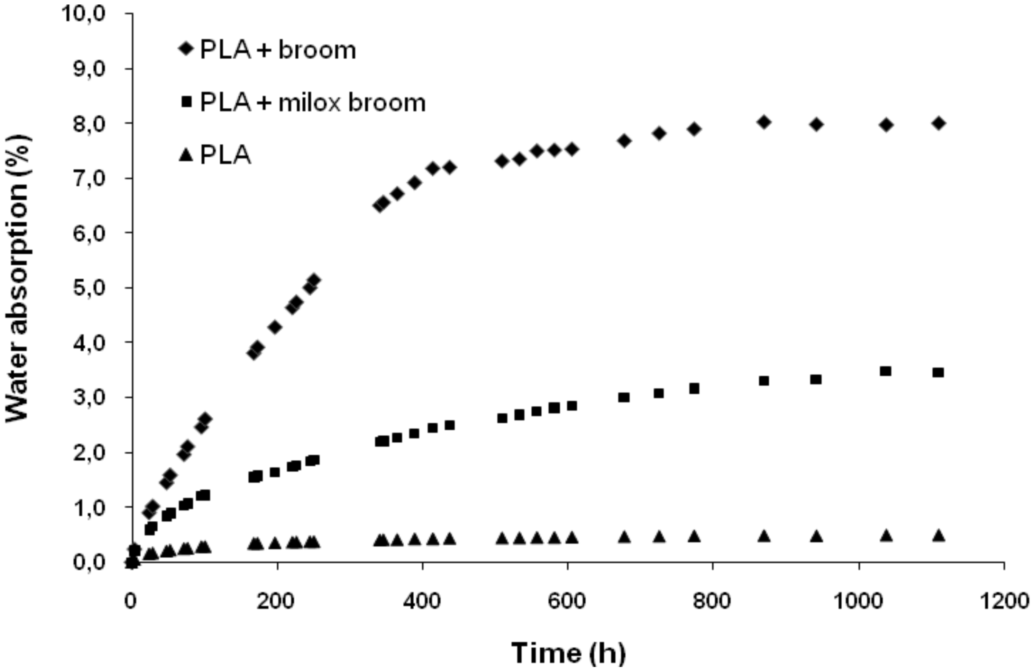

Fig. 6. Percentage of water absorption in the assayed composites

CONCLUSIONS

1. Two-stage pulping of *Cytisus scoparius* in peroxyformic acid media was assesed by Response-Surface Methodology. Phenomenological equations derived from experimental data provided a good interpretation of the dependence of experimental variables on selected operational parameters.
2. Samples obtained under selected operational conditions were assayed as reinforcing agents for PLA-based composites manufactured by injection molding. Reinforcement resulted in a stiffer material, with a decrease in the tensile strength, and little variations for impact strength.
3. Reinforcement with MILOX-processed samples was effective for reducing the percentage of water absorption respect to untreated broom samples reinforcement.
4. Reinforcement did not affect thermal properties of PLA significantly.

ACKNOWLEDGMENTS

The authors are grateful to the Spanish Ministry of Science and Innovation for supporting this study, in the framework of the research Project “Properties of new prebiotic food ingredients derived from hemicelluloses” (reference AGL2008-02072, which was partially funded by the FEDER Program of the European Union).

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Article submitted: September 7, 2010; Peer review completed: October 2, 2010; Revised version received and accepted: October 18, 2010; Published: October 19, 2010.