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Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams

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ABSTRACT

The influence of formulation variables of wood flour-reinforced phenolic foams (WRPFs) on density, compressive mechanical properties and morphology of the material was studied applying an experimental design. Variables studied were wood flour weight fraction (1.5–8.5 wt.%) and blowing agent amount (1.5–3.5 wt.%). The responses were apparent density and compressive modulus and strength of the material. Morphology of the foams was also observed using scanning electron microscopy and cell size distributions of the materials were determined. The incorporation of 1.5 wt.% of wood flour in phenolic foams leads to obtain a reinforced material with a compressive modulus and strength 130% and 154% of the values of the unreinforced foam, respectively, as well as to reduce blowing agent amount required for foam preparation.

1. Introduction

Filler-reinforced plastic composites market is dominated mainly by inorganic fillers such as calcium carbonate and glass fibers. In the last decade, natural fibers have attracted the attention of many researchers because they offer a great number of advantages compared to most conventional inorganic fillers such as high specific properties, low density, renewability, recyclability, biodegradability, good thermal and acoustic insulating properties and low cost [1–4]. Wood flour is one the most extensively used natural fiber due to its high mechanical properties and low density compared to other natural fibers. Wood is made up of cellulose, hemicelluloses, lignin and extractives and composed by fibrous hollow cells, which are arranged parallel each other along the trunk of the tree [5]. Several works have demonstrated improvements in material properties when wood flour or fibers were incorporated [6,7].

Phenolic foams are mainly used as insulating and structural materials in applications where fire resistance is critical such as buildings, aircrafts and so forth. These materials exhibit exceptional fire properties, low thermal conductivity, high thermal stability over a broad range of temperatures and low cost and density compared to other polymeric foams [8,9]. However, phenolic foams show high friability and relatively low mechanical performance [10–14]. Some authors have been focused on improving mechanical properties of these materials using inorganic fillers as reinforcements. The incorporation of aramid and glass fibers in phenolic foams has been found to increase mechanical performance of this material [10,11,13–15]. Nevertheless, the incorporation of natural fibers and in particular wood flour in phenolic foams has not been widely studied. The combination of wood flour and phenolic foams properties could provide a composite material with very interesting features for insulating and structural applications.

Several works have demonstrated the utility of experimental design to study the formulation of composite phenolic foam systems. For instance, Desai et al. [11] analyzed the influence of density and fiber weight fraction on compressive modulus and strength of glass fiber-reinforced phenolic foams applying a 2^2 experimental composite design with one central point. In a previous work, we studied the influence of lignin weight fraction and blowing agent amount on density and mechanical properties of lignin nanoparticle-reinforced phenolic foams using a 2^2 experimental composite design with 3 central points and 4 star points [16].

The aim of the present work is to study the influence of wood flour weight fraction and blowing agent amount on apparent density and compressive mechanical properties of wood flour-reinforced phenolic foams (WRPFs) and determine the improvement achieved in relation to the unreinforced material. The effect of the variables studied on WRPF morphology was also assessed using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and synthesis of the foams

Wood incorporated in phenolic foams was softwood *Pinus radiata* industrial chips provided by the Instituto Nacional de

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Investigación y Tecnología Agraria (CIFOR-INIA). Wood flour was obtained milling the chips in a mill *Retsch MM301* for 2.5 min at 30 Hz and sieved to a size lower than 0.15 mm. Wood flour particle size was selected with a value similar to that employed in reported works of wood polymer composites [17,18]. The phenolic resol resin and hardener (ACE 1035) used for foams preparation were supplied by Momentive Specialty Chemicals. Surfactant, catalyst, and blowing agent employed were Tween® 40 (Sigma Aldrich), phenol-4-sulfonic acid (Sigma Aldrich) and n-pentane (Panreac), respectively. The foams were synthesized with a phenolic:surfactant:catalyst:blowing agent:hardener ratio of 100:2:4:1.1–3.9:20 (by weight) according to a previous work [16]. The components were mixed with a mechanical stirrer and then, the blend was poured into a mold and cured for 1 h at 80 °C and post-cured for 24 h at 105 °C.

2.2. Experimental design

In the present work, a 2^2 central composite experimental design (11 runs: $2^2 + 3$ center points + 4 star points) was employed to study the influence of formulation variables on WRPF properties. The variables studied were wood flour weight fraction (W) and blowing agent amount (B) and their ranges were 1.5–8.5 wt.% and 1.5–3.5 wt.% (both referred to the mass of the resin), respectively. The responses measured for model development were apparent density (ρ), compressive modulus (E) and compressive strength (σ_c). Experimental conditions and results obtained for the experimental design are summarized in Table 1. The data were fitted to a second degree quadratic equation (Eq. (1)) as a function of the independent variables:

$$Z = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{11}X_1^2 + b_{22}X_2^2 \quad (1)$$

where Z are the responses measured (apparent density and compressive modulus and strength), X_1 and X_2 are the factors studied (wood flour weight fraction and blowing agent amount) and b_1, b_2, b_{12}, b_{11} and b_{22} are the regression coefficients. Analysis of variance (ANOVA) for experimental results was employed to reject non-significant effects from the model regression and to check the suitability of the models. Finally, contour maps were plotted in order to study graphically the influence of the factors within the ranges considered. Data processing was performed using *Statgraphics Centurion XV*.

In addition, scanning electron microscopy (SEM) was used to observe the morphology of the foams as well as to determine how the variables studied affect foam cell size distributions.

Table 1
Experimental conditions and results for WRPFs.

Run	W (%)	B (%)	ρ (kg/m^3)	E (MPa)	σ_c (MPa)
1	5	2.5	112.0	9.76	0.437
2	5	3.91	88.5	7.67	0.309
3	1.5	3.5	112.3	13.60	0.513
4	1.5	1.5	164.5	35.88	1.449
5	8.5	3.5	98.0	6.85	0.281
6	5	2.5	106.9	10.60	0.423
7	8.5	1.5	140.2	23.27	0.801
8	5	1.09	194.9	42.02	1.719
9	0.05	2.5	143.4	34.03	1.271
10	9.95	2.5	111.6	15.12	0.520
11	5	2.5	106.5	10.00	0.408

2.3. Apparent density

Apparent density was determined in accordance with ASTM D1622 [19]. The samples were cut in cubic specimens with a keyhole saw Bosh PST 900 PEL and polished with a Buehler MetaServ® 3000 polisher to a size of 2.54 cm. A minimum of five replicates of each sample were measured.

2.4. Compression tests

Compression tests were performed in accordance with ASTM D1621 using a universal testing machine (Zwick/Roell Z030) [20]. The same specimens employed for apparent density measurements were placed between stainless steel plates and a load was applied uniformly with a crosshead rate of 2.5 mm/min. Compressive strength was determined as the maximum value of the stress-curve obtained (strain <10%) and compressive modulus was calculated as the slope of the curve. A minimum of five replicates of each sample were tested.

2.5. Scanning electron microscopy

Morphology of specimens was observed with a scanning electron microscope JEOL JSM-6400 operating at 40 kV of voltage. The samples were introduced in liquid nitrogen and fractured. Finally, gold sputtering were carried out on the surface of the samples in order to impart them electrical conductivity.

3. Results and discussion

3.1. Density and mechanical properties of WRPF

The results obtained for apparent density of WRPF were ranged from 88.5 to 194.9 kg/m^3, as shown Table 1. The ANOVA for density, which was carried out with a significance level of 95%, is shown in Table 2. The factors with a distribution $F < 18.51$ and P-values > 0.05 exhibit statistical significance level lower than 95% for apparent density and they must be rejected from the ANOVA, as occurs with effect WB. The model for density (ρ) of WRPF with all significance effects is given by the following equation:

$$\rho\ (\mathrm{kg/m^3}) = 311.018 - 9.54662 \cdot W - 106.36 \cdot B + 0.656354 \cdot W^2 + 15.1529 \cdot B^2 \quad (2)$$

Density of WRPF decreased when wood flour weight fraction and blowing agent amount were increased (Fig. 1). The reduction in foam density when wood flour weight fraction increases can be due in part to the performance of wood flour as a nucleant agent, which favors the formation of bubbles in the foams. Fillers and reinforcing fibers can act as nucleant agents in the foaming process of polymeric foams [21,22]. When the amount of blowing agent was increased, the gas content in the formulation mixture rose, increasing gas/solid phase ratio in the foams and thus, decreasing their densities [23].

The results obtained for compressive modulus and compressive strength of WRPFs are ranged from 6.85–42.02 to 0.281–1.719 MPa, respectively, as shown Table 1. The ANOVA method for compressive modulus and strength was carried out with a significance level of 95% and are shown in Table 2. All effects had statistical significance for these responses. The models for compressive modulus and strength are given by the following equations:

$$E\ (\mathrm{MPa}) = 101.671 - 7.61369 \cdot W - 43.8121 \cdot B + 0.4919041 \cdot W^2 + 0.419357 \cdot WB + 6.1611 \cdot B^2 \quad (3)$$