STUDY OF LIGNIN NANOPARTICLE-REINFORCED PHENOLIC COMPOSITE FOAMS FORMULATION USING AN EXPERIMENTAL DESIGN

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Abstract

The formulation of lignin nanoparticle-reinforced phenolic composite foams (LRPF) was studied using an experimental design. The variables anaylzed were lignin nanoparticle weight fraction (wt.%) and blowing agent amount (1.5-3.5 wt.%) and the responses analyzed were apparent density and compressive modulus and strength. In addition, characterization of lignin nanoparticles incorporated in the material was carried out. Apparent density and compressive modulus and strength decreased as lignin nanoparticle weight fraction and blowing agent amount were increased. The greatest compressive mechanical properties of LRPF were obtained when 8.5 wt.% of lignin nanoparticles was incorporated. Compressive modulus and strength of LRPF were improved and the amount of blowing agent necessary to produce a LRPF was reduced compared to unreinforced phenolic foams.

1 Introduction

Phenolic foams are often used as insulation in applications where fire resistance is critical because they show very advantageous features such as, low thermal conductivity, high thermal stability, excellent fire properties and relatively low cost [1]. In contrast, phenolic foams exhibit low mechanical performance compared to other polymeric foams and the improvement of mechanical properties of phenolic foams with the incorporation of inorganic fillers such as aramid and glass fibers have been studied and reported in literature [2]. In recent years, the interest in developing more environmental-friendly materials has led many studies to be focused on improving performance of polymeric materials with the incorporation of bio-based reinforcements, such as natural fibers (e.g. cellulose, kenaf) and particles (e.g. wood flour, lignin) [3, 4].

Lignin is a natural heteropolymer, which exhibits low density, high availability and low cost [5]. The use of lignin in the synthesis of polymeric materials is the most promising alternative for the revalorization of lignin. Many works have demonstrated obtaining blends of lignin and thermoplastic materials with great thermal and mechanical performance [6, 7]. Regarding phenolic materials, investigations have been mainly focused on the substitution of phenol by lignin in the formulation of lignin-phenol-formaldehyde resins due to the similarity of their structures. Nevertheless, the incorporation in lignin as reinforcement in phenolic composites has not been widely reported yet.

Experimental design is a useful statistical tool, which allows reducing the runs required for study a system. Several researches have demonstrated the utility of applying experimental design to study composite foams formulation [2, 8]. The aim of this work is to study the formulation of lignin nanoparticle-reinforced phenolic composite foams (LRPFs) using an experimental design in order to analyze the influence of the formulation variables on foam properties, determine the optimal amount of lignin nanoparticle for the formulation of the material and evaluate mechanical improvements obtained in phenolic foams with the incorporation of lignin nanoparticle. In addition, the previous characterization of lignin nanoparticles was carried out in order to determine its suitability as filler in phenolic foams. In the present work a summary of the results obtained for the formulation of LRPFs published in a previous work [9] and the results for the characterization of lignin nanoparticle incorporated in phenolic foam are presented.

2 Materials and testing methods

2.1 Materials and synthesis of the foams

Foams were prepared using a phenolic resol resin and a hardener (ACE 1035) supplied by Momentive Specialty Chemicals; Tween® 40 (Sigma Aldrich), was used as surfactant , phenol-4-sulfonic acid (Sigma Aldrich) as catalyst, and n-pentane (Panreac) as blowing agent. Lignin nanoparticles were calcium softwood lignosulfonates with an average diameter of 1.6 μm (Lignotech Ibérica). LRPFs were prepared with a phenolic:surfactant:catalyst:blowing agent:hardener ratio of 100:2:4:1.1-3.9:20 (by weight). Lignin nanoparticles where mixed with the resol resin in a previous step and then, the rest of the components were incorporated. Later, the blend was poured into a mold and held for 1 h at 80 ºC and post-cured for 24 h at 105 ºC [9].

2.2 Characterization of lignin nanoparticles

Lignin nanoparticles incorporated in phenolic foams were characterized in terms of moisture, lignosulfonates content (UV-VIS spectrophotometer Varian Cary 1E) and crystallinity (DRX, spectrometer XPERT-PRO). Fourier transform infrared spectroscopy (FTIR) analysis was performed using a spectrophotometer Mattson Satellite. Differential scanning calorimetry (DSC) was performed employing a DSC821^e Mettler Toledo and thermogravimetric analysis (TGA) using a TGA/SDTA 851^e Mettler Toledo. In addition, lignin nanoparticles was observed employing a scanning electron microscope JEOL JM-6400.

2.3 Experimental set-up and procedure

The study of LRPF formulation was carried out applying a 2^2 composite experimental design with 3 central points and 4 star points (11 runs). The factors studied were lignin nanoparticle weight fraction (*L*) and blowing agent amount (*B*), and their respective ranges were 1.5-8.5 wt.% and 1.5-3.5 wt.% (both relative to the mass of the resin). The responses measured were apparent density (kg/m^3), compressive modulus (*E*) and compressive strength (σ_c). The experimental conditions for the experimental design and the results obtained for apparent density and compressive modulus and strength of LRPFs are shown in Table1.

Run	*L* (wt.%)	*B* (wt.%)	ρ (kg/m^3)	*E* (MPa)	σ_c (MPa)
1	5.00	2.50	100.5	9.57	0.466
2	8.50	3.50	91.6	8.24	0.392
3	8.50	1.50	158.0	37.20	1.639
4	9.95	2.50	100.9	10.69	0.548
5	5.00	3.91	80.3	4.30	0.270
6	1.50	3.50	126.9	15.58	0.738
7	0.05	2.50	130.2	18.66	0.878
8	5.00	2.50	108.8	10.03	0.500
9	1.50	1.50	206.2	42.19	2.394
10	5.00	2.50	98.6	9.85	0.428
11	5.00	1.09	211.5	41.34	2.145

Table 1. Experimental conditions and apparent density and compressive modulus and strength of LRPFs

Statgraphics Centurin XV was used for performing data processing. Least squares method was applied to obtain quadratic models. The effects with no significance were rejected from the models using analysis of variance (ANOVA). Finally, contour maps of the responses were plotted in order to study the influence of the formulation variables on LRPF properties.

2.3 Apparent density

Apparent density was determined in accordance with ASTM D1622 [10]. The samples were cut in with a keyhole saw Bosh PST 900 PEL in cubic specimens and polished with a Buehler MetaServ® 3000 polisher to a size of 2.54 cm. Apparent density was determined for a minimum of five replicates of each sample.

2.4 Compression tests

Compression tests were performed in accordance with ASTM D1621 using a universal testing machine (Zwick/Roell Z030) [11]. Specimens employed for apparent density measurements were also used for compression tests. Compressive modulus was calculated from the slope of stress-strain curve and compressive strength was determined as the maximum value of the curve (strain < 10%). A minimum of five replicates of each sample were performed.

3. Results

3.1 Lignin nanoparticle characterization

The results obtained of the characterization of lignin nanoparticle employed in the formulation of LRPFs using several analyses are summarized in Table 2. Lignin is an amorphous polymer; therefore the lignin nanoparticle characterized exhibited a low value of crystallinity (44.7 %). As more amorphous is the filler incorporated in a composite, greater is the adhesion between the filler and the matrix. Regarding FTIR characterization of lignin nanoparticles, the higher intensity of the band 1512 than 1606 cm^{-1} is normally characteristic of softwood lignins [5]. Presence of polar groups, such as alcohols, ketones and aldehydes in lignins yields compatibility between lignin and polar polymer matrixes [12], as is the phenolic matrix of the LRPFs. Lignin nanoparticles exhibited peaks characteristics of polar groups, such as alcohols (3411, 1210 and 1039 cm^{-1} bands). This fact suggests that lignin nanoparticle and phenolic matrix employed in the formulation of LRPF may show a great compatibility.

Analysis	
Moisture	8.10
Lignosulfonate (%, w)	71.9
Crystallinity (%)	44.7
FTIR[a]	
Alcohol (O-H) 3411 cm^{-1}	1.417
Carbonyl 1710 cm^{-1}	0.698
C-C Aromatic 1606 cm^{-1}	1
C-C Aromatic 1512 cm^{-1}	1.112
Methyl and Methylene 1462 cm^{-1}	0.945
C-O Phenolic 1210 cm^{-1}	1.460
C-O primary alcohols and C=O 1039 cm^{-1}	1.642
DSC	
T_g (ºC)	120.3
TGA	
T_{onset} (ºC)	244.7
$T_{10\%}$ (ºC)	275.3
T_{max} (ºC)	300.7
Ash $_{900\ ºC}$ (%)	14.88

[a] normalized absorbances at $\lambda = 1606\ cm^{-1}$

Table 2. Characterization of lignin nanoparticle

The glass transition temperature (T_g) of lignin nanoparticle employed in the formulation of LRPFs is in the range of T_g for lignins reported in literature 85-180 ºC [13]. The results obtained by TGA show that lignin nanoparticles exhibit high thermal stability and the values determinated are similar and even greater to those reported in literature for industrial lignins [12]. The morphology of lignin nanoparticles is shown in the image obtained by SEM (Figure 1).

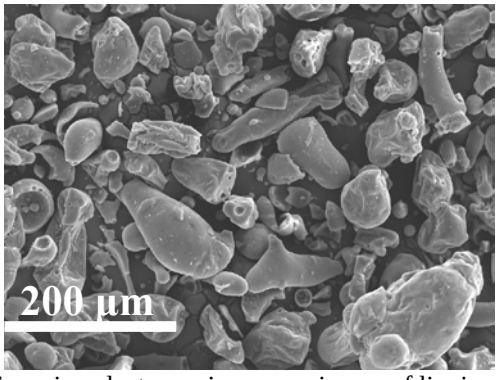

Figure 1. Scanning electron microscopy image of lignin nanoparticle

3.1 Lignin nanoparticle-reinforced phenolic foams

The influence of lignin nanoparticle weight fraction (*L*) and blowing agent amount (*B*) on apparent density (ρ), compressive modulus (*E*), and compressive strength (σ_c) was studied applying statistical methods. Results of apparent density (ρ) for LRPF were ranged from 80.33-211.5 kg/m^3, as summarized in Table 1. The ANOVA for apparent density of LRPF using a significance level of 95 % was applied and *LB* factor was rejected from the ANOVA for apparent density because had not significance. The model for apparent density as a

function of lignin nanoparticles weight fraction (*L*) and blowing agent amount (*B*) with all significant effects is given by Equation (1).

$$\rho\,(kg/m^3) = 407.92 - 12.7937 \cdot L - 168.344 \cdot B + 0.833433 \cdot L^2 + 25.3897 \cdot B^2 \quad (1)$$

R^2 = 95.24 %

The contour map for apparent density of LRPF is shown in Figure 2. When lignin nanoparticle weight fraction and blowing agent amount were increased, apparent density of LRPF were decreased. Lignosulfonates have surfactant properties [14], which favors bubbles nucleation [1]. Therefore, the amount of gas phase in the material was higher and its density decreased. As the amount of blowing agent in the formulation of the materials was increased the gas content in the foam increased [15] and hence, its density decreased.

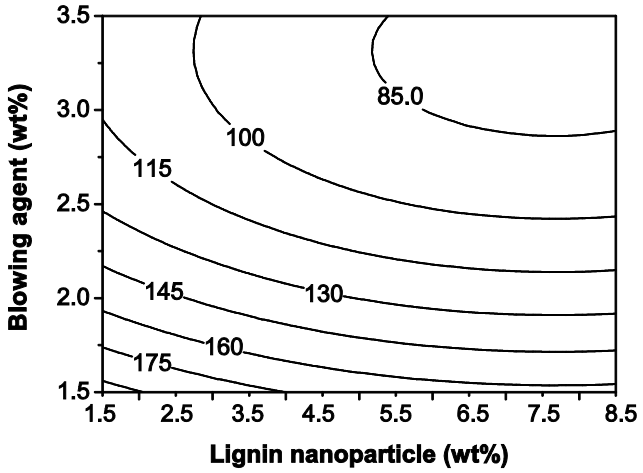

Figure 2. Contour map for density (kg/m^3) of lignin nanoparticle-reinforced phenolic foams.

Results obtained for compressive modulus (*E*) of LRPFs were ranged from 80.33-211.5 kg/m^3 (Table 1). ANOVA for compressive modulus (*E*) of LRPF was applied and all the factors exhibited a significance level higher than 95 % for compressive modulus; therefore, no one was rejected from the ANOVA. Statistical model for compressive modulus (*E*) as a function of lignin nanoparticle weight fraction (*L*) and blowing agent amount (*B*) with all significance effects is shown below:

$$E\,(MPa) = 105.884 - 3.84604 \cdot L - 53.9821 \cdot B + 0.342278 \cdot L^2 - 0.167857 \cdot LB + 8.26546 \cdot B^2 \quad (2)$$

R^2 = 95.03 %

Contour map obtained for compressive modulus of LRPF is shown in Figure 3. As lignin nanoparticle weight fraction and blowing agent amount increased, compressive modulus of LRPF decreased. This fact is due to a drop in foam density [2].

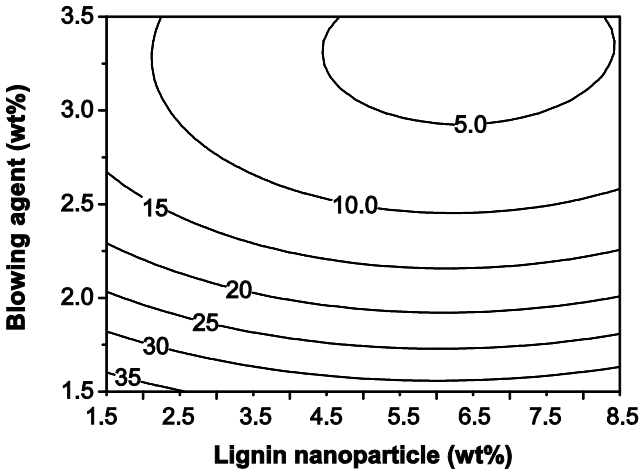

Figure 3. Contour map for compressive modulus (MPa) of lignin nanoparticle-reinforced phenolic foams.

Compressive strength obtained for LRPFs was ranged between 0.270-2.394 MPa (Table 1). ANOVA with a significance level of 95 % for compressive strength of LRPF was performed and as in the case of compressive modulus, for compressive strength all the factors exhibited a significance level higher than 95 %, hence, all of them were included in the model for compressive strength. The model for compressive strength as a function of lignin nanoparticle weight fraction and blowing agent amount is given by Equation (3).

$$\sigma_c\ (MPa) = 6.10491 - 0.297781 \cdot L - 3.1106 \cdot B + 0.0168889 \cdot L^2 + 0.0291786 \cdot LB + 0.454092 \cdot B^2 \quad (3)$$

$R^2 = 95.08\ \%$

Contour map for compressive strength of LRPF is presented in Figure 4. When lignin nanoparticle weight fraction and blowing agent amount were increased, compressive strength was decreased. As in the case of compressive modulus, this trend is due to a decrease in foam density [2].

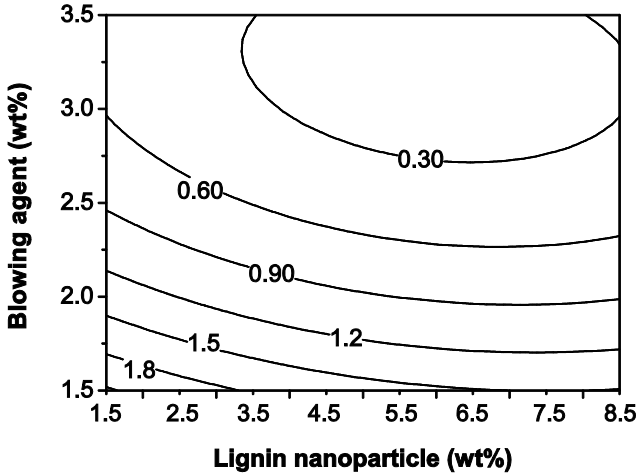

Figure 4. Contour map for compressive strength (MPa) of lignin nanoparticle-reinforced phenolic foams.

Combining Equations 1-3 can be determine that for a particular density ranged from 120-160 kg/m^3 (foams for insulating and structural applications), the greatest compressive modulus and strength is obtained at 8.5 wt.% of lignin nanoparticle, which was chosen as the optimal lignin nanoparticle weight fraction for the formulation of LRPF.

Compressive mechanical properties and blowing agent amount employed in the formulation of the foams predicted by Equations 1-3 for LRPF were compared with the respective values predicted by the models reported in a previous work for the unreinforced phenolic foam [9]. Compressive modulus and strength and blowing agent amount employed for the formulation of the materials for LRPF and the unreinforced phenolic foam of densities ranged between 120-160 kg/m^3 are summarized in Table 5.

	LRPF (8.5 wt.% of *L*)			**Unreinforced phenolic foam [9]**		
ρ (kg/m^3)	**E (MPa)**	**σ_c (MPa)**	**B (wt.%)**	**E (MPa)**	**σ_c (MPa)**	**B (wt.%)**
120	18.54	0.824	2.05	14.70	0.474	2.97
140	25.48	1.137	1.78	23.38	1.075	2.26
160	30.82	1.463	1.54	32.64	1.649	1.85

Table 5. Compressive modulus and strength and blowing agent amount employed in the formulation of the materials for LRPF formulated at 8.5 wt.% of *L* and the unreinforced phenolic foam at several densities.

Compressive modulus and strength of LRPF were highly improved with the incorporation of lignin nanoparticle in 120 kg/m^3 LRPF, as shown Table 5. Compressive modulus and strength predicted for 120 kg/m^3 LRPF are 128 and 174 % of the valued predicted for the unreinforced phenolic foam of this density, respectively. Improvements in compressive mechanical properties of 140 kg/m^3 LRPFs were negligible. Compressive mechanical properties of 160 kg/m^3 LRPF are not improved with respect to unreinforced phenolic foam of the same density (Table 5). The amount of blowing agent required for the formulation of LRPFs is lower than that required for the formulation of unreinforced phenolic foams in the range of density of 120-160 kg/m^3. The amount of blowing agent saved with the incorporation of lignin nanoparticle was to 31 %.

4. Conclusions

The influence of lignin nanoparticle weight fraction and blowing agent amount on apparent density and compressive mechanical properties of LRPF was studied applying an experimental design. In addition, the characterization of lignin nanoparticle incorporated in phenolic foams was carried out. Results showed that lignin nanoparticle exhibited appropriate physico-chemical characteristics for its incorporation in phenolic foams. Apparent density and compressive modulus and strength of LRPF decreased when lignin nanoparticle weight fraction and blowing agent amount were increased. The greatest mechanical compressive properties were obtained when 8.5 wt.% of lignin nanoparticle was incorporated in phenolic foam. Compressive modulus and strength values obtained for LRPF were up to 128 and 174 %, respectively, of the values for unreinforced phenolic foams. Moreover, the incorporation of lignin nanoparticle allow reducing blowing agent amount employed in the formulation of LRPFs up to 31 % with respect to unreinforced phenolic foam of the same density.

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