Effect of fiber loading on the properties of treated cellulose fiber-reinforced phenolic composites

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ABSTRACT

The effect of fiber loading on the properties of treated cellulose fiber-reinforced phenolic composites was evaluated. Alkali treatment of the fibers and reaction with organosilanes as coupling agents were applied to improve fiber–matrix adhesion. Fiber loadings of 1, 3, 5, and 7 wt% were incorporated to the phenolic matrix and tensile, flexural, morphological and thermal properties of the resulting composites were studied. In general, mechanical properties of the composites showed a maximum at 3% of fiber loading and a uniform distribution of the fibers in such composites was observed. Silane treatment of the fibers provided derived composites with the best thermal and mechanical properties. Meanwhile, NaOH treatment improved thermal and flexural properties, but reduced tensile properties of the materials. Therefore, the phenolic composite containing 3% of silane treated cellulose fiber was selected as the material with optimal properties.

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1. Introduction

Development of new composites reinforced with materials derived from renewable resources in substitution of synthetic compounds has increased during the last few years. Cellulose fibers are reinforcing materials with great potential for manufacturing environmental friendly composites. Light weight, low cost, recyclability, and resistance to the absorption of noise, are some of the main features of the cellulose fibers. Apart from naturally occurring plant fibers, cellulosic products can be industrially obtained using the viscose or the NMMO (N-methylmorpholine-N-oxide) processes, resulting in regenerated or man-made fibers. While the benefits of using natural fibers as reinforcement in composites have already been demonstrated [1–4], the potential of regenerated fibers in a similar use still needs to be recognized.

Depending on the intended application of the composites, the matrix must be carefully selected. Phenolic matrix composites are widely applied as structural materials in the transport industry, mainly due to their excellent fire behavior. Cellulose fiber-reinforced phenolic matrix composites have a potential application field in the automotive sector, because of the increasing trend in the use of recyclable nature materials in this area. A reduction of weight and an improvement of the mechanical and thermo-physical

properties of the composites are sought by replacing the traditionally employed glass fibers with cellulose.

Several factors are likely to influence the properties of cellulose fiber-reinforced composites. The effect of the reinforcement–matrix adhesion on the composite performance is particularly significant. A wide variety of fiber modifications have been reviewed in literature looking for an improvement on such adhesion [5–8]. Alkali treatment of the fibers and reaction with organosilanes as coupling agents have been selected in this work due to they are proven efficient methods for treating cellulose fibers [9–14]. Moreover, mentioned modifications of the fibers have been applied and optimized for the specific regenerated fibers–phenolic matrix composites in previous works [15,16]. Another factor strongly affecting the properties of composites is the fiber loading. Several authors have recently focused their efforts on the study of the fiber content effect on the properties of composites [8,9,13,17–21], but to the best of our knowledge no studies have been performed on this issue with regenerated fiber-reinforced phenolic composites. An increase in the fiber content usually leads to higher performance of the composites [8], but each system must be studied in detail to establish the most appropriate fiber loading.

In this work, the effect of fiber loading on the properties of viscose cellulosic fibers-reinforced phenolic composites was evaluated. Untreated, alkali, and silane treated cellulose fibers were used as reinforcements. Mechanical performance of the reinforced composites was measured under tensile and flexural loads and thermal stability was determined by thermogravimetric analysis

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(TGA). In addition, a scanning electron microscope (SEM) was used to observe the fracture surface morphology of the composites. We finally selected the most effective fiber loading and treatment leading to obtain the composites with better properties.

2. Experimental

2.1. Materials

Phenolic resol resin and hardener (ACE-1035) used as matrix in the composite preparation were supplied by Momentive Specialty Chemicals (USA). Viscose cellulosic fibers from eucalyptus wood of length 1.7–38 mm and linear density 1.7 dtex (0.17 g/1000 m) employed as reinforcement were supplied by Sniace (Spain). Fiber length was reduced and homogenized by milling to guarantee the uniform distribution of fiber length in the composites. Fiber length after this pretreatment varied in the range 0.1–1 mm.

Analytical grade sodium hydroxide (Panreac Química, Spain) and 3-(2-aminoethylamino) propyltrimethoxysilane, AAPS (Sigma–Aldrich®, USA), were used in the alkali and silane fiber treatments, respectively.

2.2. Composite preparation

First, phenolic resin and cellulose fibers were mixed by mechanical stirring at 800 rpm for 15 min. Then, the hardener was added and the stirring was prolonged for 2 min. The mixture was poured into a steel mold, cured in an oven for 2.75 h at 75 °C, and dried in a vacuum oven at 70 °C up to reach a constant weight. These conditions were optimized in a previous work [16]. The cellulose fiber-reinforced phenolic composites were synthesized with a resin:hardener weight ratio of 80:20, and fiber loadings of 1, 3, 5, and 7 wt% (referred to the resin + hardener mass). Composites were obtained with raw fibers (Cell-Ph), alkali treated fibers (Cell-NaOH-Ph), and silane treated fibers (Cell-AAPS-Ph). Fiber loading of the composites was also included in the code names. For example, 5%Cell-NaOH-Ph was the phenolic composite reinforced with 5 wt% of NaOH treated fibers. Properties of the composites were compared to those of the reference matrix (Unreinforced).

Cellulose fibers used as reinforcement were modified by alkali and silane treatments in order to improve adhesion properties with the phenolic matrix. Treatment conditions are detailed below and were chosen attending to previous works [15,16].

- Alkali treatment: The fibers were soaked in 1 wt% NaOH solution for 2 h at room temperature. They were further washed until pH = 7 and finally dried at 60 °C for 24 h.
- Silane treatment: The cellulose fibers were treated for 100 min at room temperature with 1.5% of AAPS silane. An acidified 80/20 wt/wt ethanol/water medium for the silane hydrolysis was used. Finally, the fibers were dried at 60 °C for 24 h.

2.3. Mechanical properties

Tensile and flexural tests of the cellulose fiber-reinforced phenolic composites were carried out using a universal testing machine (Zwick/Roell Z030) in accordance with ASTM D 638 and ASTM D 790, respectively. Test samples were cut using a computer numerical controlled or CNC milling machine (Galdabini ICP 3020) and then polished with a Buehler MetaServ® 3000 polisher to a thickness of 3.2 mm. Standard dumbbell-shaped specimens were tested at crosshead speed of 1 mm min⁻¹ in the tensile tests. Three-point flexural tests were performed using samples in the form of rectangular bars at crosshead speed of 10% min⁻¹. Tensile and flexural strength (σ) and elongation at break (ε) were obtained from the maximum values of the respective stress–strain curves. Elastic modulus (E) and strain energy density (SED) were determined from the slopes and the areas under the mentioned curves, respectively. Subscripts "T" and "F" are used to differentiate tensile and flexural properties. A minimum of five specimens were tested for each material.

2.4. Scanning electron microscopy

A scanning electron microscope (SEM, JEOL JM-6400) was utilized to observe fracture surfaces of the composites after tensile and flexural tests. Gold sputtering onto the fractured surfaces of the samples was used to impart them electrical conductivity. The operation voltage of the SEM was 40 kV.

2.5. Thermal stability

Thermogravimetric analysis (TGA) was carried out to determine the thermal stability of the composites, using Mettler-Toledo equipment (TGA/SDTA 851e). Samples of 12 mg were placed in alumina pans and heated from 30 to 900 °C at 10 °C min⁻¹ under inert nitrogen atmosphere to prevent unwanted oxidation (flow rate of 20 mL min⁻¹). Temperatures at which the materials had lost 10% and 50% of weight (T_{10} and T_{50}, respectively) and the remaining weight of the material at 600 °C (Residue$_{600 °C}$) were obtained from the thermograms.

3. Results and discussion

3.1. Mechanical and morphological properties of composites

Tensile and flexural properties of cellulose fiber-reinforced phenolic composites were plotted vs. fiber loading in Fig. 1. Properties of the untreated, NaOH, and AAPS silane treated fibers-reinforced composites were shown. The unreinforced reference matrix (fiber loading of 0%) was also included. SEM images of the tensile fracture surfaces of the composites reinforced with different contents of silane treated fibers were used to facilitate the understanding of the fiber loading effect on the mechanical properties of the composites (Fig. 2).

Fiber loading was found to change and dominate the failure mechanism of the composites. Most of the tensile and flexural properties of the composites reached a maximum in the studied fiber loading range (Fig. 1). For example, strain energy density (SED) in tensile and flexural tests reached a maximum between 3% and 5% of fiber loading, depending on the sample (Fig. 1c and g). SED provides a measure of the energy absorbed by the material during the test and thus of its resistance to the fracture. It is calculated from the area under the stress–strain curve and then SED takes into account and represents the overall behavior of the mechanical properties: strength, modulus, and elongation. Obtaining a maximum in the mechanical properties of short fiber-reinforced materials is the tendency most frequently found in the literature [22]. Incorporating low fiber loading (1%) to the phenolic matrix reduced mechanical properties for most of the materials. The largest reductions were found with the NaOH treated fiber-reinforced composites. SED in tensile and flexural tests for the 1%Cell-NaOH-Ph composite were 58% and 65% of the unreinforced material properties (Fig. 1c and g). At low fiber loading, poor fiber population caused low load transfer capacity among the fibers. As a result, accumulation of stress occurred at certain points in the matrix that brought about the rapid failure of the composites [23]. Moreover, some defects in form of air bubbles