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Dry etching plasma applied to fique fibers: influence on their mechanical properties and surface appearance

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Abstract

Plasma is a novel technique used in order to modify the surface properties of fibers used as a reinforced of polymeric composites. In this way, this paper shows the results of a research aimed to understand the effect of the dry etching plasma on natural fique fibers. Using different exposure times, the influence of plasma treatments on the tensile strength and surface appearance were investigated. Results showed that natural fibers could be effectively plasma treated without decreasing the strength and with significant modification of their surface appearance.

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Keywords: fique fiber; dry etching plasma; physical sputtering; tensile resistance; surface apperance

1. Introduction

Nowadays, the increasing environmental awareness has prompted searching sustainable materials to reduce the daily use of fossil raw materials. In consequence, natural resources have become important for industrial applications [1]. In composite industry, fibers such as hemp, flax, and sisal, are frequently used as reinforcement materials of different matrices, mainly polymeric [2], [3].

The use of natural fibers as reinforcement material of polymeric matrices provides some significant advantages to composites such as high mechanical properties per unit weight, low density and small manufacturing cost per unit volume [4]. However, their potential has not been profitable enough due to the poor compatibility between the

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composite phases. The main component of natural fibers is cellulose, which is a basic unit formed of anhydro-*d*-glucose. This molecule contains three alcohol hydroxyl groups that can form intra and inter molecular hydrogen bonds, as well as react with hydroxyl present in the air [5], leading to a hydrophilic character [6]. This hydrophilic behavior makes the fibers incompatible with the hydrophobic polymer matrices commonly used [7], [8]. Low chemical compatibility adversely affects the bonding among phases, resulting in a poor stress transfer from matrix to fibers, thus affecting the mechanical overall performance of the composite material [9], [10].

In literature, there are two main alternatives focused on the modification of physicochemical properties of matrices or fibers to improve the compatibility among composite phases. The most common alternative for industrial applications is modifying the physicochemical properties of fibers [11]. Three different procedures can be used for this purpose: using coupling agents [12]–[14]; through a graft polymerization of monomers compatible with the polymer matrix [11], [15]; and by exposing fibers to plasma treatments [16]–[18].

The application of scientific knowledge about plasma has been successfully used since the 60s in a broad number of purposes in material science [15]. Plasma is considered the fourth state of matter and consists in the ionization (partial or total) of a gas or gasses, which can be achieved by applying an electric field to the gas [19]–[22]. Plasmas are composed of positive ions and electrons [23], [24], and can be classified into two categories: hot plasmas (thermal plasmas) and cold plasmas (non-thermal plasmas) [25], [26]. Hot plasmas are characterized by very high temperature species into the ionized gas (from 4000 K to 20000 K) and a thermal equilibrium among them. Cold plasmas are characterized by electrons with much higher temperatures than those of positive ions, and in consequence, there is non-thermal equilibrium. Cold plasmas are frequently employed in material science, due to most materials exhibited changes on their microstructural composition and degradation at high temperatures. Cold plasmas can be generated using low (10^{-4} to 10^{-2} kPa [26]) or atmospheric pressure; in both cases, the ionization is started and maintained by using direct current (DC), radio frequency (RF) or microwave (MW) power, with or without an additional electric (bias) or magnetic field.

As a general point of view, cold low-pressure plasmas fulfill three main purposes: functionalization of surfaces, deposition of thin films, and etching [15], [19], [25]. Although surface alterations are complex when cold plasma is used, it is reported that this has no effect on bulk properties [27]–[30], which represents its main advantage. According to Hua and co-workers [31], plasma species do not penetrate deeper than 100×10^{-10} m (100 Å) from the material surface. Those surface alterations are achieved after a few minutes of plasma treatment [30].

Etching processes are focused on removing some material from the surface [23], and there are two main alternatives to be attained: using a purely chemical process (wet etching), or using a physical or chemical-physical process (dry etching). Dry processes have several advantages over wet processes because they are direct methods [32], which can be developed in a wide range of pressure [25]. Dry etching treatments could be carried out by physical sputtering, chemical reaction or ion-assisted mechanism. On the physical sputtering procedure, the material is removed by purely physical processes. Ions in the plasma transfer significant amounts of energy and momentum to the substrate, causing the atoms removal. On chemical reaction and ion-assisted mechanisms, the surface material is converted into high vapor pressure products to facilitate the removal [32].

This paper shows the results of a research aimed to use dry etching plasma for treating fique fibers, in which the exposure time to the same energy was variable. The influence of the physical sputtering on the mechanical properties was determined through tensile tests, and the changes on the surface appearance were assessed using a Scanning Electron Microscope (SEM). This research explores this plasma technique as improver of interfacial properties of polymeric composite materials.

2. Experimental details

2.1. Fiber obtention

Fique fibers were obtained from the local market. Individual fique fibers were obtained from fabrics. All fibers were cut to an average length of 10 cm because of the space available in the plasma equipment.

2.2. Dry etching plasma treatment

Fibers were exposed to a physical sputtering treatment. In a previous research [18], it was found as a preliminary result, that the employed technique increased the superficial roughness of *Guadua angustifolia* bamboo fibers; similar conclusions using different dry plasma etching treatments on natural fibers were obtained by other researchers [16], [17], [33]–[36].

In this research the treatment was performed using a DC sputtering (etching) system and employing Argon (Ar) gas. Fibers were exposed to ion bombardment for different times and to the same energy; the exposure times were 200, 400, 600, 800 and 1000 s. All treatments were carried out using an average current of 30 ± 3 mA and a working pressure of 10^{-2} kPa.

2.3. Tensile tests

The aim of tensile tests was to study the influence of treatments applied on the fibers tensile strength. The mechanical tests followed the guidelines established on ASTM 1557-14 [37]. The load application rate was 1.5 mm/min, in order to get a fiber failure in maximum 30s, complying with the recommendation of ASTM 1557-14. Before mechanical tests, all fibers were placed on paper frames, as shown in Fig. 1, to avoid deviation of axial load due to incorrect positioning of the fiber on testing grips. After setting the testing grips, the paper frame was carefully cut.

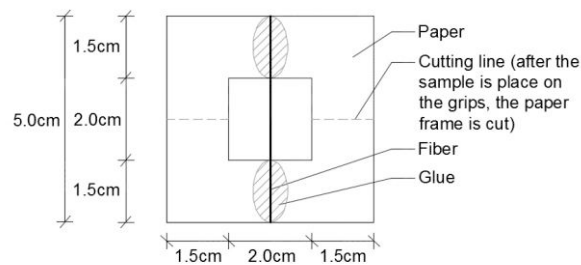


Fig. 1. Paper frames used on tensile tests.

The ultimate tensile resistance, σ_t , was calculated using Eq. 1, where P_{max} indicates the failure load of each fiber and A gives the cross-sectional area. Do to the fact that natural fibers have irregular cross-sections [38]–[40], the cross-sectional area was measured using micrographs obtained at fracture planes of individual fibers after mechanical tests. Micrographs were obtained using a stereo microscope Nikon SMZ 800.

$$\sigma_t = \frac{P_{max}}{A} \quad (1)$$

Statistical analysis was performed to identify significant differences among tensile resistances for different treatment times. Initially, using a Shapiro-Wilk test, it was verified whether each data set fulfilled a normal distribution. The homoscedasticity among data sets was verified using a Levene test. An ANOVA analysis was applied in the cases to satisfy both criteria of normality and homoscedasticity. In the case where normality and/or homoscedasticity were not satisfied, the Kruskal-Wallis test was used [41]. The significance level for every case was 0.05.

2.4. Scanning electron microscope

In order to assess the influence of etching treatment on surface appearance of fibers, treated and nontreated specimens were observed using a scanning electron microscope Tescan Vega 3 SB, working in secondary electron mode.

3. Results and discussion

3.1. Tensile tests

Fig. 2 shows the tensile resistance results. For each treatment time, the tensile resistance was calculated as an average of at least five specimens tested for each treatment time.

The ANOVA analysis made for the tensile resistance of fique fibers indicates that there are no significant differences among treatment times applied. Researchers who have evaluated the influence of dry etching plasma on tensile strength of different fibers have also concluded that there are no alterations on the mechanical property [17]. Seki et al. [42] found that the tensile strength of jute fibers treated using an oxygen plasma, slightly decreased as a consequence of micro pits and cracks caused by ion bombardment. Ceria et al. [43] and Cheng et al. [44] used oxygen and nitrogen atmospheric plasmas to treat wool fabrics; they found that the tensile strength is positively affected by applied treatment. They attributed this behavior to an increment of inter-fiber frictional force leads on a stronger cohesion inside the fabric structure.

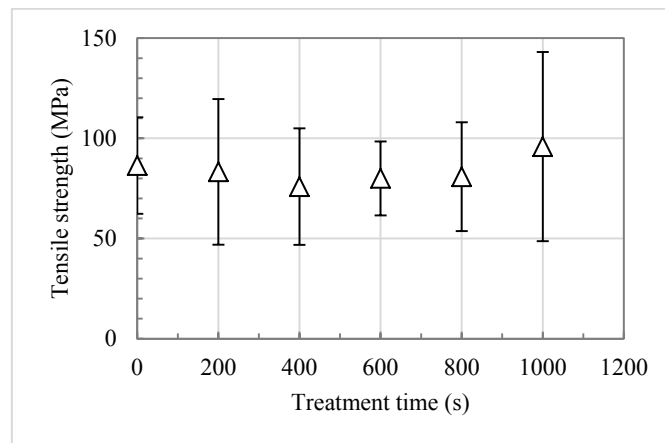


Fig. 2. Tensile strength for fique fibers.

3.2. SEM analysis

Fig. 3 shows the SEM micrographs for fique fibers. Treated fibers exhibit a rough and coarser surface, even with the formation of some cracks. This behavior is attributed to etching effect caused by ion bombardment on the fibers surface. Similar results were found in other research works [36], [44]–[47].

Untreated fique fiber shows a mild surface with some continuous and slight ridges (Fig. 3a). According to Bogaerts et al. [23], the sputter-etching mechanism begins with the removal of material surface atoms, forming little and isolated microcracks (Fig. 3b), which increase with higher treatment times (Fig. 3c and 3d). For treatment times above 800s, those little-isolated microcracks coalesce together and the surface tends to become continuous (Fig. 3e and 3f).

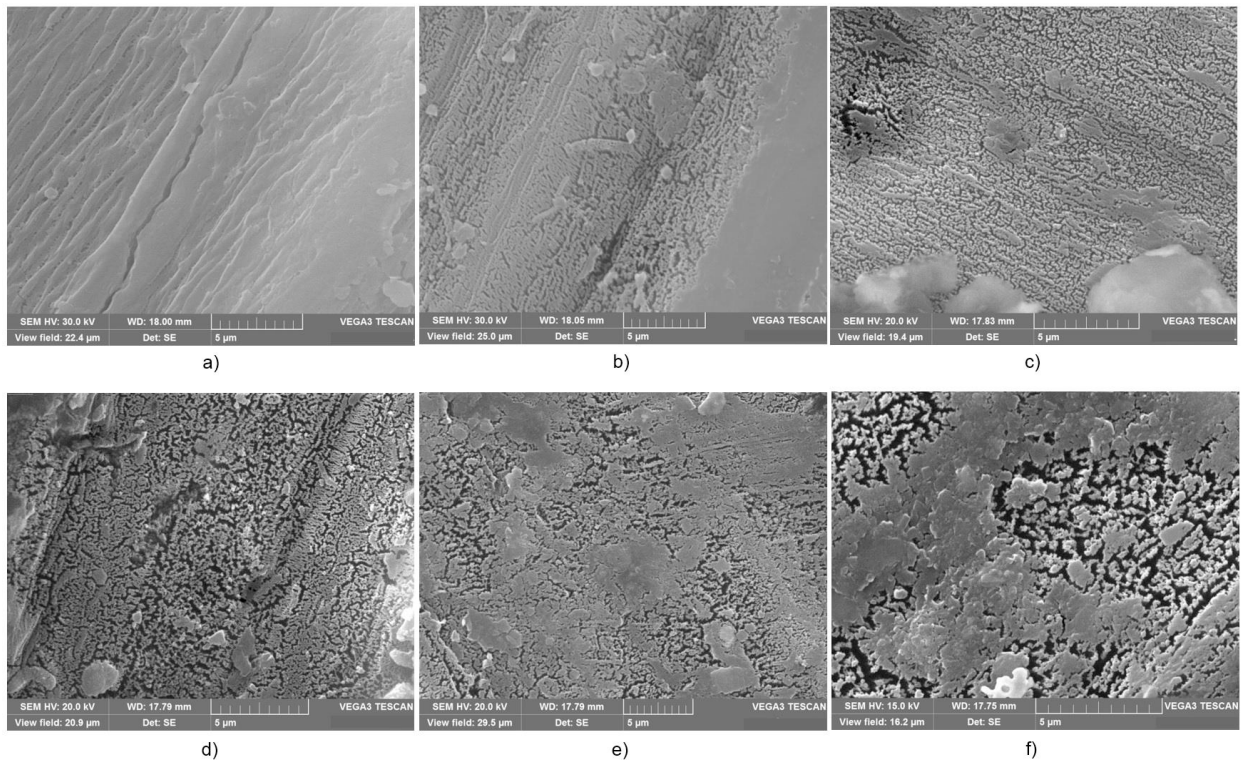


Fig. 3. SEM micrographs for fique fibers.

4. Conclusions

The statistical analysis made on the mechanical tests concluded that the tensile resistance has no alteration produced by ion bombardment. Although these results are promising, need to be correlated with other experimental results.

SEM images suggest that using plasma dry etching for treating fibers could increase the bonding among phases of composite materials because the treatment causes rough and coarser fiber surfaces.

From mechanical results and SEM images it can be concluded that the coalesce effect does not affect the tensile resistance of treated fibers.

The encouraging results obtained suggest to propose a new research in this field. This compatibilization technique could be used to increase the adherence between polymer composite phases.

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