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Manufacture and Mechanical Behavior of Green Polymeric Composite Reinforced with Hydrated Cotton Fiber

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Abstract

Composites using natural fibers as reinforcement and biodegradable polymers as matrix are considered environmentally friendly materials. This paper seeks the mechanical and morphological characterization of a biocomposite of polyurethane (PU) derived from a blend of vegetable oils doped with alumina trihydrate (ATH) and reinforced with hydrated cotton fiber fabric (HCF). The comparison and study were performed based on the properties of the: (i) pure PU; (ii) PU doped with ATH containing 30% of the final mass (PU+30%ATH); (iii) composite of PU reinforced with 7 layers of cotton fiber fabric (PU+7CF); (iv) composite of PU+30%ATH reinforced with 7 layers of CF (PU+30%ATH+7CF); (v) composite of PU+30%ATH reinforced with 7 layers of hydrated cotton fiber fabric (PU+30%ATH+7HCF). The mechanical properties obtained according to the tensile test for the composite PU+30%ATH+CF with fibers oriented at 0° showed a significant increment in tensile strength (60 MPa) and the modulus of elasticity (4.7 GPa) when compared to pure PU (40 MPa) and (1.7 GPa) respectively. PU+30%ATH also presented a rising tensile strength (31 MPa) and Young modulus (2.6 GPa). For the composite with addition of water, results presented a significant decrease in strength (31.3 MPa) and stiffness (0.9 GPa) than the composite with no water. Electron microscopy (SEM) analyses exhibited that the samples with addition of water showed the presence of large amounts of pores and the lower interaction between matrix and fiber. These results may explain the lower mechanical properties of this material.

Key words: Natural fiber, polyurethane, biodegradable, alumina trihydrate.

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1- Introduction

The development of new materials in order to improve the quality of products comes from the beginning of civilization, where production and treatment of materials technologies have developed over the centuries. It might even be said that the human race divided its history based on the material technologies developed over the time, characterized by the Stone, Bronze and Iron Ages. Therefore, the investigation surrounding new material applications and developments have an astonishing impact over society and must always be treated as an important scientific research topic [1].

Over the last two decades, the interest around the investigation of polymers and composites from renewable sources have grown as a result of the increasing environmental concern surrounding the fossil resources exhaustion, as it can be demonstrated by the exponentially increasing number of patents and publications on these materials [2,3]. Synthetic fibers (aramids, glass, carbon) are widely used as reinforcement in plastic [4]. However, due to recent environmental restrictions, the polymer industry has been developing new materials with good physical and mechanical properties, low cost, and lower environmental impact than those conventionally used [5]. Natural fibers are inserted against this background, which are resistant, light-weighted, non-abrasive, and serve as an excellent reinforcing agent for plastics [6-8].

The field of employment of natural fibers is quite wide, ranging from the classic applications in the textile industry to the reinforcement of thermoplastic and thermoset polymer matrices [9,10]. Also, the automotive industry started using composites with vegetable fibers, which highly enhances the application field for these materials [9].

Among vegetable fibers, cotton fiber fabrics (CF) present an advantage in the composite manufacture, since they are processed industrially and in large scale for the textile industry, thus, the obtainment of fiber is quite easy and its reproducible properties are well standardized [11,12]. Cotton is one of the natural fibers that do not present a matrix of lignin, having basically a pure cellulosic matrix, still, it does not present stiffness characteristics of the lignocellulosic fibers (like sisal) [13,14].

The term “biopolymers” usually refers to naturally occurring long chain molecules, although, it may also refer to products that have been derived from these natural materials. Moreover, a biopolymer made from annually renewable resources which will biodegrade can appear to solve the major problems associated with plastics like the limited fossil origin and its environmental harmful discard [15].

Among the biopolymers, it stands out the polyurethane (PU) derived from castor oil, once it is compatible with living tissues and has been successfully used in medicine for the manufacture of prostheses [16-17].

According to the National Fire Protection Association, there were more than 1.34 million fires reported in the US in 2016. Those fires had 3,390 deaths and 14,650 civilian fire injuries confirmed. Moreover, the property damage was evaluated in 10.6 billion US dollars [18]. Therefore, the usage of materials that possess certain resistance to fire is increasing over the globe.

Since most of the polymers are highly flammable materials, they are often doped with fire retardants [19]. The aluminum hydroxide reigns among the most used fire retardants. It is responsible for half of the entire amount of fire retardants used in plastics [20]. Its most impressive characteristics are the non-emission of toxic gases and its relative low price [21]. However, in order to obtain a good fire resistance, large amounts of ATH (40% – 70%) are necessary, which harm the material density and may impair its mechanical properties [22].

The mechanical properties of polymeric composites along with fibers depend on some factors such as fiber-matrix adhesion. The interface interaction between matrix and reinforcement must be strong enough to successfully transfer the stress through the whole material. To improve fiber-matrix adhesion, one of the alternatives is to chemically or physically modify the fibers prior to incorporation into the polymer matrix [23].

The presence of free water and OH groups, especially in the amorphous regions, impairs the fiber adhesion capacity in the matrix [24]. Although, according to Szycher (2013) [25], the reaction between isocyanate and water is very strong and mostly happens consuming 3 mol of isocyanate for each mol of water, producing carbonic gas and urea. Consequently, it is reasonable to assume that there would be no water left in a polyurethane based composite. Instead, the reaction between isocyanate and water would produce carbonic gas, which would act as blowing agent inside the polymer structure.

Therefore, this work proposes a study of the mechanical and morphological behavior of the polymeric composite with PU doped with ATH and reinforced with hydrated cotton fiber fabric (HCF).

2- Material and Methods

The polymerization of the PU matrix derived from a vegetable oil blend (kindly supplied by Kehl) was performed by mixing the reagents AG201 (isocyanate) and AG201-R (bio-based polyol), with a ratio of 1: 1. The reinforcement was made by 07 (seven) layers of unidirectional CF (kindly supplied by Toalhas São Carlos).

First of all, the molding area was delimited by a tacky tape responsible for fixing and sealing the vacuum bag against air intake. Soon after, a thin layer of carnauba wax was placed in the area to facilitate demolding at the end of the process. Next, the first layer of

Peel Ply was placed inside the specified area followed by the PU (resin), which was poured on the Peel ply sheet. Subsequently, 4 layers of CF were positioned over the resin, then, a new amount of polymeric matrix was poured on those CF layers. Next, the last 3 CF layers were placed over the second PU film, followed by the second layer of Peel Ply and the resin flow mesh respectively. Finally, the vacuum bag was sealed with the tacky tape and the material cure occurred under vacuum for 24 hours.

2.1 - Mechanical Test

The plates were cut in two directions in order to obtain specimens with fiber orientation of 0° and 90°, also, the specimen dimensions followed the ASTM D3039/3039M 14 standard [26] , which normalizes the tensile mechanical test in composite materials.

The tests were done in a Jinan Shijin WDW-100E Universal Testing Machine (UTM) with a 100 kN load cell. The UTM provided the strength data used to calculate the material true stress. The testing speed was 2 mm/min. The true strain values were obtained by Digital Image Correlation (DIC) with the aid of the software GOM Correlate, moreover, the camera Canon Rebel 5, controlled by the software EOS Utility 2, was used to take a picture of the material being tested each 5 seconds.

2.3- Morphology

The samples morphologies were verified using a scanning electron microscope (SEM EVO MA 15) attached to an Oxford Instruments detector to EDS X-Max 20 mm^2. The samples were cut in order to analyze their fracture zones resulting from the tensile test.

3 - Results and discussion

Da Silva et al. (2017)[27] characterized the tensile properties of the pure PU, the PU+7CF and PU+ATH+7CF (which has a matrix of PU doped with 30% of ATH as final mass) composites with fibers oriented in 0°, 45° and 90°. That study stated that the mean value and standard deviation of the elasticity modulus and the maximum stress were 1.703±0.260 GPa and 39.71±3.36 MPa for the pure PU matrix. Table 1 shows the mechanical properties of the PU+7CF and PU+ATH+7CF laminates.

Table 1 : Mechanical Properties of PU+7CF and PU+ATH+7CF composites. [Adapted from Silva (2018)[27]]

COMPOSITES	E [GPa]	σ_{max} [MPa]	Poisson (v)
PU	1.715	39.715	0.440
PU+ATH	2.607	31.630	0.317
PU+7CF-0°	3.702±0.407	78.340±5.620	0.417±0.002
PU+7CF-45°	2.127±0.077	32.690±0.740	1.111±0.032
PU+7CF-90°	1.079±0.363	11.560±1.210	0.081±0.006
PU+ATH+7CF-0°	4.733±0.527	60.280±2.070	0.195±0.020
PU+ATH+7CF-45°	2.425±0.106	19.790±1.230	0.502±0.012
PU+ATH+7CF-90°	2.223±0.163	10.440±0.370	0.037±0.011

Figure 1 (A) and (B) show the data obtained in the tensile tests for the PU+ATH+7HCF orientated at 0° and 90° respectively. The values for tensile strength and Young modulus decreased in relation to the data showed in Table 1. A possible explanation for the reduction in strength and stiffness of the composite while hydrating the cotton fibers is the expansion of the matrix, once the ultimate load with and without hydration was the same, therefore, the main aspect influencing the stress resistance decrease was the increasing area around 100%. Moreover, the PU matrix in the composites with no hydrated fibers has a dense body with no pores and the hydrated cotton fiber composite showed uncountable pores in its constitution. Furthermore, the figure shows the digital image correlation (DIC) used to acquire the true strain data in the tensile test.

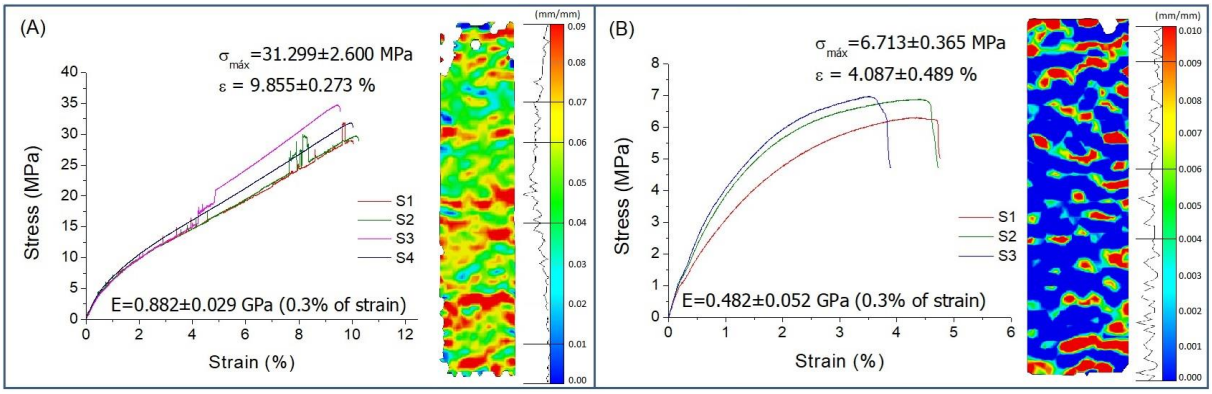

Figure 1 : Stress-Longitudinal strain and DIC of PU+ATH+7HCF at (A) 0° and (B) 90°.

Figure 2 (A) and (B) show SEM images of the fracture of the composite PU+ATH+7CF oriented at 0° and 90° respectively. Figure 2 (C) and (D) show the images for the composite PU+ATH+7HCF oriented at 0° and 90° respectively. SEM images demonstrated the differences in the structure of the polyurethane matrix in the composite of cotton fiber and in the composite with hydrated cotton fiber. The images for the hydrated fibers show the presence of a non-porous phase (indicated with arrow) with a high concentration of alumina that was not observed in the samples of non-hydrated fibers.

The porous part evident in the hydrated samples is a consequence of the very strong reaction between isocyanates and water. According to Szycher (2013) [25] a small amount of water may have a drastic influence on the reaction sequence and on the final molecular structure of the polyurethane. Thus, the water used in the hydration process of the cotton fiber reacted with the isocyanate and produced carbon dioxide molecules that were encased inside the polyurethane, causing the various pores present in the material. Therefore, the comparison between the hydrated fiber composite mechanical properties with the dense PU is not appropriate, once the matrix was a porous polyurethane. The presence of pores and the lower interaction between matrix and fiber may explain the lower mechanical properties of this material. Also, EDX analysis shown in Figure 2 (E) and (F) exhibit the occurrence of a non-porous phase with a high concentration of

aluminum, indicating that water harmed the flame-retardant homogenization in the matrix structure, once the porous phase shows only a small amount of ATH.

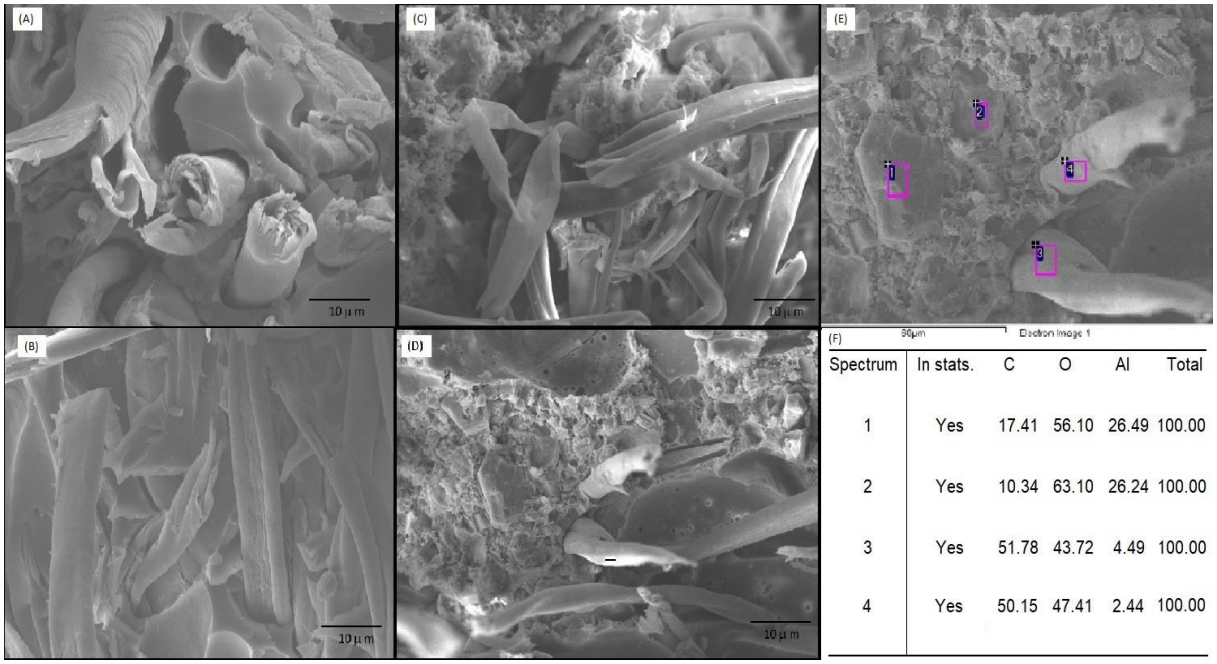

Figure 2 : SEM images of the fracture of the polymer composite of PU+ATH+7CF cotton oriented at 0°(A) and 90° (B), PU+ATH+7HCF oriented at 0°(C) and 90° (D), PU+ATH+7HCF EDX analysis (E) and (F).

4 - Conclusion

From the results, it was observed that the addition of water in the fiber caused an expansion in the polymeric matrix, consequently, decreasing the mechanical properties of the composite. These results are in accordance with the SEM images which showed samples with addition of water presenting a large number of pores. Therefore, the matrix in this case was an expanded polyurethane, which increased the composite volume, did not interfere in the ultimate load and decreased the ultimate stress and stiffness.

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