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ORIGINAL PAPER

Effects of Dry Etching Plasma Treatments on Natural and Synthetics Fibers: a Comparative Study

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Abstract
Nowadays, natural and synthetic fibers are becoming a valuable resource for composite industry. The use of natural and synthetic fibers as reinforcement of polymeric matrices has many advantages: it betters mechanical properties per unit of weight, decreases the cost of manufacturing per unit of volume and, among other things, it is environmentally friendly. Despite all of this, the low compatibility between the constituents can result in a poor mechanical behavior. However, plasma treatments can modify the surface of the fibers used as reinforcement, so the bond between the phases of the composite can be improved by its use. In this work, we present the results of a comparative study of the effects produced by dry etching plasma treatments on Young's modulus and surface morphology of Guadua angustifolia, Fique, and Nylon fibers. Natural and synthetic fibers were exposed to physical bombardment with argon ions during different time intervals. Scanning electron microscopy (SEM) analysis showed that all treated fibers exhibited rough surfaces and that the surface roughness augmented by increasing the bombardment time. The results of Young's modulus as a function of bombardment time displayed a significant increment in Guadua and Fique fibers but did not change significantly in Nylon fibers. The serious damages produced in the natural fibers by ion bombardment as determined by SEM analysis could be considered as the main cause of the observed increase in Young's modulus. Other causes, however, can not be ruled out as responsible for the increment in Young's modulus in natural fibers and the almost null effect in synthetic fibers.

Keywords Dry etching plasma · Young's modulus · SEM · Circular economy · Guadua *angustifolia* fiber · Fique fiber · Nylon fiber

Introduction

The mechanical behavior of composite materials depends on the mechanical properties of its constituents like, for example, the reinforcement material, the distribution of their constituents, reinforcement length, the matrix, and other characteristics. The interaction between constituents plays an essential role on composite performance and the physicochemical interactions between composite components seems to be the responsible of stress transfer from the matrix to the reinforcement.Luna (2019), Luna et al. (2018), Daniel and Ishai (2006), Albella (2003), Sun and Stylios (2005), and Sun (2016)

The physical dry etching processes, led by cold plasmas, are clean processes mainly used in the removal of material from different surfaces. This represents an alternative to chemical processes (wet etching) that produce non-environmentally friendly waste materials. Dry etching is carried out by ion bombardment on a surface where the ions in the plasma are accelerated to a surface. Then, using a bias voltage, they transfer significant amounts of energy and momentum to the surface, causing both atoms removal and damage on the surface. Sun and Stylios (2005), Sun (2016), Barra et al. (2015), Rodríguez et al. (2015), and Sánchez-Cruz et al. (2020)

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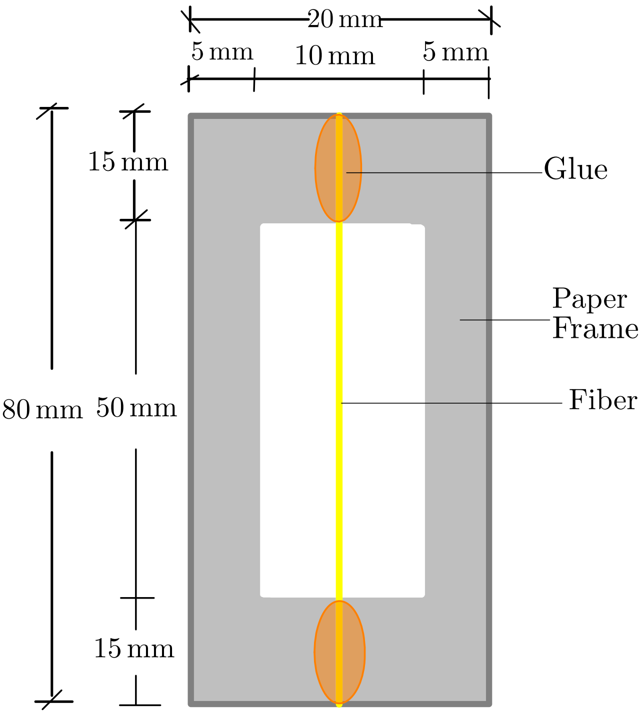

Fig. 1 Paper frame used for mechanical tests

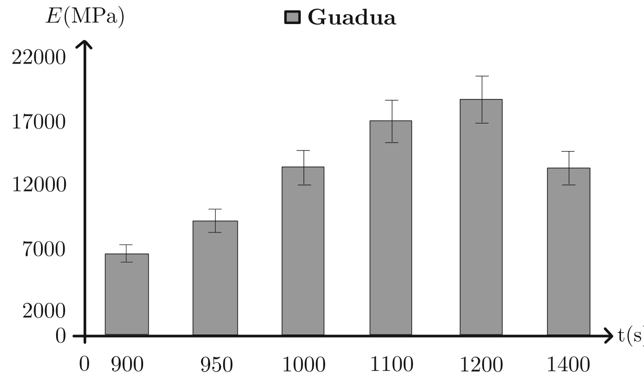

Fig. 3 Young's modulus as a function of bombardment time for Guadua

The use of natural fibers in composite industry has increased in the last two decades. This shows in the fact that the use of high-performance fiber-reinforced composites from natural renewable materials in the construction and automotive industry is less expensive, biodegradable, and environmentally friendly. In addition to these characteristics, the natural fiber composites (NFC) can provide the solutions needed since they do not only support the policies of circular economy, but they are also sustainable and lightweight. Besides this, they possess high strength to weight ratio. (Elseify et al. 2021; Bledzki et al. 1996; Bledzki and Gassan 1999; Rijswijk et al. 2001; Mohanty et al. 2002; Faruk et al. 2013).

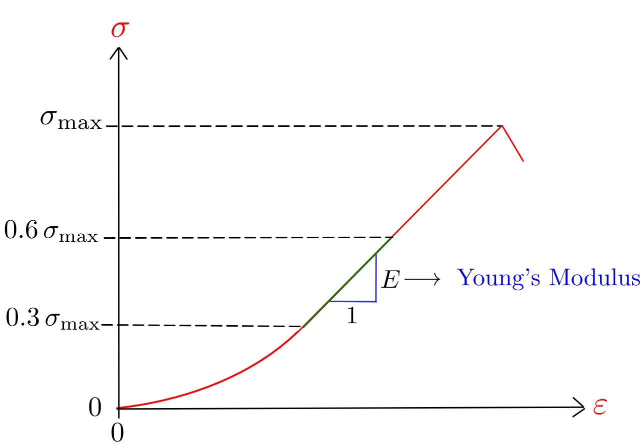

Fig. 2 Stress (σ) - strain (ε) curve. Young's modulus (E) is determined from the curves slope between 30 and 60%

Nevertheless, the potential of natural fibers in composite industry has not been completely profited, due to the low chemical compatibility between components, which leads to an inadequate mechanical performance of composite materials as a consequence of the low adherence between composite phases (Barkoula et al. 2008; Kushwaha et al. 2010; Song and Zhao 2015).

In this research, the effects produced on the mechanical properties and surface appearance by dry etching plasma processes on natural and synthetic fibers like Guadua, Fique, and Nylon were studied. The influence of different treatment times on fiber tensile strength and on the appearance of the surfaces was determined and correlated in an effort to understand the behavior of the mechanical properties of composite materials. This work is a part of a more extensive study of the application of plasma techniques on natural and synthetic fibers as a possible improver of interfacial properties of polymeric composite materials (Luna 2019). In this case, all treatments were carried out using the same ions energy and different treatment times. This was done to produce changes on the surfaces of natural and synthetic fibers and to study and correlate the effects on their mechanical properties.

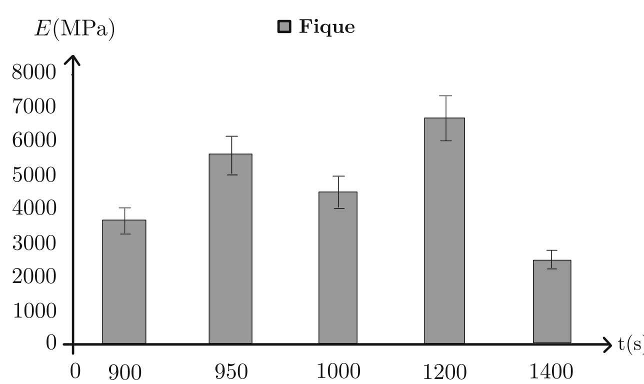

Fig. 4 Young's modulus as a function of bombardment time for Fique

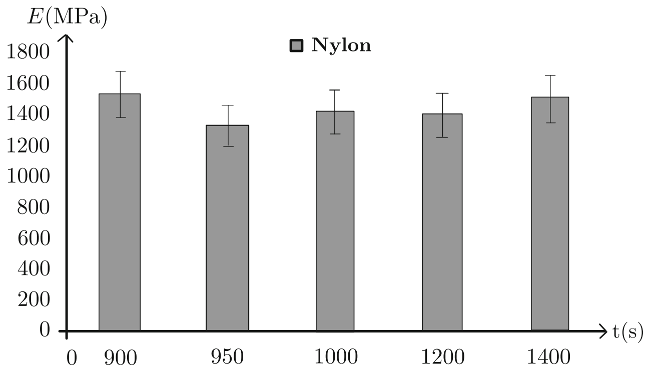

Fig. 5 Young's modulus as a function of bombardment time for Nylon

Experimental Details

Dry etching plasma treatments were carried out using a commercial dry etching system. Guadua, Fique, and Nylon fibers were exposed at the same time and under the same conditions to an Argon ion bombardment during different time intervals (900, 950, 1000, 1200, and 1400s).

All treatments were carried out using an Argon pressure of 10^{-2} mbar at a power of ~0.5 Watts. Tensile tests were performed following the guidelines of ASTM C1557, and using a load rate of 1.0mm/min for Guadua and Fique and 5.0mm/min for Nylon fibers. Before mechanical tests, all fibers were placed on paper frames working with a gage

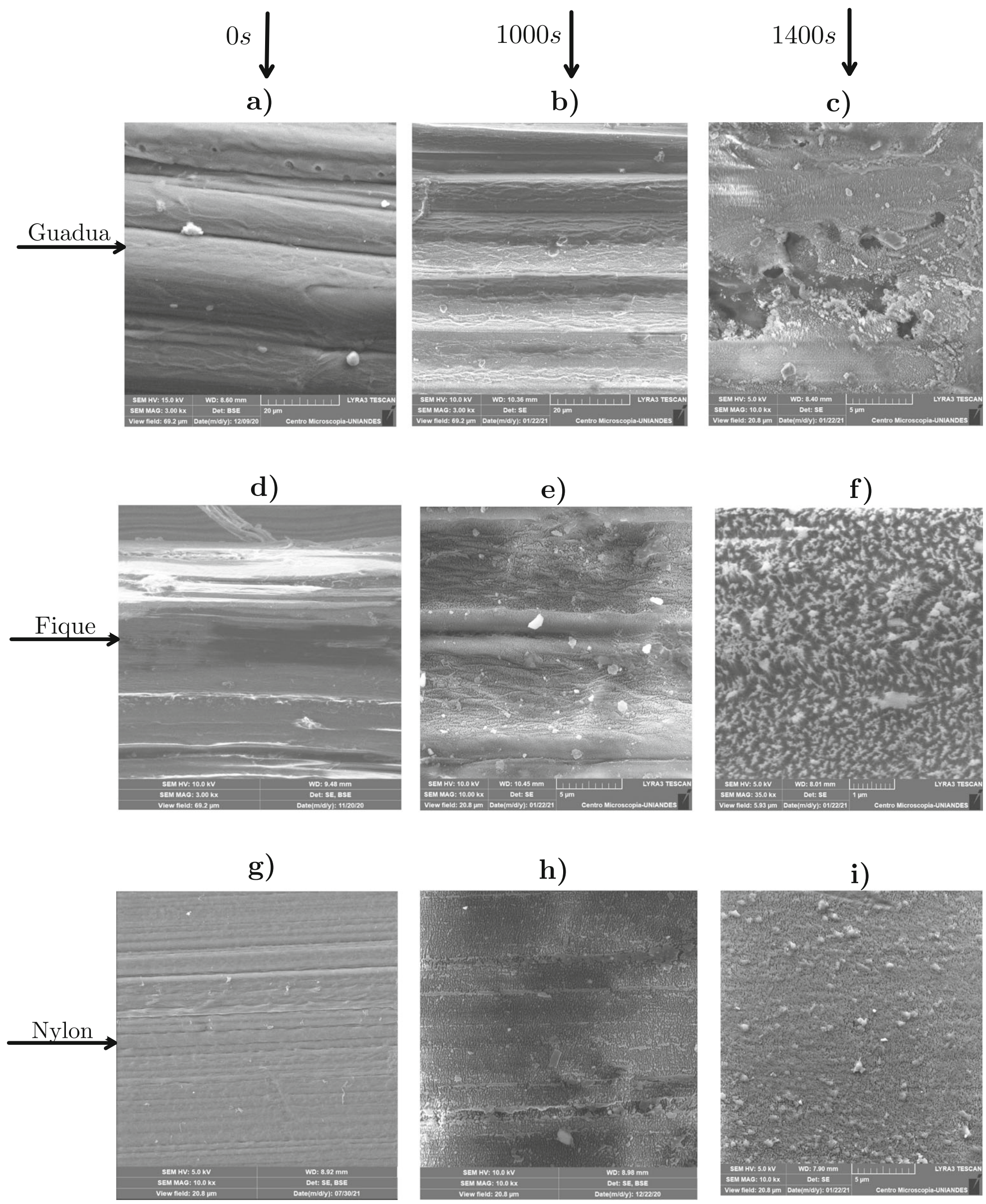

Fig. 6 SEM micrographs for Guadua, Fique, and Nylon fibers. Untreated, figures, a, d, and g respectively, and treated fibers with different bombardment times

length of 50mm, to avoid deviation of axial load due to incorrect positioning (see Fig. 1).

For each treatment time and for each fiber, 6 tensile test were performed. Young's modulus (E) of each fiber was calculated as the slope, between 30 and 60% of maximum tensile strength σ, from the stress (σ)-strain(ε) curves as shown in Fig. 2.

The fiber's strain (ε) was calculated using Eq. (1), where ΔL is the fiber's elongation and $L_0 = 50$ mm.

$$\varepsilon = \frac{\Delta L}{L_0} \tag{1}$$

The surface morphology was determined by SEM analysis using a scanning electron microscope Tescan Vega 3 SB.

Results and Discussion

Figures 3, 4, and 5 display Young's modulus as a function of bombardment times for Guadua, Fique, and Nylon fibers respectively.

As it can be observed, Young's modulus changed with treatment time for Guadua and Fique. However, it did not change appreciably for Nylon fibers.

The increase of Young's modulus for Guadua and Fique fibers observed up to 1200 s can be related, mainly, with damages produced in the fibers surfaces. This happens because untreated fibers of Guadua, Fique, and Nylon (Fig. 6 a, d, and g respectively) show a mild surface with continuous and slight ridges. However, in all treated fibers, a higher roughness was observed, which increased with the treatment times.

The treated fibers of Guadua and Fique (Fig. 6 b and e respectively) display, additionally, some microcracks on the fibers, which increase in number with treatment times.

High treatment times ($>$ 1200s) show additional damages on the fibers surfaces which, appear mainly as voids, (Fig. 6 c and f).

The results of Young's modulus for Nylon (Fig. 6 g, h, and i) do not permit to establish a definite trend for this results. There are not substantial differences among modulus of elasticity determined for untreated and treated Nylon fibers. From SEM analysis the presence of some microcraks and voids are observed just only at high treatment times ($>$ 1200 s) (Fig. 6 i).

The damaged surfaces in Guadua and Fique fibers produced by different bombardment times as observed by SEM microscopy could be related with the different behaviors of the observed Young's modulus. On the other hand, the lighter damages produced by ion bombardment on Nylon fibers (Fig. 6 h and i) could be one of the main reasons that explain the small differences observed in Young's modulus as a function of the bombardment time.

The apparent maximum of Young's modulus observed in Guadua and Fique fibers for bombardment times between 1000 and 1300 s can be attributed both to the higher roughness of the surfaces and the cracks formation. However, treatment times larger than 1300 s showed a decrease in Young's modulus, which, can be associated to the voids formation as observed by SEM analysis (Fig. 6 c and f for Guadua and Fique respectively).

Conclusions

The Argon ions bombardment affected the roughness surfaces of all the fibers, but the damages produced by bombardment with Argon ions are more appreciable in the surfaces of Guadua and Fique than in those of Nylon fibers.

Young's modulus increased with Argon ions bombardment in Guadua and Fique fibers but did not show noticeable changes in Nylon fibers. The former one can be associated with the higher damages, as observed by SEM in the surface of the natural fibers.

An apparent maximum of Young's modulus is observed in Guadua and Fique fibers for bombardment times between 1000 and 1300 s, this can be attributed mainly to the higher roughness of the surfaces and the cracks formation. Nevertheless, treatment times larger than 1300 s showed a decrease in Young's modulus, which can be associated with the voids formation as determined by SEM analysis.

Results obtained through SEM images suggest that ion bombardment times in guadua and fique fibers can produce an increase of the bonding between composite phases, because the higher roughness in the treated fibers surface increment the mechanical grip between the reinforcement and the polymer matrix. On the other side, in the case of nylon fibers, because the damages in the fibers surfaces produced by ion bombardment are lighter than that produced in natural fibers, the effects on Young's modulus are not remarkable. In this case, ion bombardment with higher energy would be necessary in order to produce similar effects on the surface to those observed on natural fibers. Results of previous research using a composite material with a polyester matrix reinforced with guadua fibers treated by ion bombardment showed sensible increments in Young's modulus (Luna 2019).

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Author Contribution SMG participated in samples preparation, tensile strength measurements, SEM measurements, analysis of results, and was the major contributor in writing the manuscript. AMC supervised and managed the research, participated in the design of the experiments, boosted the analysis of results, and contributed to writing the manuscript. PLT was the promoter of the research and participated in the analysis of mechanical results, and contributed to writing the manuscript. All authors read and approved the final manuscript.

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Availability of Data and Materials The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests

References

Albella JM (ed) (2003) Láminas delgadas y recubrimientos, preparación propiedades y aplicaciones. Consejo superior de investigaciones científicas, Madrid

Barkoula NM, Alcock B, Cabrera NO, Peijs T (2008) Fatigue properties of highly oriented polypropylene tapes and all-polypropylene composites, 16. https://doi.org/10.1177/096739110801600203

Barra BN, Santos SF, Bergo PVA, Alves C, Ghavami K, Savastano H (2015) Residual sisal fibers treated by methane cold plasma discharge for potential application in cement based material. Ind. Crop. Prod. 77:691–702. https://doi.org/10.1016/j.indcrop.2015.07.052

Bledzki A, Gassan J (1999) Composites reinforced with cellulose based fibres. Profress in Polymer Science 24:221–274. https://doi.org/10.1016/S0079-6700(98)00018-5

Bledzki A, Reihmane S, Gassan J (1996) Properties and modification methods for vegetable fibers for natural fiber composites. J. Appl. Polymer Sci. 59:1329-1336. https://doi.org/10.1002/(SICI)1097-4628(19960222)59:8%3C1329::AID-APP17%3E3.0.CO;2-0

Daniel IM, Ishai O (eds) (2006) Engineering mechanics of composite materials, 2nd edn. Oxford University Press, USA

Elseify LA, Midani M, El-Badawy A, Jawaid M (eds.) (2021) Manufacturing automotive components fron sustainable natural fibers composites. Springer briefs in Materials, SBN 978-3-030-83025-0

Faruk O, Bledzki AK, Fink H (2013) Progress report on natural fiber reinforced composites. Macromol Mater Eng, 19

Kushwaha PK, Kumar R, Yu X, Wang C, Wei W, Zhang S (2010) Studies on performance of acrylonitrile-pretreated bamboo- reinforced thermosetting resin composites. Journal of REINFORCED PLASTICS AND COMPOSITES, 29. https://doi.org/10.1177/0731684409103701

Luna P (2019) Mechanical behavior of a composite material using a polyester matrix reinforced with guadua angustifolia bamboo fibers. Ph.D. Thesis, Universidad Nacional de Colombia

Luna P, Mari?o A, Lizarazo-Marriaga J (2018) Dry etching plasma applied to guadua angustifolia bamboo fibers: influence on their mechanical properties and surface appearance. Non-Conventional Materials and Technologies 7:332–340. https://doi.org/10.21741/9781945291838-30

Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources : opportunities and challenges in the green materials world. J. Polym. Environ. 10:19–26. https://doi.org/10.1023/A:1021013921916

Rijswijk K, Brouwer WD, Beukers A (2001) Application of natural fibre composites in the development of rural societies

Rodríguez L, Fangueiro R, Orrego C (2015) Effect of chemical and plasma dbd treatments on pseudostem plantain fiber properties. Rev. LatinAm. Metal. Mat 35:295–304. www.rlmm.org

Sánchez-Cruz ML, Patiño-Castro WA, Cárdenas-Pulido JW (2020) Methods of surface treatment and its effect on the physical and mechanical properties of guadua fibers métodos de tratamiento superficial y su efecto en las propiedades físico mecánicas de fibras de guadua. Scientia et Technica A?o XXV, 25

Song W, Zhao F (2015) Interfacial characterization and optimal preparation of novel bamboo plastic composite engineering materials. Bioresources, pp 5049–5070. https://doi.org/10.15376/biores.10.3.5049-5070

Sun D, Stylios GK (2005) Investigating the plasma modification of natural fiber fabrics-the effect on fabric surface and mechanical properties. Text. Res. J. 75:639–644. https://doi.org/10.1177/0040517505057637

Sun D (2016) Surface modification of natural fibers using plasma treatment. wiley, pp 18–39. https://doi.org/10.1002/9781118911068.ch2

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