# Characterization of NaOH-Treated Colombian Silverskin Coffee Fiber as a Composite Reinforcement

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The effects of an alkali treatment with NaOH (5%, 10%, and 15%) was studied relative to the tensile and flexural mechanical properties of Colombian coffee silverskin fiber (CCSF)/polyester biocomposites. The CCSF was treated with NaOH for 30 min and then dried at 50 °C for 5 h. Laminates with a 35.1% volume fraction of fiber were prepared using a hand lay up manufacturing technique. Scanning electron microscopy was used to study the fiber morphology. The results revealed that the specific maximum tensile and flexural strengths increased by 36.3% and 25.1%, respectively, the specific tensile and flexural moduli increased by 31.6% and 147.0%, respectively, and the tensile toughness was 67.9% higher compared with the untreated biocomposite. The flexural toughness decreased by 62.0%. The results suggested that mercerization is an effective method to treat CCSF/polyester biocomposites.

*Keywords: Alkali treatment; Coffee silverskin; Polyester; Biocomposite; Tensile; Flexural*

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## INTRODUCTION

In recent years, researchers have been evaluating new materials to reduce the impact of industry on the environment. This has led to reducing the use of petroleum materials by combining them with biodegradable materials to produce composites that are not only eco-friendly and economical, but also have improved properties.

Natural fibers are an alternative that can help solve ecological and environmental problems (Goda *et al.* 2006), as they replace glass fiber, aramid, carbon, or nylon as reinforcing materials in polymeric matrices to enhance the mechanical properties (Kim and Netravali 2010; Marinho *et al.* 2015; Sanjay *et al.* 2015; Luna *et al.* 2016). These fibers increase the tensile and flexural resistance of materials (de Morais *et al.* 2016).

One of the biggest hindrances to the combination of natural fibers with the most commonly employed types of synthetic polymeric matrix is the poor interfacial bonding of fibers and polymers, which determines the resistance of composites (Pietak *et al.* 2007; Pickering *et al.* 2016). This issue is caused by the physicochemical incompatibility between fibers and matrices. Fibers are hydrophilic because of their cellulosic nature, while typical matrices are normally hydrophobic (Mahdi *et al.* 2015). To reduce this problem, surface modification methods have been developed that use physical or chemical treatments (Faruk *et al.* 2012; Gurunathan *et al.* 2015). A chemical method called alkali treatment, or mercerization, uses sodium hydroxide (NaOH) to partially remove hemicellulose, lignin, pectin, and waxes from the fiber (Qin *et al.* 2008) (Eq. 1), and allows the reorientation of cellulose. This increases the surface roughness and results in mechanical coupling. This method has been studied with different fibers, such as sisal, abaca, bamboo, hemp, and jute, and its effects depend on many factors, including alkali concentration, immersion time, fiber origin, fiber volume fraction, and curing temperature. It has been reported that at high alkali concentrations there is a larger degradation of fiber (Zuluaga *et al.* 2009).

$$Fiber - OH + NaOH \rightarrow Fiber - ONa + H_2O \tag{1}$$

Coffee silverskin is the primary residue from the coffee industry and is disposed as industrial waste. Narita and Inouye (2014) reported that it has a high fiber content and could be a source of bioactive substances, used for feed, fertilizer, fermentation or as direct fuel. Because of the large potential of using coffee silverskin as a reinforcement material and the abundance of coffee fields in Colombia, the authors explored the effect of NaOH treatment on the morphology of Colombian coffee silverskin fiber and the tensile and flexural properties of reinforced polyester composites. The current research determined the effects of alkali treatment on the mechanical properties and microstructure of Colombian coffee silverskin composites.

## EXPERIMENTAL

### Materials

Colombian coffee silverskin fiber (CCSF) was provided by Carcafé Ltd. (Pitalito, Colombia). The fiber was obtained after the hulling-polishing process. All of the samples were randomly selected and had an average length of 4 to 8 mm. The steps from raw fruit to CCSF are shown in Fig. 1. The selected matrix was Cristalan 856 (98% polyester resin, cobalt naphthenate 2%) supplied by Químicos S.A.S. (Neiva, Colombia). The resin catalyst was MEK peroxide 2% (9% Oxy-active, Químicos S.A.S., Neiva, Colombia) and was used at a ratio of 100:1 by weight. The properties of neat polyester resin were given by the manufacturer specifications and are listed in Table 1.

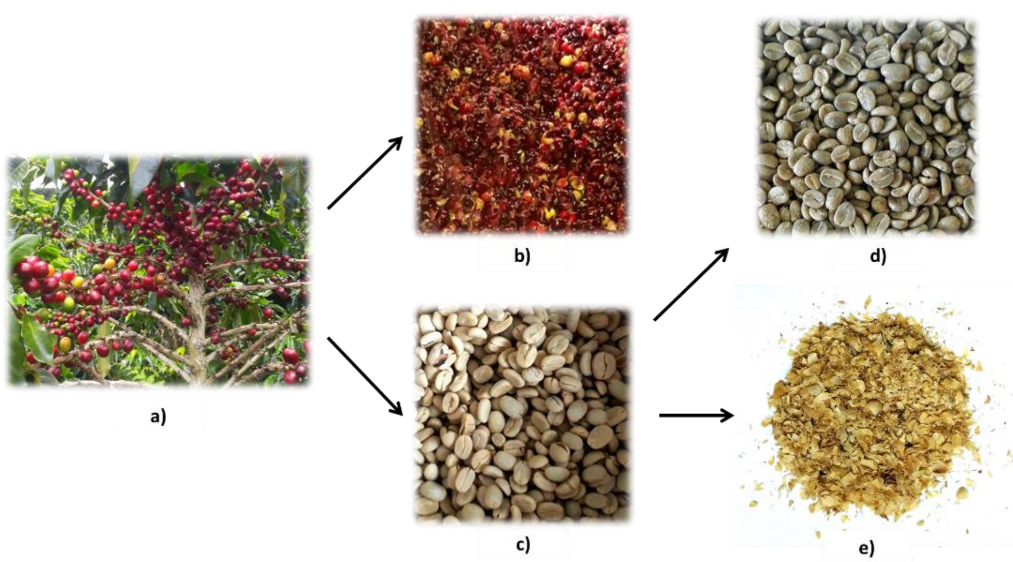


**Fig. 1.** Steps from raw fruit to CCSF: (a) coffee plant, (b) coffee husk, (c) dry coffee bean with silverskin, (d) coffee bean, and (e) coffee silverskin

**Table 1.** Properties of Neat Polyester Resin

| Density, g/cm$^3$ | Young's modulus, GPa | Tensile strength, MPa | Poisson's ratio |
|---|---|---|---|
| 1.35 | 3.38 | 20 | 0.25 |

The coffee silverskin fibers were treated with an NaOH solution with 5, 10, and 15 wt.%/vol for 30 min at room temperature (27 °C) and a ratio of 1:10 by weight. The fibers were washed with distilled water until a neutral pH was obtained, and then they were dried in an oven at 50 °C for 5 h. The untreated silverskin (0% NaOH) was also dried in the oven at the same conditions. The dried fibers were stored in sealed plastic bags to avoid contamination. Biocomposite laminates (520 x 140 mm) were prepared by a hand lay up technique, which is given in Fig. 2. First, the polyester resin and MEK peroxide were mixed. The CCSF was impregnated with the matrix and put into a mold frame. Later, it was consolidated with a hydraulic press for 24 h at 1 bar and 27 °C. The prepared composites had a fiber volume of 35.1%.

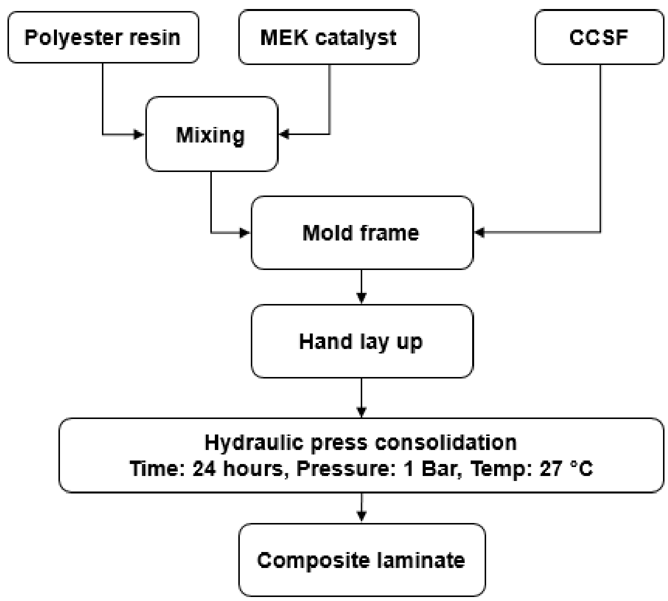


**Fig. 2.** Process flow chart showing the fabrication route of the CCSF/polyester composite

## Chemical Analysis

Some fiber specimens were sent to Nutrianálisis Laboratories in Bogotá, Colombia to determine the moisture percentage (using method 930.15 of AOAC International for humidity) and contents of cellulose, hemicellulose, and lignin (with Van Soest sequence from Agric. Handbook No. 379). The results are listed in Table 2.

## Tensile Test

The tensile properties of the CCSF/polyester biocomposites were studied using a universal testing machine (TINIUS OLSEN 50ST, Horsham, USA) according to ASTM D3039/D3039M (2014) with a load carrying capacity of 50 kN. Coupons for the tensile test were cut according to this standard. A crosshead speed of 2 mm/min was used for the tensile test. Five specimens were tested for each treatment condition.

## Flexural Test

The flexural properties were determined by means of a three-point bending configuration test with the same testing machine used for the tensile test and conducted according to ASTM D790 (2015) with a 250-kN load cell. Coupons for the flexural test were cut according to this standard, and the span-to-depth ratio was 40:1. Five specimens were tested for each treatment condition.

## Morphological Analysis

The surfaces of the untreated and treated fibers were observed using scanning electron microscopy (SEM) (NeoScope JCM 5000, JEOL, Tokyo, Japan). For the SEM analysis, CCSF samples were mounted on a stub and coated with gold using a sputter coater (Cressington Sputter Coater 108auto, Cressington Scientific Instruments, Watford, UK) for 180 s prior to SEM observation. The micrographs were obtained at 10 kV. Moreover, the tensile morphology damage was observed using a microscope (Zeiss SteREO Discovery.V12, Carl Zeiss Microscopy GmbH, Jena, Germany) on a 2-mm scale.

# RESULTS AND DISCUSSION

## Fiber Composition

According to the compositions tabulated in Table 2, mercerization partially decreased the hemicellulose and lignin content by up to 20% and 4.5%, respectively. This behavior was expected in accordance with the literature (Faruk *et al.* 2012; Cai *et al.* 2016; Pickering *et al.* 2016). The decrease of hemicellulose content is due to its dissolution in alkali (Ray *et al.* 2001; Dittenber and GangaRao 2012). Cai *et al.* (2016) also reported that reduction in lignin and hemicellulose content is due to the destruction of their acetyl and carboxyl groups or because of their dissolution under strong alkali solutions. The results in Table 2 show a decreasing trend from 5% NaOH.

Furthermore, the cellulose content slightly changed because mercerization rearranged cellulose chains from cellulose I (parallel conformation) to cellulose II (anti-parallel conformation) (Qin *et al.* 2008). The selected method used to determine the content of this polysaccharide did not differentiate the cellulose conformations.

**Table 2.** Chemical Analysis of NaOH-Treated Colombian Coffee Silverskin Fiber

| NaOH Treatment | Humidity (%) | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|---|
| 0% | 1.18 | 58.00 | 14.15 | 24.02 |
| 5% | 3.03 | 57.26 | 12.10 | 23.58 |
| 10% | 2.76 | 60.42 | 11.45 | 23.33 |
| 15% | 2.36 | 59.88 | 11.33 | 22.94 |

## Effect of the Alkali Treatment on the Mechanical Properties

As was mentioned earlier, alkali treatment improves the mechanical properties of the composites by modifying the surface of the fibers (Pickering *et al.* 2016). This can be observed in the enhancement of the specific strength and toughness. There is an optimum alkali concentration to achieve better properties that depends on the fiber (Manalo *et al.* 2015), and natural fibers have a porosity that is associated with their original structure. Mercerization creates vacancies by degrading part of the fiber structure, which can then be penetrated by resin and enhance its mechanical performance (Rong *et al.* 2001). The average properties obtained in this research are listed in Tables 3 and 4.

**Table 3.** Average Tensile Properties of the CCSF Composites

| NaOH (%) | Volume Fraction | Spec. Max Strength ($MPa/gcm^3$) | Max. Strain ($x10^{-3}$ mm/mm) | Spec. Tensile Modulus ($GPa/gcm^3$) | Spec. Tensile Toughness ($x\ 10^{-2}$ kJ/g) |
|---|---|---|---|---|---|
| 0 | 0.40 | 6.59 ± 0.02 | 3.26 ± 0.23 | 1.85 ± 0.16 | 1.21 ± 0.09 |
| 5 | 0.33 | 7.34 ± 0.45 | 3.15 ± 0.37 | 2.23 ± 0.07 | 1.30 ± 0.23 |
| 10 | 0.34 | 8.15 ± 1.11 | 4.10 ± 0.46 | 2.17 ± 0.44 | 2.03 ± 0.29 |
| 15 | 0.34 | 8.98 ± 0.75 | 3.59 ± 0.30 | 2.43 ± 0.06 | 1.77 ± 0.32 |

**Table 4.** Average Flexural Properties of the CCSF Composites

| NaOH (%) | Volume Fraction | Spec. Max. Strength ($MPa/gcm^3$) | Max. Strain ($x10^{-3}$ mm/mm) | Spec. Flexural Modulus ($GPa/gcm^3$) | Spec. Flexural Toughness ($x\ 10^{-2}$ kJ/g) |
|---|---|---|---|---|---|
| 0 | 0.37 | 28.12 ± 1.39 | 2.32 ± 0.24 | 13.74 ± 2.83 | 4.42 ± 0.57 |
| 5 | 0.37 | 35.17 ± 3.09 | 1.76 ± 0.19 | 16.35 ± 3.56 | 3.79 ± 0.56 |
| 10 | 0.34 | 32.96 ± 1.03 | 1.25 ± 0.15 | 28.35 ± 3.51 | 2.66 ± 0.42 |
| 15 | 0.33 | 29.36 ± 1.46 | 0.90 ± 0.10 | 33.94 ± 1.14 | 1.68 ± 0.09 |

*Specific ultimate strength and fracture strain*

As was expected, the specific strength increased with the treatment concentration because of an increase in the fiber superficial roughness. For instance, at 15% NaOH, the specific tensile strength increased by 36.3% compared with the untreated composite, which indicated a better coupling between the fiber and matrix. For the 5% NaOH treatment, the highest specific flexural strength was obtained, 35.17 $MPa/gcm^3$, which was 25.1% higher than that of the untreated composite. For the 10% and 15% NaOH treatments, this property was also higher than the untreated composite, but declined, which can be explained by the decrease in the load transfer because of the degradation of cellulose chains (Manalo *et al.* 2015). The literature indicated that the mechanical properties depend mainly on the adhesion of the fiber-matrix (Manalo *et al.* 2015). Therefore, it was concluded that the NaOH treatment improved the interlocking of the CCSF and polyester resin. Figure 3a shows the behavior of the specific ultimate strength.

It is interesting to note that the highest tensile strain was found with the 10% NaOH-treated composite, which was 25.5% higher than that of the untreated composite. The observed decrease in the tensile strain as the NaOH increased above 10% was explained by the increase in the fiber-matrix adherence. The flexural strain decreased sharply as the NaOH concentration increased, which indicated that the NaOH treatment increased the brittle behavior of the CCSF/polyester composite. Figure 3b shows the behavior of the fracture strain.

*Specific modulus*

According to previous research, if cellulose I changes to cellulose II, then the Young's modulus must decrease due to microfibrils losing their crystalline structure, such that they will deform much more (Gomes *et al.* 2007). However, for the alkali treatment of the composites with 15% NaOH, the tensile and flexural moduli were 31.6% and 147.0%

higher, respectively, than that of the untreated composite. This increase in the Young's modulus indicated an increase in the stiffness (Rong *et al.* 2001) after mercerization, which suggested there was better interlocking between the fiber and matrix. Figure 3c shows the behavior of the specific modulus.

*Specific toughness*

The specific tensile toughness increased, while the flexural toughness decreased. The highest tensile toughness was achieved with the 10% NaOH treatment, and it was 67.9% higher compared with that of the untreated CCSF. After the 15% NaOH treatment, the flexural toughness decreased by 62.0%. These results meant that the mercerization treatment increased the structural stability which coincided with the improvement of the fibre-matrix coupling. Figure 3d shows the behavior of the specific toughness.

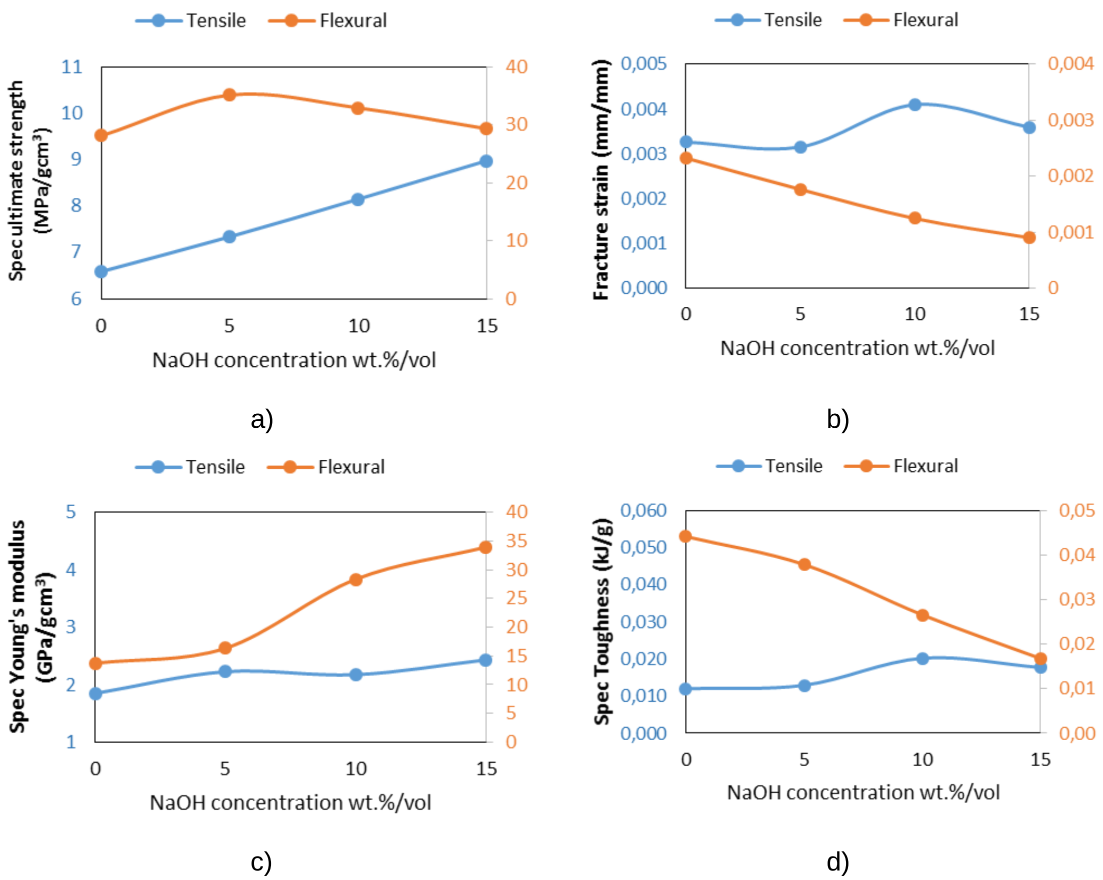


**Fig. 3.** Tensile and flexural properties of the NaOH-treated CCSF/polyester composites: (a) specific ultimate strength, (b) fracture strain, (c) specific modulus, and (d) specific toughness

## Morphology Examination

Images obtained by SEM revealed noticeable morphological differences between the untreated CCSF and 15% NaOH-treated CCSF. Natural fibers derived from plants consist mainly of cellulose fibrils embedded in a lignin matrix. Each fiber consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules. Each cell wall is made up of three main components, which are cellulose, hemicellulose, and lignin. The lignin-hemicellulose combination acts as a matrix, while microfibrils comprised of cellulose molecules act as fibers (John and Thomas 2008; Dittenber and

GangaRao 2012). The untreated coffee silverskin fiber surface had a denser lignin-hemicellulose layer, relatively flat morphology, and very low porosity. Figure 4a shows the SEM micrographs of the untreated CCSF.

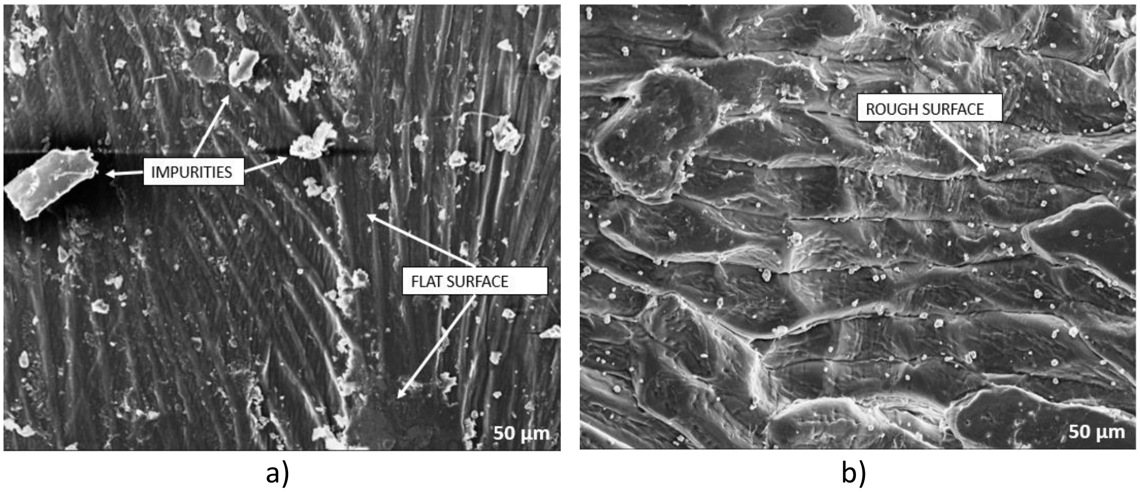


**Fig. 4.** SEM micrographs of the CCSF: (a) untreated and (b) 15% NaOH-treated

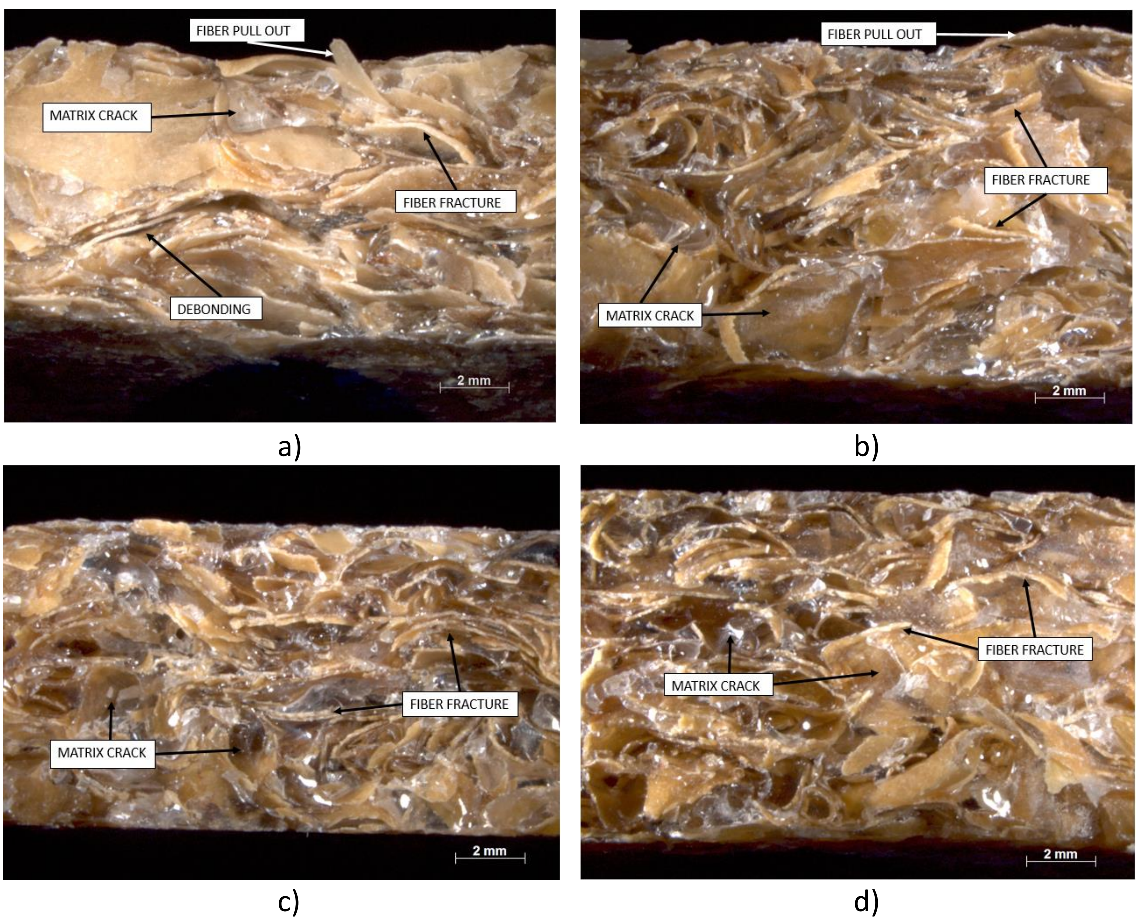


**Fig. 5.** Tensile damage of the NaOH-treated CCSF/polyester composite coupons: (a) untreated, (b) 5% NaOH-treated, (c) 10% NaOH-treated, and (d) 15% NaOH-treated

The NaOH treatment promoted a total or partial degradation of the lignin-hemicellulose matrix, which consequently increased the porosity. The SEM micrographs of the 15% NaOH-treated CCSF showed a rough surface, NaOH corrosion, and microfibrils under the lignin-hemicellulose layer. Figure 4b shows the SEM micrographs of the 15% NaOH-treated CCSF. It is well known that a higher porosity promotes higher fiber-matrix adherence and improves the mechanical performance of composites.

CCSF/polyester showed different damage morphology for untreated silverskin, 5%, 10% and 15% NaOH-treated composites. The microscope observations conducted to reveal the tensile test damage morphology with untreated silverskin are shown in Figures 5a. This figure shows debonding, matrix cracks, fiber fracture, and fiber pull out as the main damage characteristics. Debonding between the fiber and the matrix coupling area reduced the composite stress transfer capacity. This result is a consequence of a poor fiber-matrix interface. For the 5% NaOH-treated coupon (Fig. 5b) the debonding disappeared, which is evidence of an increase in the fiber-matrix adherence.

Figures 5c and 5d show the damage morphology for the 10% and 15% NaOH-treated composites with no evidence of fiber pull out. It was seen that the fiber-matrix coupling improved, the composite were brittle, and there were fiber fractures in the fiber-matrix coupling area and matrix cracks. It was determined that as the alkali concentration increased, the composites exhibited brittle behavior. This result was evidence of an increase in the fiber-matrix adherence and implied that the fiber absorbed the polyester matrix, which explained the brittle and flat fracture surface for the composites treated with higher NaOH concentrations.

## CONCLUSIONS

1. The NaOH treatment changed the structure and chemical composition of the Colombian coffee silverskin fiber (CCSF), and improved the mechanical adherence and chemical bonding between the CCSF and polyester resin.
2. The specific tensile and flexural strengths of the CCSF/polyester composites increased as the NaOH concentration increased.
3. The specific stiffness moduli of the CCSF/polyester composites increased as the NaOH concentration increased.
4. As the NaOH concentration increased, the specific tensile toughness of the CCSF/polyester composites increased.
5. The specific flexural toughness of the CCSF/polyester composites decreased as the NaOH concentration increased.
6. The SEM images of the coffee silverskin fiber surface after the 15% NaOH treatment showed a rough surface and the removal of lignin-hemicellulose.
7. The micro-scale damage from the tensile test of the untreated material included fibre fractures, matrix cracks, debonding, and fibre pull out. The treated material experienced fibre fractures and matrix cracks.

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## REFERENCES CITED

ASTM D3039/D3039M (2014). “Standard test method for tensile properties of polymer matrix composite materials,” ASTM International, West Conshohocken, USA.

ASTM D790 (2015). “Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials,” ASTM International, West Conshohocken, USA.

Cai, M., Takagi, H., Nakagaito, A. N., Li, Y., and Waterhouse, G. I. N. (2016). "Effect of alkali treatment on interfacial bonding in abaca fiber-reinforced composites," *Compos. Part A-Appl. S.* 90, 589-597. DOI: 10.1016/j.compositesa.2016.08.025

de Morais, J. A., Gadioli, R., and De Paoli, M.-A. (2016). "Curaua fiber reinforced high-density polyethylene composites: Effect of impact modifier and fiber loading," *Polímeros* 26(2), 115-122. DOI: 10.1590/0104-1428.2124

Dittenber, D., and GangaRao, H. (2012). "Critical review of recent publications on use of natural composites in infrastructure," *Compos. Part A-Appl. S.* 43(8), 1419-1429. DOI: 10.1016/j.compositesa.2011.11.019

Faruk, O., Bledzki, A. K., Fink, H.-P., and Sain, M. (2012). "Biocomposites reinforced with natural fibers: 2000-2010," *Prog. Polym. Sci.* 37(11), 1552–1596. DOI: 10.1016/j.progpolymsci.2012.04.003

Goda, K., Sreekala, M. S., Gomes, A., Kaji, T., and Ohgi, J. (2006). "Improvement of plant based natural fibers for toughening green composites—Effect of load application during mercerization of ramie fibers," *Compos. Part A-Appl. S.* 37(12), 2213-2220. DOI: 10.1016/j.compositesa.2005.12.014

Gomes, A., Matsuo, T., Goda, K., and Ohgi, J. (2007). "Development and effect of alkali treatment on tensile properties of curaua fiber green composites," *Compos. Part A-Appl. S.* 38(8), 1811-1820. DOI: 10.1016/j.compositesa.2007.04.010

Gurunathan, T., Mohanty, S., and Nayak, S. K. (2015). "A review of the recent developments in biocomposites based on natural fibres and their application perspectives," *Compos. Part A-Appl. S.* 77, 1-25. DOI: 10.1016/j.compositesa,2015.06.007

John, M., and Thomas, S. (2008). "Biofibres and biocomposites," *Carbohyd. Polym.* 71(3), 343-364. DOI: 10.1016/j.carbpol.2007.05.040

Kim, J. T., and Netravali, A. N. (2010). "Mercerization of sisal fibers: Effect of tension on mechanical properties of sisal fiber and fiber-reinforced composites," *Compos. Part A-Appl. S.* 41(9), 1245-1252. DOI: 10.1016/j.compositesa.2010.05.007

Luna, P., Lizarazo-Marriaga, J., and Mariño, A. (2016). "*Guadua angustifolia* bamboo fibers as reinforcement of polymeric matrices: An exploratory study," *Constr. Build. Mater.* 116, 93–97. DOI: 10.1016/j.conbuildmat.2016.04.139

Mahdi, E., Hernández, D. R., and Eltai, E. O. (2015). "Effect of water absorption on the mechanical properties of long date palm leaf fiber reinforced epoxy composites," *Journal of Biobased Materials and Bioenergy* 9(2), 173-181. DOI:

10.1166/jbmb.2015.1508

Manalo, A. C., Wani, E., Zukarnain, N. A., and Karunasena, K.-t. L. (2015). "Effects of alkali treatment and elevated temperature on the mechanical properties of bamboo fibre-polyester composites," *Compos. Part B-Eng.* 80, 73-83. DOI: 10.1016/j.compositesb.2015.05.033

Marinho, J. F., Braga, N. F., Krohn, A., Myata, F. S., Silveira, L. H., Neto, A. C., and Fechine, G. J. M. (2015). "Melt processing of polymer biocomposites," *Polímeros* 25(2), 133-136. DOI: 10.1590/0104-1428.1847

Narita, Y., and Inouye, K. (2014). " Review on utilization and composition of coffee silverskin," *Food Research International.* 61, 16-22. DOI: 10.1016/j.foodres.2014.01.023

Pickering, K. L., Efendy, M. G., A., and Le, T. M. (2016). "A review of recent developments in natural fibre composites and their mechanical performance," *Compos. Part A-Appl. S.* 83, 98-112. DOI: 10.1016/j.compositesa.2015.08.038

Pietak, A., Korte, S., Tan, E., Downard, A., and Staiger, M. P. (2007). "Atomic force microscopy characterization of the surface wettability of natural fibres," *Appl. Surf. Sci.* 253(7), 3627-3635. DOI: 10.1016/j.apsusc.2006.07.082

Qin, C., Soykeabkaew, N., Xiuyuan, N., and Peijs, T. (2008). "The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites," *Carbohyd. Polym.* 71(3), 458-467. DOI: 10.1016/j.carbpol.2007.06.019

Ray, D., Sarkar, B. K., Rana, A. K., and Bose, N. R. (2001). "The mechanical properties of vinyl ester resin matrix composites reinforced with alkali-treated jute fibres," *Compos. Part A-Appl. S.* 32, 119-127.

Rong, M. Z., Zhang, M. Q., Liu, Y., Yang, G. C., and Zeng, H. M. (2001). "The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites," *Compos. Sci. Technol.* 61(10), 1437-1447. DOI: 10.1016/S0266-3538(01)00046-X

Sanjay, M. R., Arpitha, G. R., and Yogesha, B. (2015). "Study on mechanical properties of natural - glass fibre reinforced polymer hybrid composites: A Review," *Materials Today: Proceedings* 2(4-5), 2959-2967. DOI: 10.1016/j.matpr.2015.07.264

Zuluaga, R., Putaux, J. L., Cruz, J., Vélez, J., Mondragon, I., and Gañán, P. (2009). "Cellulose microfibrils from banana rachis: Effect of alkaline treatments on structural and morphological features," *Carbohyd. Polym.* 76(1), 51-59. DOI: 10.1016/j.carbpol.2008.09.024

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