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Effect of enzyme and plasma treatments of bark cloth from *Ficus natalensis*: morphology and thermal behavior

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Bark cloth fabric has been in production in Uganda since the thirteenth century. In a move to preserve its cultural heritage, the United Nations Educational, Scientific and Cultural Organization (UNESCO) proclaimed in 2005 that Ugandan bark cloth is a "Masterpiece of the Oral and Intangible Heritage of Humanity." Plant fibers require surface treatment before aimed at impurity reduction and for enhancement of fiber to matrix adhesion in composites. An exploratory investigation of enzymatic and plasma treatment of bark cloth is reported. The morphology of the fabric was investigated using scanning electron microscope. Thermal behavior of the fabric was studied using thermogravimetric analysis and differential scanning calorimetry. Fourier transform infrared spectroscopy and ultraviolet–visible (UV–vis) spectrophotometer were used to evaluate the surface functional groups. Enzyme-treated fabrics were cleaner and thermally stable compared to plasma and untreated fabrics.

Keywords: bark cloth; *Ficus natalensis*; natural fiber; cellulose; enzyme; plasma

Introduction

Utilization of natural vegetable fibers as fillers in polymer composites is on the rise due to numerous advantages such as low specific weight, renewability, greenhouse gas emission mitigation, and less energy requirement in processing compared to synthetic fibers. Bark cloth is a naturally occurring non-woven fabric, produced in Uganda from majorly three tree species: *Antiaris toxicaria*, *Ficus brachypoda,* and *Ficus natalensis*. The most commonly used species is *F. natalensis* which after various processing routes is used in art and design to produce fashion articles.

For efficient processing and mechanical properties of natural fiber-reinforced composite structures, there is a need for fiber surface treatment in order to enhance fiber to matrix adhesion and the wettability of the fibers. Bark cloth being a natural fibrous non-woven fabric, the surface microfibers have plant material in the form of flakes and waxes for which if the fabric were to effectively undergo further processing, there is a need of dissolving the impurities.

Rwawiire, Luggya, and Tomkova (2013) studied the morphology, thermal, and mechanical properties of bark cloth; it was observed that the material is made up of naturally bonded microfibers entangled in specific aligned angles, a pattern acquired through its early extraction processes. The effect of alkaline treatment showed that the fabric becomes thermally stable; however, the softness to touch is lost leading to a coarse fabric after treatment. The thermo-physiological and comfort properties of the fabric were found to be comparable to those of other conventional natural fibers such as cotton (Rwawiire & Tomkova, 2014). Bark cloth fabric chemical composition was shown to be made up of 69% cellulose (Rwawiire, Tomkova, Militky, Kale, & Prucha, 2015).

With an increase in greenhouse gas emissions coupled with industrial pollution arising from chemical processing, avenues for cleaner production environments are being explored. Enzymes solve the problem, in that they are environmentally friendly and attached with less or no health risk to humans. In the quest for cleaner production environments, enzymes are part of the solution. Enzymes are biocatalysts which act on substrates and accelerate biochemical reactions. The textile industry has applied enzymes for desizing, scouring, and decoloring dye house waste water (Sricharussin, Ree-iam, Phanomchoeng, & Poolperm, 2009). Commercial enzymes which contain pectinase, hemicellulase, xylanase, laccase, and cellulase have been widely used by researchers elsewhere for treatment of wood fibers and other bast fibers (Alix et al., 2012; Bourmaud, Morvan, & Baley, 2010; Jiang, Zhang, & Wang, 2009; Joko et al., 2002; Mamun & Bledzki, 2013; Samanta, Basu, & Ghosh, 2008). Enzymes are utilized in less quantity; therefore, less water and energy is utilized in their application making them environmentally friendly (Marek et al., 2008).

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Plasma treatment is another type of textile surface modification treatment which can tailor the properties of textile substrates to achieve better physical, chemical and mechanical properties (Oliveira, Erkens, Fangueiro, & Souto, 2012). Plasma has been used to increase hydrophobicity of textile substrates of various types of fibers. Although several works (George, Sreekala, & Thomas, 2001; Höcker, 2002; Kalia, Kaith, & Kaur, 2009; Kalia, Thakur, Celli, Kiechel, & Schauer, 2013) have documented plasma treatment of natural fibers, to our knowledge, this is the first report in the scientific world investigating the bark cloth fabric surface treatment with enzymes and plasma. Despite the fact that bark cloth has been around dating as far back as thirteenth century, there has been limited data or scientific study on bark cloth. Therefore, in this study, for the first time, the effect of enzyme and plasma treatments on bark cloth with the view for polymer reinforcement is explored. The fabric morphology was studied using scanning electron microscope (SEM), thermal behavior using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), whereas surface functional groups characterization was done using Fourier transform infrared spectroscopy (FTIR). Ultraviolet–visible (UV–vis) spectrophotometer was used to analyze the dissolved plant material so as to understand the effectiveness of the commercial enzymes.

Materials and methods

Materials

Bark cloth from *F. natalensis* was extracted using the method described by Rwawiire and Tomkova (2014). Two commercial enzymes Texazym DLG neu and Texazym BFE supplied by INOTEX spol. s.r.o, Czech Republic was utilized.

Enzyme treatment

DLG enzyme was used together with BFE to form a mixture. The bath ratio was 1:30; 0.3 g of DLG and 0.6 g of BFE were utilized in 900 ml of distilled water. 0.2 g/l of Texawet DAF an antifoaming agent was added and the mixture was conditioned at 55 °C for 90 min as per the manufacturer's directives in a neutral environment.

Another bath was prepared using BFE enzyme with the same bath ratio of 1:30. 0.6 g of the enzyme was mixed with the antifoaming agent and the bath maintained at 55 °C for 90 min. Sodium bicarbonate was added so as to set the pH 9. Caution was taken such that both enzymes are not heated with a direct heat source.

Plasma treatment

Bark cloth fabrics were treated with plasma using laboratory device, Universal Plasma Reactor 100W,

Figure 1. Universal plasma reactor with bark cloth fabrics.

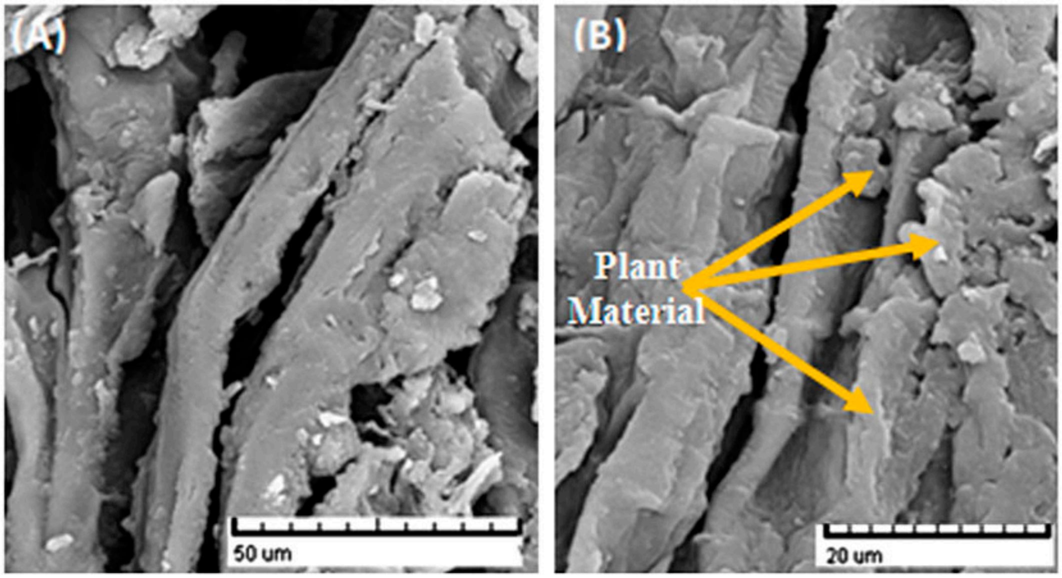

Figure 2. Morphology of untreated bark cloth: (A) ×1000 (B) ×2000.

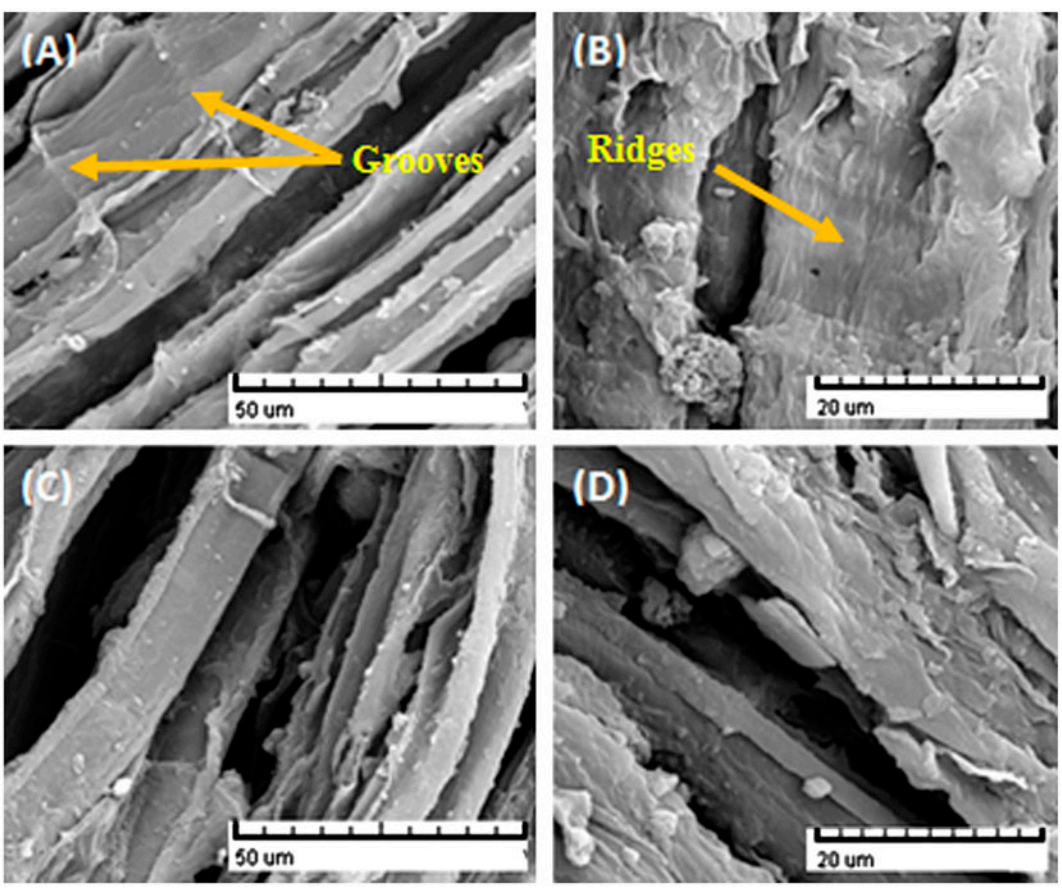

Figure 3. Enzyme-treated bark cloth: (A) and (B) BFE enzyme; (C) and (D) DLG enzyme.

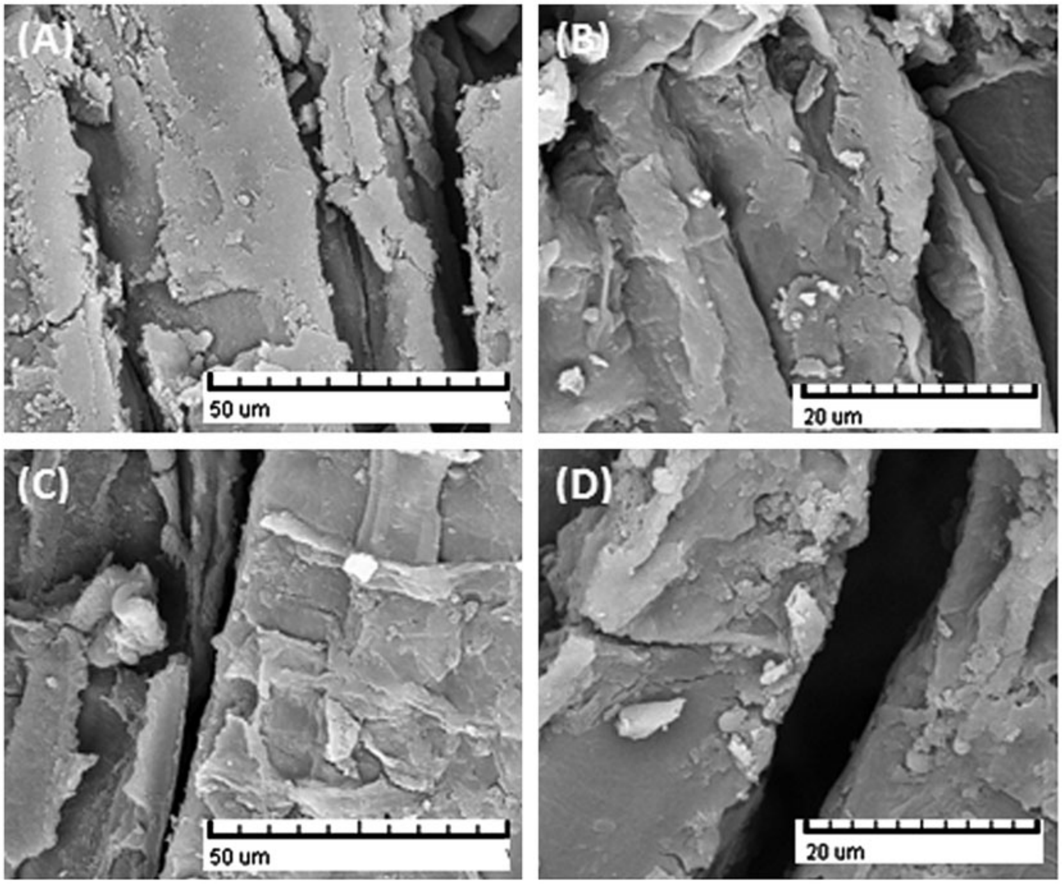

Figure 4. Plasma-treated bark cloth: (A) and (B) 30 s; (C) and (D) 60 s.

model FB-460, Class 2.5 (Figure 1). The cut fabrics were put in the reactor for the duration of 30 s, 45 s, and 60 s, respectively.

Characterization methods

Fabric morphology

The surface morphologies were investigated using a Vegas-Tescan SEM with accelerating voltage of 20 kV.

FTIR

Nicolet iN10 MX scanning FTIR microscope was used to provide the spectrum of the sample. *In situ* infrared absorbance spectra for both plasma- and enzyme-treated samples were obtained in the range of 4000–700 cm^{-1}.

Thermogravimetric analysis

TGA of samples weighing 7–8 mg was carried out using a Mettler Toledo TGA/SDTA851^{e} under air atmosphere heating from room temperature (25 °C) to 400 °C at a heating rate of 10 °C/min.

DSC analysis

Samples weighing approximately 10 mg were placed in aluminum crucibles and sealed. The specimens were heated in air atmosphere from 30 to 400 °C at a heating rate of 10 °C/min using the Perkin Elmer Differential Scanning Calorimeter DSC6.

UV–vis spectroscopy

The VWR UV-1600PC spectrophotometer was utilized in analysis of the degraded plant material–enzyme liquid mixture. The concentrate of both enzymes was diluted by 50% and the spectra obtained.

Results and discussion

Fabric morphology

Untreated

The fabric morphology is made up of a dense network of microfibers that are naturally bonded and aligned at specific angles (Rwawiire et al., 2013). Figure 2 shows that the fabric microfibers are embedded with plant material in the form of flakes, waxes, and other impurities. The fabric surface morphology is inherited through the extraction phase and the types of grooved pummeling hammers used. *F. natalensis* bark cloth undergoes lengthy refining processes which helps it to dissolve other plant material and drying in sunshine gives it a rich terracotta color.

Enzyme treated

The morphology shows that treatment with commercial enzyme BFE led to ridges and grooves along the microfibers (Figure 3). DLG enzyme is a textile auxiliary agent, it catalyzes decomposition of hemicelluloses and partially lignin in the binder layers of bast fibers. Whereas BFE catalyzes pectin layer decomposition, therefore it is the right enzyme for elementarization of natural fibers. The combination of DLG and BFE treatment led to change in mass of the substrates by 31% whereas BFE alone led to 30% change in mass of the substrates. The change in mass of the weighed substrates shows that the enzymes used dissolved a considerable amount of plant material in form of waxes, pectins, and other impurities. Because the main function of BFE enzyme is to dissolve impurities, it is observed that its performance was better than DLG and the surfaces are fairly cleaner compared to DLG. The loss in weight of the substrates was more with the DLG enzyme, due to the fact that the nature of DLG affects cellulose unlike BFE.

Plasma treated

Plasmas are used to modify lignocellulosic fibers, therefore it aids in surface activation of the fiber network (Höcker, 2002). Bark cloth fabric is made up of cellulose; therefore, the only reactive functional group is the hydroxyl group. Treatment with atmospheric plasma leads to oxidation of the cellulose. The morphology of plasma-treated fabrics (Figure 4) shows no striking visible difference on the surface.

Surface functional groups

Functional groups assignments and their respective bonding interactions of untreated and treated bark cloth substrates can be deduced using FTIR (Figures 5 and 6).

The transmittance peaks and their respective surface functional groups. Broad absorption bands at 3353 cm^{-1} and 3403 cm^{-1} are due to hydrogen bonding (O–H) stretching vibrations of cellulose and hemicelluloses (Célino, Goncalves, Jacquemina, & Fréoura, 2014). The BFE enzyme absorbance intensity at the above band was less than DLG enzyme meaning that more

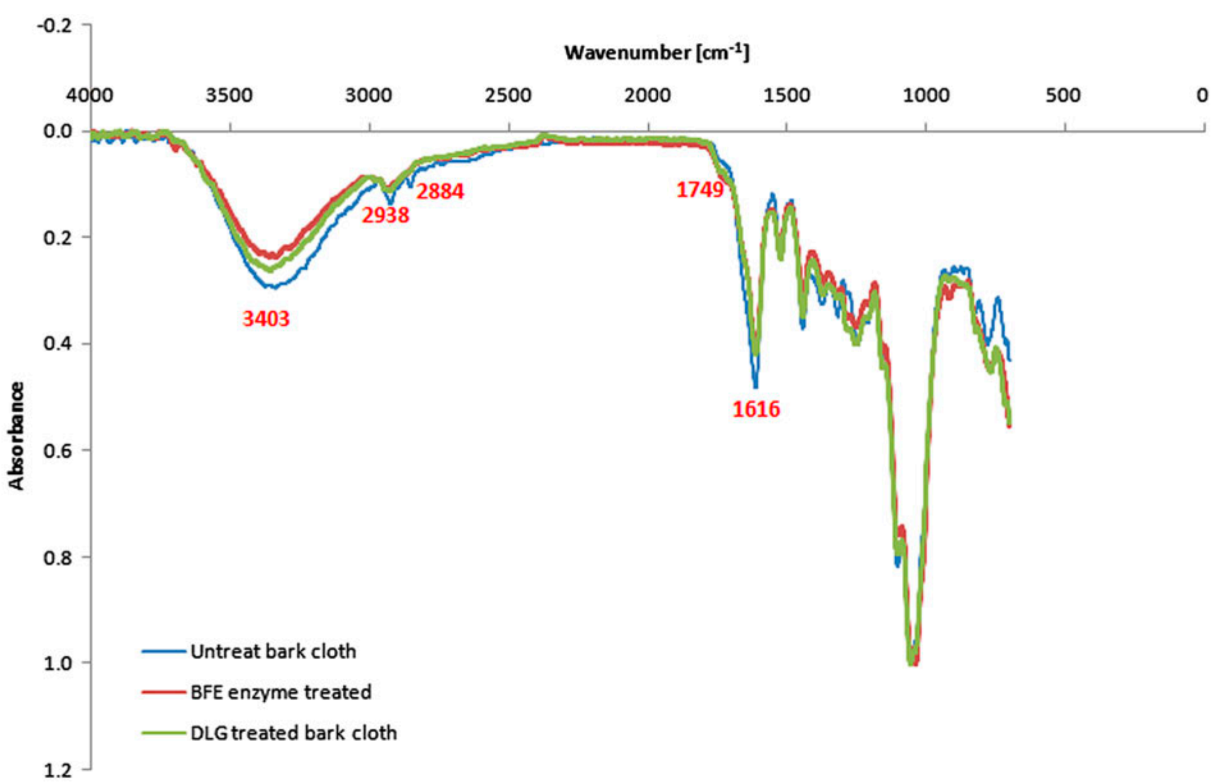

Figure 5. Spectra of enzyme-treated bark cloth.

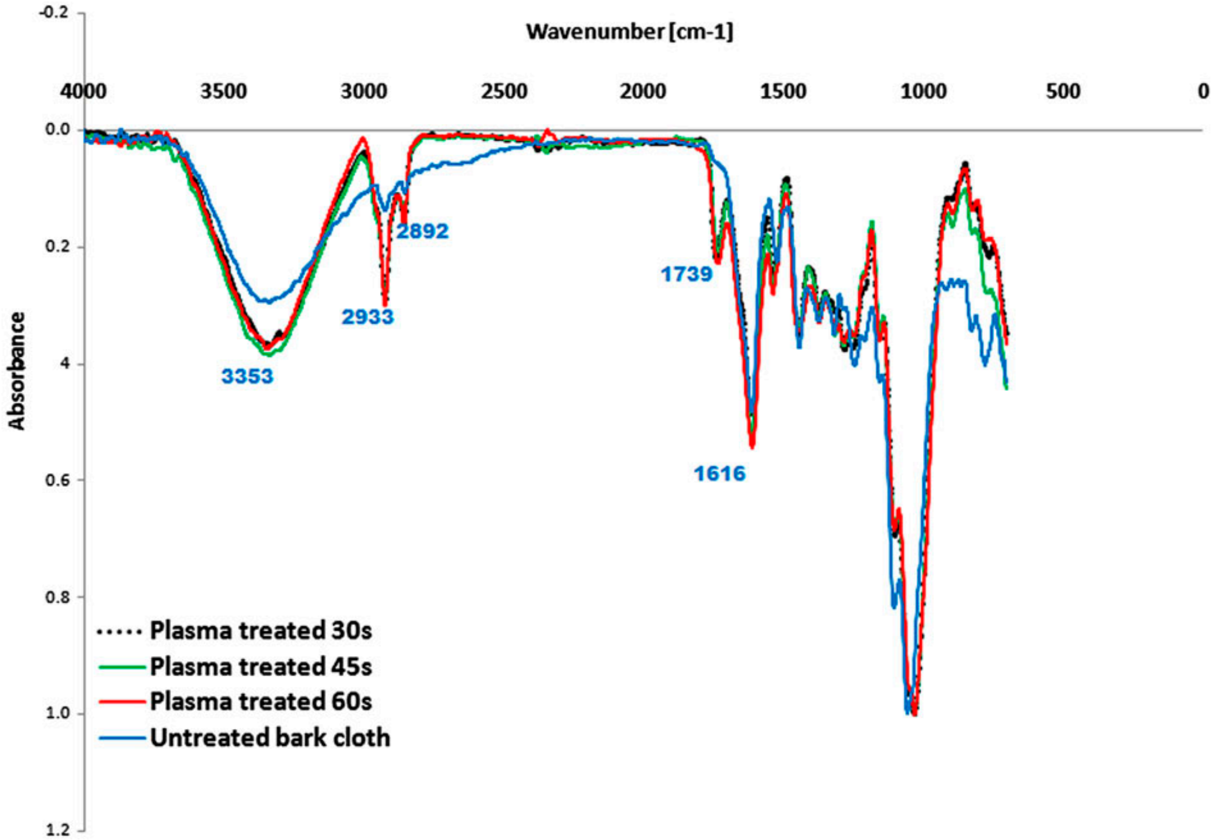

Figure 6. Spectra of plasma-treated bark cloth.

hemicelluloses were effectively dissolved by the enzymes. Plasma treatment excited the OH reactive bonds of cellulose, therefore, increasing the absorption peak intensity. The bands at 2933 $cm^{-1}$and 2938 cm^{-1} correspond to CH and CH_3 stretching vibrations of cellulose and hemicelluloses (Sarikanat, Seki, Sever, & Durmuskahya, 2014). The decrease in the absorption band of enzyme-treated fabrics is attributed to the lower content of hemicelluloses of the fabric structure which is further confirmed by the band at 1749 cm^{-1} that is decreased and is due to carbonyl groups (C=O) stretching and vibration of acetyl groups of hemicelluloses.

After this peak, the sudden leveling off shows that the hemicelluloses are removed from the fiber. Aromatic vibration of benzene ring in lignin may be at 1615 cm^{-1}. The absorption band at 1529 cm^{-1} was owing to CH_2 bending in lignin. In order to study the morphological behavior of plasma-treated fabrics, three times (30, 45, and 60 s) were chosen for comparison purposes. It is observed that the absorption bands of cellulose and hemicelluloses were greatly enhanced by plasma treatment meaning that the surfaces were activated (Figure 6). It is also observed that the time of exposure of fabrics to atmospheric plasma was directly proportional to the increase in activated surfaces of cellulose-OH groups; however, exposure time had no considerable difference between each other with the CH and CH_2 groups of hemicelluloses.

Thermal properties

One of the drawbacks for natural fibers is their limited thermal stability. Therefore, a study of their thermal behavior is of utmost importance for material engineers. For natural fibers, the thermogravimetric behavior is directly proportional to the chemical constituents of the fibers (Monteiro, Calado, Rodriguez, & Margem, 2012). Figure 7 shows the thermogram of bark cloth, whereas Table 1 is the summary of the parameters obtained from the figure. The first stage from 30 to 100 °C is attributed to evaporation of water accounting for about 5% loss in weight. The weight loss is higher in enzyme-treated fabrics than plasma due to the fact that the enzymes degraded the plant material in form of waxes and impurities however this led to thermal stabilization of the fabrics. Untreated and plasma-treated fabrics were less thermally stable

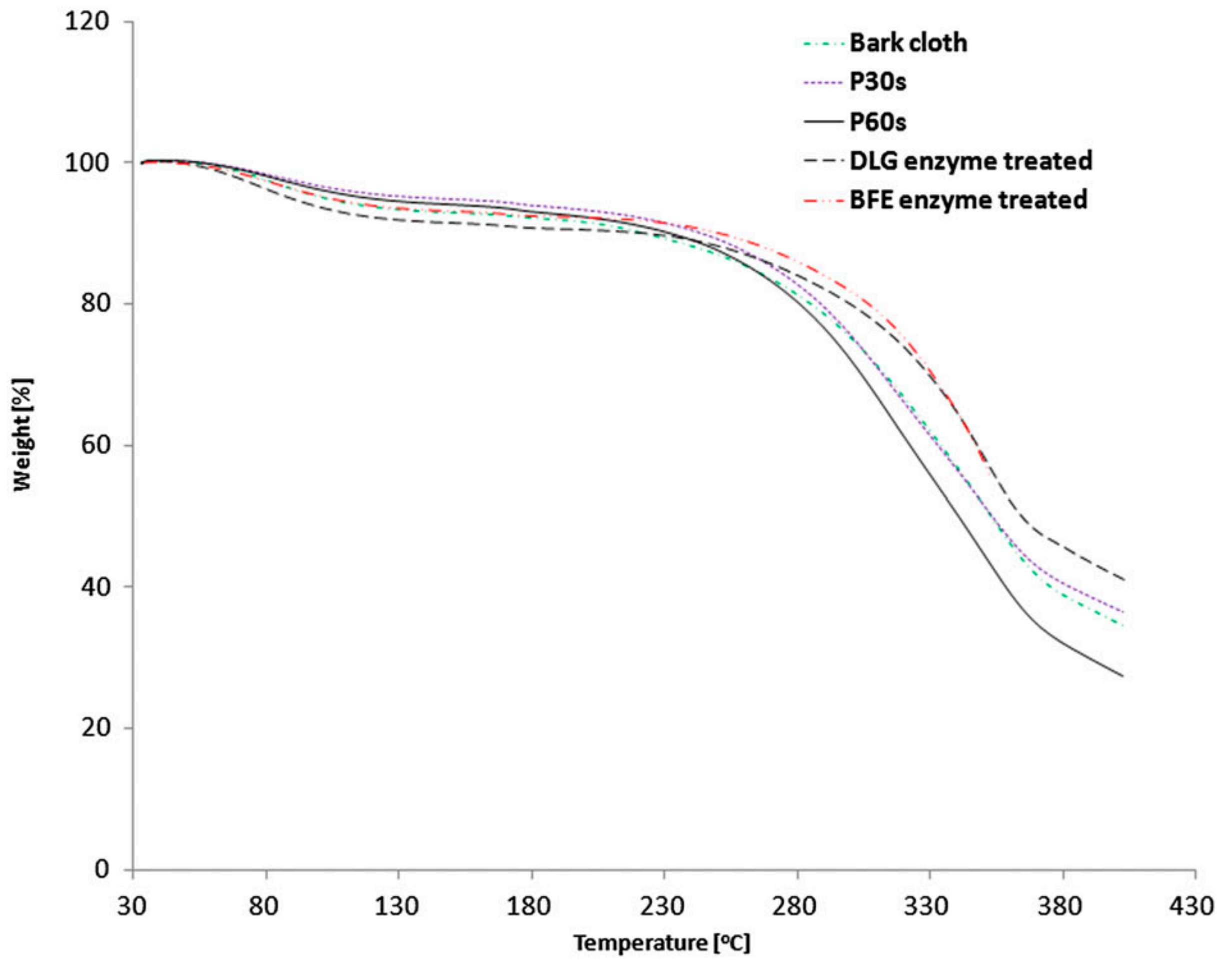

Figure 7. Thermogravimetric behavior of bark cloth.

Table 1. TGA results.

	First stage weight loss (%)	Degradation onset, T_o (°C)	Second stage peak (°C)
Untreated	6	206	260
DLG enzyme	7	237	280
BFE enzyme	6	230	285
Plasma 60 s	4	210	261
Plasma 30 s	4	221	261

compared to enzyme-treated fabrics. In terms of moisture evaporation, it was observed that plasma-treated fabrics had less moisture followed by BFE enzyme-treated fabrics. This is attributed to the fact that plasma made the surface hydrophobic, whereas the BFE enzyme did not degrade the fabric compared to the action by DLG enzyme.

Thermal behavior of the fabrics using DSC is shown in Figure 8, whereas Table 2 shows the summarized parameters obtained. The first peak corresponds to water loss, whereas a small second peak may be due to decomposition of hemicelluloses. Onset is due to decomposition of cellulose which is in agreement with the weight loss as can be observed from the TGA thermogram in Figure 7. The last peak at temperature 374 °C is attributed to decomposition of lignin. Treatment with enzymes made the fabrics stable because of their effect on the plant material, waxes, and other impurities.

UV–vis spectra

The diluted solution containing the dissolved plant material and enzymes as viewed under the UV–vis spectrophotometer showed a couple of close peaks within the wavelength of 200–250 nm (Figure 9). BFE enzyme solution mixture showed peaks at wavelength of 218, 226, 228, 238, and 248 nm, whereas DLG enzyme solution mixture absorbed at wavelength 214, 226, and 242 nm.

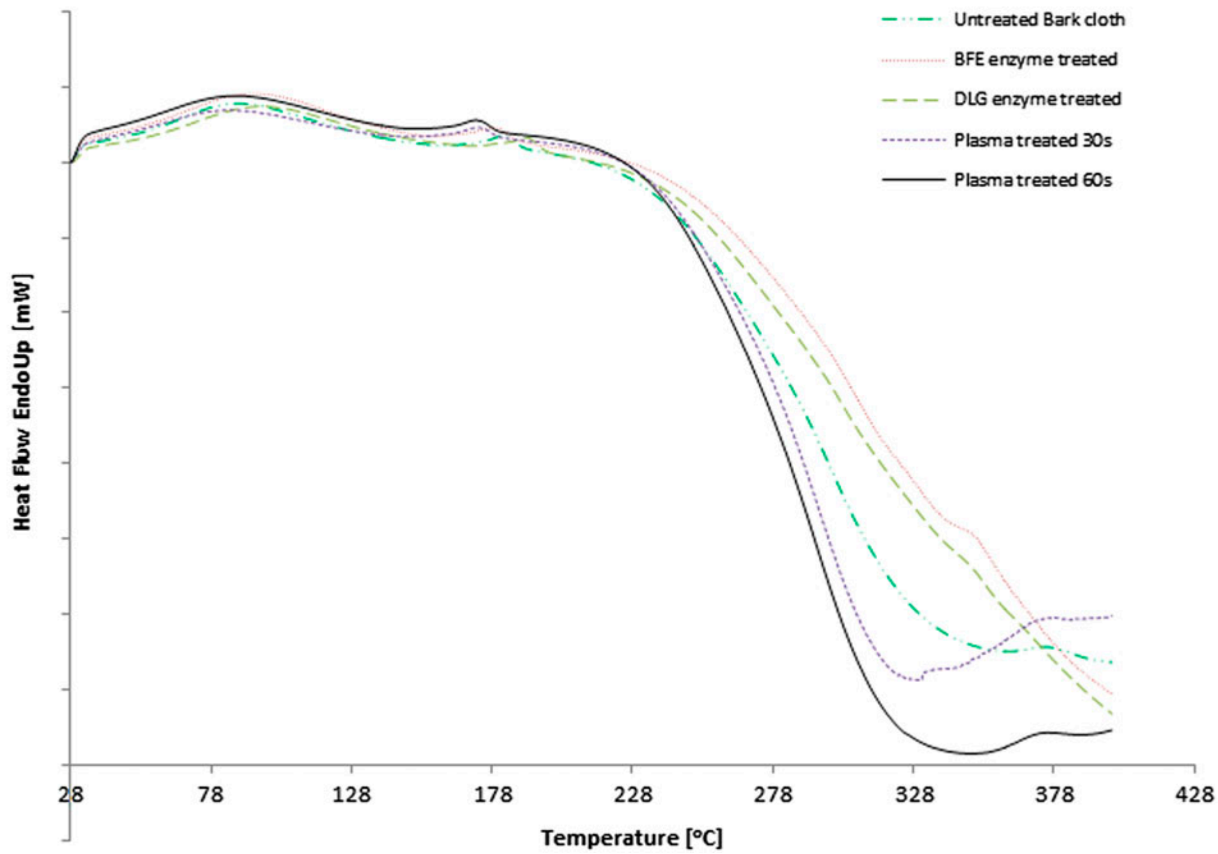

Figure 8. DSC of untreated, enzyme- and plasma-treated bark cloth.

Table 2. DSC results.

	Exothermic peaks		Onset of
	First (°C)	Second (°C)	Degradation (°C)
Untreated	88	183	233
DLG enzyme	97	192	239
BFE enzyme	95	180	246
Plasma 60 s	88	175	232
Plasma 30 s	87	175	231

A broad peak for both DLG and BFE was at wavelength of 226 nm. The spectra therefore shows that the dissolved plant material solution absorbs strongly in the UV range and the dissolved enzyme–plant residue mixture may be composed of aldehyde and aromatic rings which could mean that hemicelluloses and lignin were probably opened up in the fabric structure by enzyme treatment.

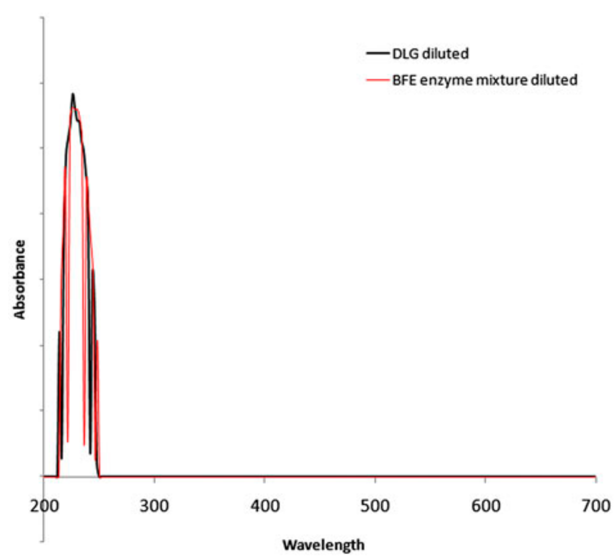

Figure 9. UV–vis spectra of dissolved components.

Conclusion

Enzyme- and plasma-treated bark cloth were characterized using FTIR, DSC, TGA and SEM.

Investigation of the thermal behavior has showed that bark cloth is stable below 200 °C; therefore, plasma and enzyme treatments can be explored for surface modification of bark cloth in preparation for polymer composite reinforcement.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

Alix, S., Lebrun, L., Marais, S., Philippe, E., Bourmaud, A., Baley, C., & Morvan, C. (2012). Pectinase treatments on technical fibres of flax: Effects on water sorption and mechanical properties. *Carbohydrate Polymers, 87*, 177–185.

Bourmaud, A., Morvan, C., & Baley, C. (2010). Importance of fibre preparation to optimize the surface and mechanical properties of unitary flax fibre. *Industrial Crops and Products, 32*, 662–667.

Célino, A., Goncalves, O., Jacquemina, F., & Fréoura, S. (2014). Qualitative and quantitative assessment of water sorption in naturalfibres using ATR-FTIR spectroscopy. *Carbohydrate Polymers, 101*, 163–170.

George, J., Sreekala, M. S., & Thomas, S. (2001). A review on interface modification and characterization of natural fibre reinforced plastic composites. *Polymer Engineering & Science, 41*, 1471–1485.

Höcker, H. (2002). Plasma treatment of textile fibres. *Pure and Applied Chemistry, 74*, 423–427.

Jiang, H., Zhang, Y., & Wang, X. (2009). Effect of lipases on the surface properties of wheat straw. *Industrial Crops and Products, 30*, 304–310.

Joko, K., Tokuda, S., Kikumoto, N., Sugai, J., Hayashi, T., & Arai, M. (2002). Enzymatic function on jute fiber with various commercial enzymes. *FIBER, 58*, 22–28.

Kalia, S., Kaith, B. S., & Kaur, I. (2009). Pretreatments of natural fibres and their application as reinforcing material in polymer composites – A review. *Polymer Engineering & Science, 49*, 1253–1272.

Kalia, S., Thakur, K., Celli, A., Kiechel, M. A., & Schauer, C. L. (2013). Surface modification of plant fibres using environment friendly methods for their application in polymer composites, textile industry and antimicrobial activities: A review. *Journal of Environmental Chemical Engineering, 1*, 97–112.

Mamun, A. A., & Bledzki, A. K. (2013). Micro fibre reinforced PLA and PP composites: Enzyme modification, mechanical and thermal properties. *Composites Science and Technology, 78*, 10–17.

Marek, J., Antonov, V., Bjelkova, M., Smirous, P., Fischer, H., Janosik, S. (2008). Enzymatic bioprocessing – New tool of extensive natural fibre source utilization. *2008 International Conference on Flax and Other Bast Plants*, Saskatoon, Canada.

Monteiro, S. N., Calado, V., Rodriguez, R. J. S., & Margem, F. M. (2012). Thermogravimetric behavior of natural fibers reinforced polymer composites? An overview. *Materials Science and Engineering: A, 557*, 17–28.

Oliveira, F. R., Erkens, L., Fangueiro, R., & Souto, A. P. (2012). Surface modification of banana fibres by DBD plasma treatment. *Plasma Chemistry and Plasma Processing, 32*, 259–273.

Rwawiire, S., Luggya, G. W., & Tomkova, B. (2013). Morphology, thermal, and mechanical characterization of bark cloth from *Ficus natalensis*. *ISRN Textiles*, *2013*, 1–8. doi:10.1155/2013/925198

Rwawiire, S., & Tomkova, B. (2014). Thermo-physiological and comfort properties of Ugandan barkcloth from *Ficus natalensis*. *The Journal of The Textile Institute, 105*, 648–653.

Rwawiire, S., Tomkova, B., Militky, J., Kale, B. M., & Prucha, P. (2015). Effect of layering pattern on the mechanical properties of bark cloth (*Ficus natalensis*) epoxy composites. *International Journal of Polymer Analysis and Characterization, 20*, 160–171.

Samanta, A. K., Basu, G., & Ghosh, P. (2008). Enzyme and silicone treatments on jute fibre. Part I: Effect on textile-related properties. *The Journal of The Textile Institute, 99*, 295–306.

Sarikanat, M., Seki, Y., Sever, K., & Durmuskahya, C. (2014). Determination of properties of Althaea officinalis L. (Marshmallow) fibres as a potential plant fibre in polymeric composite materials. *Composites Part B: Engineering, 57*, 180–186.

Sricharussin, W., Ree-iam, P., Phanomchoeng, W., & Poolperm, S. (2009). Effect of enzymatic treatment on the dyeing of pineapple leaf fibres with natural dyes. *ScienceAsia, 35*, 31–36.