Environmentally Friendly and Animal Free Leather: Fabrication and Characterization

Nabanita Saha*, Fahanwi Aśabuwa Ngwabebhoh, Hau Trung Nguyen, Petr Saha

Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Trida Tomase Bati 5678, 760 01 Zlín, Czech Republic

***Corresponding/reference author**: nabanita@utb.cz*

Abstract

Environmentally friendly and animal free leather also known as "vegan leather" or ''artificial leather'', is an alternative biomaterial produced without the use of any animal component. This biobased material compared to traditional leather shows similar physico-chemical and mechanical properties. Moreover, recent studies show that this class of materials are gradually gaining market in the fashion industry as leather substitutes. In the present study, efforts toward the preparation of such biobased materials using novel formulations agro-waste components is accomplished. Different compositions of the leather-like materials are successfully fabricated using waste maple leave (5-10%) and apple fruit (0-10%) pulp, mixed with additives such as kombucha biomass cellulose (25-40%), biodegradable polyesters (0-25%), and poly(ethylene) glycol diglycidyl ether (5-15%) as well as plasticizers (5-20%). The prepared biocomposite materials are characterized for morphology, mechanical, adhesion, and water absorptive properties. SEM results confirm that the fabricated biocomposites are porous and breathable. In addition, tensile, DMA, and adhesion analysis showed that the materials are flexible with considerable mechanical strength. To conclude, this material may be considered as a prospective leather alternative for application in leather accessories, such as handbags and upper shoe sole.

Keywords: Animal free leather, Vegan leather, Biocomposites, Environment friendly.

INTRODUCTION

Over the last decades, the gradual push toward the development of leather analogues has been trailed by scientific researchers and the footwear industry, leading to the design of various synthetic and natural materials [1]. However, the fashion industry with its ever-changing trends and styles tries to offer affordable market products to attract consumers, but this sector is unknown to most of the buyers as one of the major key players toward global pollution via production of massive quantities of wastes [2, 3]. Moreover, the increase in the manufacturing of leather fashion products from natural resources like animal skin is gradually becoming a critical issue to sustainability for current and future generations. Therefore, the development of alternative sources and design of eco-friendly materials is essential [4].

Amongst all, bacterial cellulose (BC) also known as microbial cellulose commonly produced by *Gluconacetobacter xylinus* via the formation of a gelatinous 3D interconnected nanofibril film and similar to the structural make-up as well as chemical composition of pure cellulose, stands as a promising alternative source for sustainable material design in the fashion industry [5, 6]. This biopolymer, possesses enhanced mechanical properties and presents several distinct advantages such as no lignin, hemicellulose or pectin contents, unique porous interconnected structure, high crystallinity, high water holding capacity, and high in situ and ex situ moldability. As such, these unique features have contributed to the wide applications of BC in biomedicine, pulp and paper, foods and composites industry [7, 8]. Recently, BC has been used as a reinforcement or filler matrix for the production of analogue leather materials. Nam et al. in a recent research study prepared a multi-layered BC composite material supported by denim and hemp fibres as a potential leather substitute [9]. In addition, a "Malai biocomposite material has" been fabricated from BC grown using agro-waste coconut water and leaf fibres as main components via molding into a 3D assembly [10]. The materials prepared showed soft hardness and good appearance to that of conventional leather.

However, the growing market interest and commercial feasibility of these alternative materials has been relatively modest, due to the high cost production, low breathability, and among other limitations. Herein, a novel formulation approach by combining preparation simplicity, low cost and eco-friendliness by investigating the conversion of agro residues to produce animal free leather materials was studied. In essence, kombucha biomass cellulose (KBC), maple leave pulp (MLP) and apple fruit pulp (AP) processed from agro-waste residues in combination with different biodegradable polyester polymers were blended to form biocomposite materials. The prepared biocomposite materials were then characterized for their morphological, mechanical, adhesion, and water absorptive properties for potential prospective application in the textile and shoe industries.

EXPERIMENTALS

Preparation of KBC and MLP

Basically, kombucha biomass cellulose (KBC) was fabricated from black tea and waste apple juice extracts. In brief, different ratios of produced extracts for both samples were added into cultured Hestrin–Schramm medium, sterilized by autoclave at 120 °C for 15 min and then transferred into 1% (v/v) suspension of *Gluconacetobacter xylinus* CCM 3611. The mixture was statically incubated at 30 °C for 15 days, forming KBC membranes that were harvested and washed with distilled water and stored at 4 °C for further usage.

Maple leave pulp (MLP) was extracted via an alkali treatment process as previously reported with slight modifications [11]. Briefly, dried collected maple leaves were treated with 8-12% NaOH solution for 1-2 h, washed to neutral pH, blended in a NutriBullet® blender and centrifuged using a Thermo Scientific™ Sorvall Lynx 4000 centrifuge (Waltham, MA USA). The precipitate was then collected and dried in an oven at 50 °C overnight to constant weight and stored for further use.

Fabrication animal free leather

In the present study, different mixture blends of varying percentage compositions were formulated and their physico-chemical properties analyzed. In essence, the compositions were based on either of the following components including maple leave pulp (MLP) used as filler, kombucha biomass cellulose (KBC), polyvinyl alcohol (PVA), polycaprolactone (PCL) and polylactic acid (PLA) used as polymer matrix, and poly (ethylene glycol) diglycidyl ether (PEDGE) applied as the crosslinker, as well as glycerol (GL) and epoxidized sunflower oil (ESFO) used as plasticizers. All compositions of the different components in the blends were calculated in terms of weight percent as shown in **Table 1**. Basically, four samples (S1, S2, S3 and S4) of varying compositions were investigated in this study. All four formulations, which includes S1, S2, S3 and S4 were prepared by the blending of two separate pre-mixtures. Firstly, MLP, KBC, GL, ESFO and PVA fiber were mixed using a micro ball mill (Lab Wizz 320, Laarmann Group, Netherlands) to produce a finely mixed paste. The second mixture was then prepared by mixing the produced fine paste with PCL and/or PLA (dissolved in dichloromethane), to form a uniform blend. The mixture was molded (thickness ≈2 mm) under gentle pressing using a press machine of 5-20 kN force to form sheets. All the samples were air dried at ambient temperature to constant weight and then cured at 120 °C for 30 min. The samples were cooled down to room temperature and stored for further analysis and application.

Table 1. Compositions of environmentally friendly and animal free leather

Samples	Components and weight percentage of each composition (w/w%)								
	KBC	MLP	AP	PVA	PCL	PLA	GL	ESFO	PEDGE
S1	35	10	-	15	20	-	5	10	5
S2	30	10	10	10	15	-	5	10	10
S3	25	5	-	25	10	5	20	-	15
S4	40	5	-	5	20	10	10	5	5

Characterization methods

Surface morphological properties of the prepared biocomposite materials were examined using the instrument Nova NanoSEM (FEI™, Brno, Czech Republic) at an accelerating voltage of 5 kV. Changes in the storage (E') and loss (E") modulus as well as thermal transitions of the prepared samples (cut in dimensions of 50 mm length and 7 mm width) were measured using a Q-800 dynamic mechanical analyzer (DMA) (TA instruments, Delaware, USA) in the temperature range between -25 to 150 °C at a heating rate of 3 °C/min under the tension deformation mode. Tensile tests to measure the tensile and tear strength as well as elongation at break were performed following the ASTM D882 standards using the Instron 5567 (Instron, USA) instrument at room temperature (25 °C) and a crosshead speed of 10 mm/min. Adhesion test of the fabricated samples was conducted following the pull-off method as described by ASTM D 4541 using an Elcometer 510 adhesion tester (Elcometer, Manchester, UK).

The water uptake capacity of the prepared materials was also evaluated by the static water absorption method based on the BASF standards of leather technology [12]. In brief, samples (15 mm width x 20 mm length) were cut and completely immersed in distilled water for 24 h to reach equilibrium absorption. Readings were recorded within different time intervals in triplicates and the average value recorded. The water absorptivity percentage was then calculated using the equation below.

$$\text{Water absorptivity } \% = \frac{W_0}{W} \times 100$$

where, Wo and W are the weights of the samples before and after immersion (g), respectively.

RESULTS AND DISCUSSION

Characterization of animal free leather materials

Morphological analysis: The morphologies of the polymeric matrix of S1, S2, S3 and S4 biocomposites were evaluated by SEM. As shown in **Figure 1**, the images present a good adhesion interaction between the blended fibers and particulates of the different mixture components. It is worth noting that uniform dispersion of all components in a given matrix is highly necessary to achieve stable adhesion and good mechanical properties [13]. In addition, results showed voids and pores for all investigated biocomposites' polymeric matrix. The porosity of the prepared biocomposites was further analyzed using a Bendtsen porosity tester apparatus (N3500 model, Paper-testing association) and obtained results as provided in **Table 2**, confirmed the materials to be porous due to the recorded airflow through the materials. In comparison to a procured commercial polyurethane (PU) leather-like material (as control), no airflow was recorded, indicating that the prepared biocomposite materials in the present study were breathable making them suitable for leather apparel application. Furthermore, S4 compared to the other samples based on visual analyses showed good fiber-matrix adhesion due to its uniform and considerable smooth appearance.

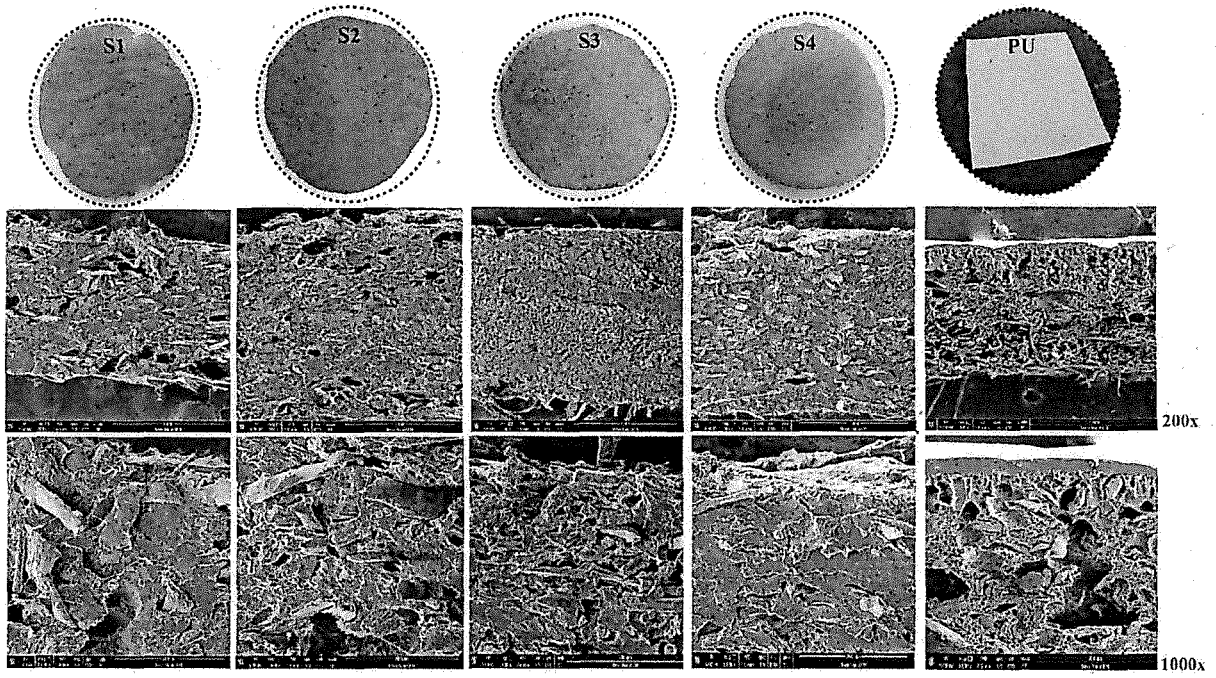

Figure 1. Cross sectional SEM images showing the different biocomposites and commercial PU material.

Mechanical analysis: **Figure 2**a shows the stress-strain plot for the prepared biocomposites. As observed, S2 and S3 were stiffer compared to compared to S1 and S4.

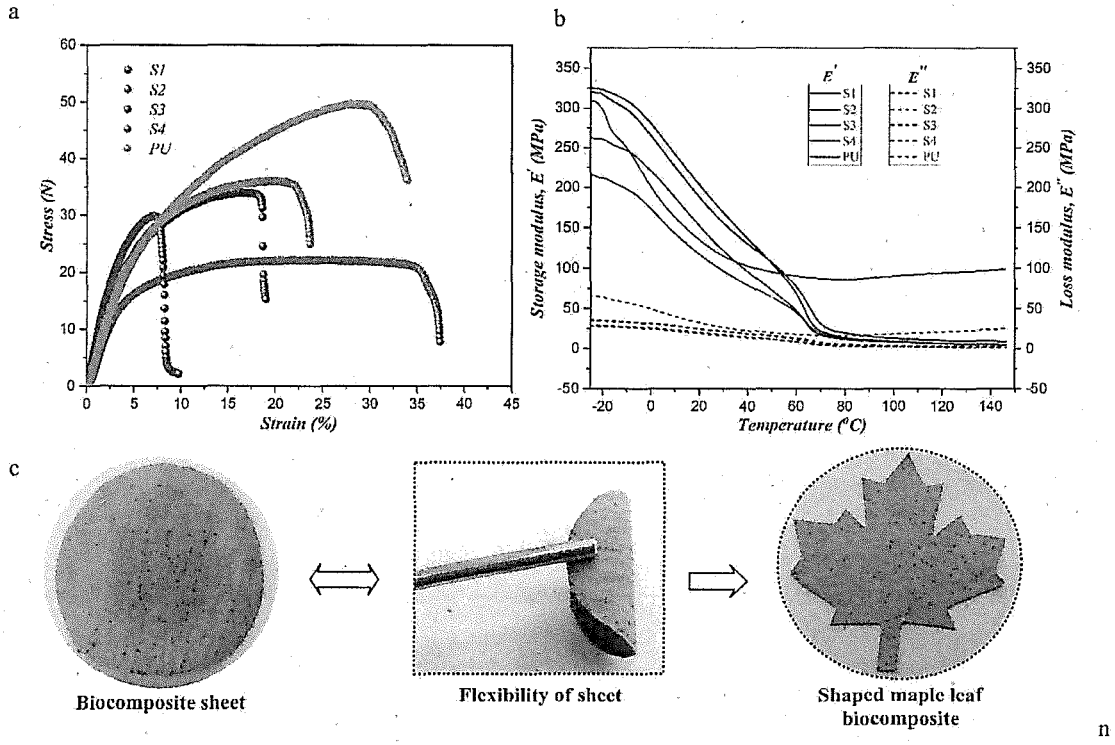

Figure 2. a) stress-strain curves and b) DMA thermograms of biocomposite samples S1, S2, S3, S4 and commercial PU.

This may be attributed to the low KBC content present in the both samples. In addition, the crosslinking density generated as a result of high incorporated PEDGE may have attributed to the stiffness of the materials. A further comparison of prepared

biocomposite with PU-based leather-like showed that the tensile parametric values of PU as provided in **Table 2,** was 3 times higher than that of the materials in the present study. This indicates that more research study, which is currently under progress is required to improve the mechanical properties of the fabricated biocomposites. The mechanical response from tension deformation as a function of temperature on the viscoelastic properties of the fabricated biocomposites are elucidated in **Figure 2**b. As observed, the elastic modulus gradually decreases with increasing temperature. A further slight sharp decrease between 50 to 70 °C is visualized, which corresponds to the α-relaxation of amorphous PLA and PVA. However, the effect of the amount of incorporated KBC in the polymer matrix could be observed. By increasing the amount of KBC (S1 and S4), the elastic modulus before Tg decreased compared to S2 and S3 samples. This indicated that the addition of KBC in the polymer matrix increased segmental motion of the other polymer chains thereby decreasing the stiffness of the materials. However, these effects are mostly related to the adhesion ability at the fiber-matrix interface. As described in a previous study by Kakroodi et al. [14] on the enhancement of elastic modulus following the mixing PCL and PLA, it can be mentioned in the present study that the inclusion of PLA in the polymer matrix, greatly affected the overall elasticity following the elastic modulus obtained especially for S4 (**Table 2**), and which in turn increased the strength of the materials.

Table 2. Comparison of mechanical analysis for biocomposite and synthetic leather materials

Samples	Tensile strength (MPa)	Elongation at break (%)	Tear strength (N/mm)	Elastic modulus (MPa)	Porosity (mL/min)
S1	1.59	14.70	23.95	104.11	1360
S2	1.37	19.20	20.57	133.89	1520
S3	1.33	6.95	19.98	140.27	812
S4	1.68	16.42	25.25	84.95	610
PU	5.28	31.54	79.20	106.10	0

Adhesive property analysis: Pull-off strength analysis was evaluated in order to determine de-cohesion or de-adhesion effect of the prepared materials. In brief, when sample failure occurs between the coating and the substrate, the failure mechanism is denoted as de-adhesion, while occurrence within the coatings is described as de-cohesion [15]. The observed types of failures corresponding to each sample is described in **Figure 3**a. With the exception of S4, all investigated samples showed 100% glue failure. This be attributed to the poor interaction of the glue with the biocomposites. The pull-off force for samples S1, S2, S3, S4 and PU were determined as 6.07, 4.68, 4.48, 7.11, 4.84 MPa, respectively.

Water absorption performance: Water sensitivity has proven to be another important property for the practical application of leather materials. The water absorption property of the formulated biocomposite samples was analyzed in order to further understand their physico-chemical characteristics. **Error! Reference source not found.**b shows the water absorptive capacity of the fabricated different biocomposite materials within a time interval of 24 h following leather material quality assessment by BASF. Results achieved showed that the water absorptivity of the biocomposite materials were slightly different by varying in the range of 20 – 52%. However, the highest and lowest absorption capacities were obtained for S2 and S3 samples. The high water absorption for S2 was attributed the KBC and incorporated AP which great increase in swelling capacity of material. On the other hand, the low swelling for S3 was due to the low weight of ratio of KBC and the high crosslinked network structure obtained with the large amount of incorporated PEDGE as crosslinker. This decreased free volume in the materials' matrix and consequently reduced the uptake of water. Summarily, low water absorptivity was achieved for all investigated samples, indicating a good interface adhesion between the biocomposite material components attributed to the presence of strong hydrogen bonding interactions, which tend to stabilize the materials' matrix that to some extent reduced the extent of water absorbance [16].

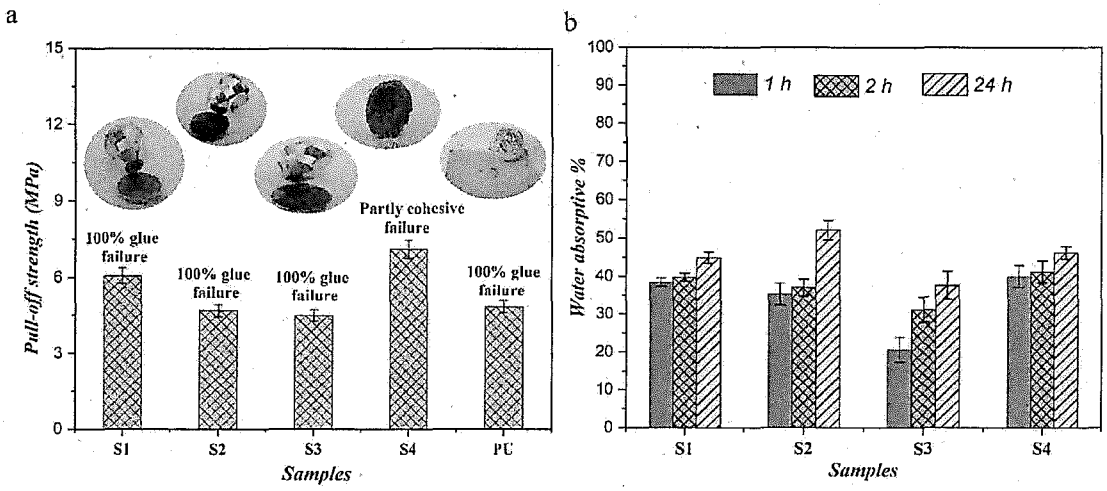

Figure 3. a) Pull-off strength for the different biocomposites samples (S1, S2, S3, and S4) and commercial PU leather material as control and b) water absorptivity of the biocomposites materials.

CONCLUSION

In the current study, environmentally friendly new formulations of animal free leather materials were produced and successfully characterized. The materials were mainly produced from agro-waste sources of KBC, maple leave pulp as filler extracted from dry waste leaves, and additives such as biodegradable polyesters and plasticizers. SEM analysis showed the materials were porous and breathable. The tensile test and DMA analysis demonstrated the materials to be flexible with considerable mechanical strength. Results deduced that sample S1 and S4 showed superior physico-chemical and flexible properties compared to S2 and S3. This was typically attributed to the incorporated amounts of KBC, PVA, PCL and PLA, which enhanced the mechanical stability in the polymeric matrix of the samples. While adhesive analysis depicted that partial cohesion mechanism with substrate was obtained just for S4. In addition, the water absorptivity evaluation indicated that the values obtained were slightly higher compared to the required value (max. 25%) for upper shoe sole by BASF. Although the present formulated samples still show some demerits, including low mechanical integrity compared to conventional synthetic polyurethane and animal leather, more research is still in progress toward improving the performance of this materials for possible commercialization as leather alternative in the fashion industry.

ACKNOWLEDGEMENTS

This work is supported by the Ministry of Education, Youth and Sports of the Czech Republic – NPU Program I (LO1504), Internal Grant Agency (Project No. IGA/CPS/2019/009), Tomas Bata University in Zlin, Czech Republic.

REFERENCES

1. Fernandes, M., et al., *Development of novel bacterial cellulose composites for the textile and shoe industry.* Microbial Biotechnology, 2019. **12**(4): p. 650-661.
2. Rathinamoorthy, R., *Consumer's Awareness on Sustainable Fashion*, in *Sustainable Fashion: Consumer Awareness and Education*, S.S. Muthu, Editor. 2019, Springer Singapore: Singapore. p. 1-36.
3. McNeill, L. and R. Moore, *Sustainable fashion consumption and the fast fashion conundrum: fashionable consumers and attitudes to sustainability in clothing choice.* International Journal of Consumer Studies, 2015. **39**(3): p. 212-222.
4. Vaisanen, T., et al., *Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: A review.* Waste Management, 2016. **54**: p. 62-73.
5. Ng, F.M. and P.W.J.T.D.J. Wang, *Natural self-grown fashion from bacterial cellulose: a paradigm shift design approach in fashion creation.* 2016. **19**(6): p. 837-855.
6. Garcia, C. and M.A. Prieto, *Bacterial cellulose as a potential bioleather substitute for the footwear industry.* Microbial Biotechnology, 2019. **12**(4): p. 582-585.
7. Iguchi, M., S. Yamanaka, and A.J.J.o.m.s. Budhiono, *Bacterial cellulose—a masterpiece of nature's arts.* 2000. **35**(2): p. 261-270.
8. Picheth, G.F., et al., *Bacterial cellulose in biomedical applications: A review.* 2017. **104**: p. 97-106.
9. Nam, C. and Y.A. Lee, *Multilayered Cellulosic Material as a Leather Alternative in the Footwear Industry.* Clothing and Textiles Research Journal, 2019. **37**(1): p. 20-34.
10. Material District. *Malai biocomposite.* 2019 March 08, 2019]; Available from: https://materialdistrict.com/material/malai/.
11. Chen, H., et al., *Effect of alkali treatment on microstructure and mechanical properties of individual bamboo fibers.* 2017. **24**(1): p. 333-347.
12. BASF, *Pocket book for leather technologist.* 4th ed. 2007, Aktiengesellschaft, 67056 Ludwigshafen, Germany. 454.
13. Kong, I., et al., *Study of properties of coconut fibre reinforced poly (vinyl alcohol) as biodegradable composites.* 2016. **11**(1): p. 135-143.
14. Kakroodi, A.R., et al., *Facile production of biodegradable PCL/PLA in situ nanofibrillar composites with unprecedented compatibility between the blend components.* Chemical Engineering Journal, 2018. **351**: p. 976-984.
15. Dmitruk, A., et al., *Pull-off strength of thermoplastic fiber-reinforced composite coatings.* 2018. **32**(9): p. 997-1006.
16. Wan, Y., et al., *Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites.* 2009. **69**(7-8): p. 1212-1217.

Nabanita Saha

From: PPS2019 <PPS2019@csir.co.za>
Sent: Wednesday, September 18, 2019 9:04 PM
To: Nabanita Saha
Subject: PPS2019: S02-112 Paper Acceptance

Dear Dr. Nabanita Saha,
Your contribution "*Environmentally Friendly and Animal Free Leather: Fabrication and Characterization*", with Reference number S02-112, has been accepted as **KEYNOTE** presentation in the symposium S02 - Bio-based and Biodegradable Polymers to the **PPS2019** Conference of the Polymer Processing Society.
A very large number of contribution has been submitted and accepted for the PPS20199 which will be held in Pretoria, South Africa during November 18-22 (including postconference tour on November 22nd), 2019. We expect PPS2019 to be a very fruitful event with diverse topics.
In order to allow an optimal organization of the Conference, it would be extremely useful for us if you could finalize your registration as soon as possible. Early bird on or before 30th September 2019.
Thank you if you already completed your registration.

==========

PPS2019 Conference Secretariat
PPS2019@csir.co.za / www.pps2019.com

==========