



Conversion of finished leather waste incorporated with plant fibers into value added consumer products – An effort to minimize solid waste in Ethiopia



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ABSTRACT

Presently, the leftovers from leather product industries are discarded as waste in Ethiopia. The objective of the present study was therefore, to prepare composite sheets by incorporating various plant fibers like enset (*Ensete ventricosum*), hibiscus (*Hibiscus cannabinus*), jute (*Corchorus trilocularis* L.), palm (*Phoenix dactylifera*) and sisal (*Agave sisal*) in various proportions into the leather waste. Resin binder (RB) and natural rubber latex (NRL) were used as binding agents for the preparation of the composite sheets.

The composite sheets prepared were characterized for their physicochemical properties (tensile strength, elongation at break, stitch tear strength, water absorption, water desorption and flexing strength). Composite sheets prepared using RB having 10% hibiscus, 20% palm and 40% sisal fibers showed better mechanical properties than their respective controls. In composite sheets prepared using NRL having 30% jute fiber exhibited better mechanical properties than its control. Most of the plant fibers used in this study played a role in increasing the performance of the sheets. However, as seen from the results, the contribution of these plant fibers on performance of the composite sheets prepared is dependent on the ratio used and the nature of binder. The SEM studies have exhibited the composite nature of the sheets and FTIR studies have shown the functional groups of collagen protein, cellulose and binders. The prepared sheets were used as raw materials for preparation of items like stiff hand bags, ladies' purse, keychain, chappal upper, wallet, wall cover, mouse pad and other interior decorating products. By preparing such value added products, we can reduce solid waste; minimize environmental pollution and thereby securing environmental sustainability.

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1. Introduction

Africa's livestock population represents over 14%, 20% and 28% of the global cattle, sheep and goats population respectively and with the estimate of 220 million cattle heads, 214 million sheep and 257 million goats flock (FAO, 2013). Ethiopia, one of the east African Countries, is blessed for having diverse agro ecology that made it suitable to be the home for many livestock species. The livestock population of the country according to the estimates of (FAO, 2015) is 55.694 million bovine; 26.537 million sheep and 25.035 million goats. This fact made Ethiopia to rank 1st in Africa

and 10th in the world in its livestock population (EFDRE, 2015). The huge livestock resource according to John (2007) is basis for the development of a vibrant leather and leather products industry in the country.

Tanning, a series of collagen stabilizing processes by the tanning agents, such that the skin/hide is no longer susceptible to putrefaction or rotting (HMIP, 1995), is an age long art which has transcended generations (Thosmason, 1985). The leather industry generally uses hides and skins as raw materials, which are the by-products of meat and meat products industry. In this respect, the leather industry could have easily been distinguished as an environmentally friendly industry, since it processes waste products from meat production (Lang et al., 1999). However, the leather industry has commonly been associated with high pollution due to the bad smell, organic wastes and high water consumption caused during manufacturing processes (Taylor et al., 1998).

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Different forms of biological wastes emerge during the transformation of hides and skins into leathers, in the leather industries all around the world; have negative impacts on the environment (Ozgunay et al., 2007). From one ton of wet-salted hide, only about 200 kg is converted into finished leather and the rest is discarded as waste (Lang et al., 1999).

Recently, due to the increase in population and very high competition on resource; natural resources are being exploited substantially as an alternative to synthetic materials. For this reason, utilization of natural fibers for the reinforcement of the composites has been receiving increasing attention. Natural fibers have many remarkable advantages over synthetic fibers. Nowadays, various types of natural fibers (Taj et al., 2007) have been investigated for use in composites including flax, hemp, jute straw, wood, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm, sisal, coir, water hyacinth, pennywort, kapok, paper mulberry, banana fiber, pineapple leaf fiber and papyrus (Wikipedia, home page, 2010). Composites are a versatile and valuable family of materials that can solve problems of different applications. They facilitate the introduction of new properties in the materials. Recycling and renewing natural resources are giving a new dimension in discovering new materials (Khan et al., 2010).

Nowadays alternative options for utilizing tannery solid wastes are taking worldwide significance for preparation of different products, among which is crust leather trimmings/finished leather scraps used for making leather boards and production of bricks (Zhang et al., 2006).

The objective of the present work therefore, is to prepare leather composite sheets, from finished leather scrap, in combination with plant fibers of enset, hibiscus, jute, palm and sisal using resin binder (RB) and natural rubber latex (NRL).

2. Materials and methods

2.1. Materials

Finished leather scraps were collected from ELICO (Ethiopian Leather Industry Corporation). Texbinder LS was purchased from Textan Co. India. Natural rubber latex, Polyethylene glycol and $Al_2(SO_4)_3$ were purchased from Sastha PLC Chennai India. Plant fibers such as Jute (*Corchorus trilocularis* L.), Hibiscus (*Hibiscus Cannabinus*), and Palm (*Phoenix dactylifera*) were collected from Chennai and Andhra Pradesh, India. The fibers of sisal (*Agave sisalana*) and Enset or Ethiopian banana (*Ensete ventricosum*) were collected from Ethiopia and other chemicals used in this study were of laboratory grade chemicals.

2.2. Methods

Preparation of leather fiber (LF) and plant fibers (PFs):

Finished leather scrap was cut into small pieces of convenient size to use in the pulverizing machine (length 5–10 cm and width 2–3 cm) using Swing ARM Clicker (Porielli S. 20, VIGEVANO-ITALIA) and converted into leather fiber (LF) with the help of Hinged Hammer Pulverizing machine (Sturtevant, SDL868, USA). Similarly, all long uneven plant fibers were cut into small pieces to convert them into smooth and short fibers. The average fiber size ranged between 1.5 and 2.5 cm in length and 0.2–0.7 mm in width according to the procedure of Satyanarayana et al. (1990).

2.3. Optimization of binders

Leather sheets (LS) were prepared using leather fiber and two different binders namely resin binder (RB) and natural rubber latex

(NRL) at different levels of (30, 60, 90, 120 and 150 ml) and tested for their tensile strength to take the optimum result as reference for the binders.

2.4. Preparation of NRL leather sheets (NRL-LS)

About 130 g of fiberized leather fiber was soaked in 1000 ml of water for 12 h, minced in the food mincing machine (La Minerva C/E 680 N) (three times minced to reduce the particle size) and made into fine paste. To this paste 120 ml of NRL, 10 ml of PEG and 4% of $Al_2(SO_4)_3$ was added and mixed thoroughly. Later, 10 ml of 1:3 ratio diluted H_2SO_4 is added and pH adjusted to below 5 by thorough mixing, the mixture was diluted using 4000 ml water so that slurry was formed. Then the sample was poured into the sheet making machine of (30 cm × 30 cm) and wet sheet was pressed using hydraulic press (polyhydron 4DL10SGS-10) at a pressure of 217.5 kPa for 10 s. The pressed sheet was air dried and plated using hydraulic press at a pressure of 13,789 kPa at 80 °C for 10 s.

2.5. Preparation of RB leather sheet

The process was same as above (NRL-LS preparation) the change is only binder, instead of NRL, RB was used.

2.6. Preparation of plant fiber incorporated leather composite sheets

To the prepared LF, already extracted and fiberized PFs were added individually in the proportions of 10%, 20%, 30% and 40%, mixed with the LF, and then fiberized in the fiberizer machine (SDL868, USA). Composite sheets containing LF and different species of PFs were then prepared separately following the same procedure as that of control sheet. The details of the composite sheets prepared are noted as follows:

1. Composite sheets made from finished leather scraps and binders served as a control.
2. Composite sheet made from finished leather scraps (FLS) and enset fiber labeled as FLS-E
3. Composite sheet made from finished leather scraps (FLS) and hibiscus fiber labeled FLS-H
4. Composite sheet made from finished leather scraps (FLS) and jute fiber labeled FLS-J
5. Composite sheet made from finished leather scraps (FLS) and palm fiber labeled FLS-P
6. Composite sheet made from finished leather scraps (FLS) and sisal fiber labeled FLS-S

2.7. Characterization of control and composite sheets

Finished leather scraps (FLS) and composite sheets (CSs) were characterized for their physicochemical properties such as mechanical studies, thermal stability, formation and changes in the functional groups (FT-IR) and surface morphology.

2.7.1. Mechanical properties

Mechanical properties were assessed using three dumbbell shaped specimens of 4 mm wide and 10 mm length. Tensile strength (MPa), elongation at break (%) and stitch tear strength (N/mm) were measured using Universal Testing Machine (INSTRON model 3369) at an extension rate of 5 mm/min. Water absorption and desorption (%) capacities of the different control leather and composite sheets were determined according to Sekar et al. (2007). Flexing endurance was also assessed using SATRA fiber board flexing (TER 74) machine according to (STM 129) test method.

2.7.2. Physical characterization

Fourier transform infrared (FTIR) measurements were carried out to determine the formation and changes in the functional groups of recycled leather composite sheets. The spectra were measured at a resolution of 4.0 cm^{-1} in the frequency range of $4000\text{--}600 \text{ cm}^{-1}$ using Nicolet 360 FTIR Spectrometer. Thermo gravimetric analysis (TGA) was used to analyze the thermal stability of control and composite sheets. TGA and DSC (differential scanning calorimeter) measurements were performed using TGA instrument/TGA Q 50 and DSC instrument/DSC Q 200. A 2 g of sample was placed in a platinum pan, and test was carried out in a programmed temperature range of $32\text{--}800 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. under nitrogen atmosphere at flow rate of $60 \text{ ml}/\text{min}$. Surface morphology of the samples was visualized by scanning electron microscope (SEM Model LEICA stereo scan 440 instruments).

3. Data analysis

Measurements on physical characteristics of control and composite sheets were recorded and mean values were compared between leather with fibers of different plant types and binders used. Descriptive statistics was employed using Statistical Package for Social Sciences (SPSS version 20) software as mean and standard deviation of the four individual experiments ($n = 4$).

Origin 8.0 Software was also used for FTIR, TGA and DSC graphs.

4. Results and discussion

4.1. Mechanical properties of composites

The mechanical studies of composite sheets are important properties because the products produced have to bear the mechanical stress when used by the consumer. Products with good mechanical properties last long and are commercially viable in the market. Keeping these facts in mind, mechanical properties of the composite sheets prepared in this experiment were examined.

The mechanical properties such as tensile strength, elongation at break, stitch tear strength, flexing strength were examined. Apart from these properties water absorption and desorption properties of the composites prepared were also determined.

As presented in Fig. 1, optimum values in tensile strength (TS) of both binders (modified resin binder and natural rubber latex) were obtained at the level of 120 ml and is taken as reference level to prepare controls as well as other composite sheets prepared.

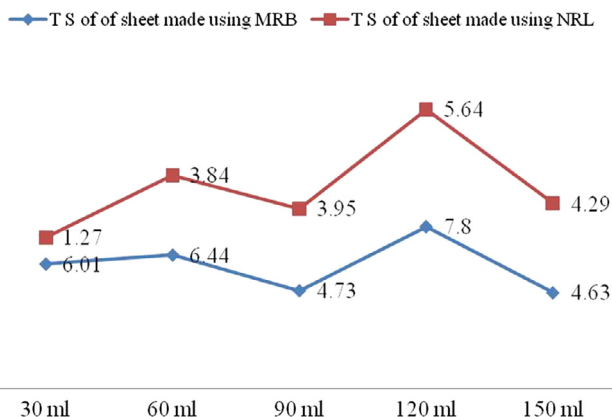


Fig. 1. Optimum values of the two binders in the leather sheet preparation to standardize the binders.

Results in Table 1 showed mechanical properties of controls and composite sheets made from FLS-E fiber mix with RB and NRL binders. The tensile strength values of composite sheets prepared using RB in the dry as well as the in wet condition showed lower values than their respective controls. The tensile strength values of these composite sheets did not meet the required standard set by Central Leather Research Institute shoe design and development center (CLRI-SDDC) ($7.0\text{--}4.0 \text{ MPa}$) in the wet condition for the insole/shank board of footwear as per the SATRA TM2:1995 test method because their value is in the range of ($2.09 \pm 0.02\text{--}2.60 \pm 0.36 \text{ MPa}$). However, this product can serve for other purposes. In the case of composite sheets prepared using NRL, even though, the results are lower than their control, they are fit for insole board making, since all results meet the required standard value ($4.49 \pm 0.45\text{--}5.89 \pm 1.06 \text{ MPa}$), with its optimum in sample 2 (10% PF) ($7.44 \pm 0.24 \text{ MPa}$). Elongation at break values of composite sheets made using RB showed lower values than their respective control, but in case of NRL all do have better values than their respective control. Results of stitch tear strength revealed that sample 2 (10% PF) of composite sheets made using RB and all sheets made using NRL do meet the required standard ($50\text{--}70 \text{ N}/\text{mm}$) set by CLRI-SDDC as per the SATRA TM5:2000 test method. In sample 3 (20% PF) and sample 4 (30% PF) the results are above the value of their control, this indicates that the plant fiber contributed to the stitch tear strength of the composite sheets and optimum result is seen in sample 4 (30% PF). In their water absorption results, all composite sheets made using RB have better values than their control and all meet the standard values required for insole board making but in composite sheets made using NRL except sample 3 (20% PF) all including the control did not meet the required standard value which means it is not comfortable if used for insole board as it can't absorb water to the required level and enable to create more moisture inside the shoe. The water desorption values of all composite sheets in both binders are fit for needed product preparation with their optimum values of ($88.69 \pm 0.74\%$) in sample 4 (30% PF) for RB and ($78.17 \pm 2.57\%$) in sample 2 (10% PF) for NRL. In the case of flexing strength, composite sheet prepared using RB fail to meet the required standard set for insole board by CLRI-SDDC as per (SATRA TM3:1999) test method. All composite sheets prepared using NRL, meet the standard optimum value.

As presented in table 2, FLS-H fiber composite sheets were prepared using synthetic polymer (RB) and natural rubber latex (NRL). In this experiment, the tensile strength of the control is better in NRL ($9.43 \pm 2.74 \text{ MPa}$) than in the RB ($7.94 \pm 1.15 \text{ MPa}$). This difference in tensile strength among the controls might be due to the compatibility of the binder to the leather fiber or the nature/quality of the binder. The optimum tensile strengths of the composite sheets (FLS-H) in NRL and RB were ($7.69 \pm 1.70 \text{ MPa}$) and ($9.21 \pm 0.04 \text{ MPa}$) respectively. The optimum results in both composite sheets were obtained in sample 2 (10% PF) in the dry state. According to the CLRI-SDDC, in wet condition the required tensile strength for industrial and high quality footwear; fashion and comfort footwear; and light use footwear are 7.0 ; 6.0 ; and 4.0 MPa respectively. (This is as per the SATRA TM2:1995 test method). As per this standard requirement, among the prepared composite sheets only those made using NRL meet the required tensile strength value for all levels of footwear preparation even though values are lower than the control ($8.65 \pm 0.64 \text{ MPa}$) but the composite sheets prepared using RB did not meet the required value for any footwear. The tensile strength values of these composite sheets prepared using NRL is lower than their respective control, whereas those prepared using RB exhibited higher values. The optimum result in elongation at break of composite sheets made using RB ($12.34 \pm 0.63\%$) is seen in sample 2 (10% PF), however, the value is lower than the control sheet ($14.78 \pm 2.98 \text{ MPa}$). Com-

Table 1
Mechanical property of FLS-E fiber composite sheets.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|---------------------|-----------|------------------------|-------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| ENSET | | | | | | | | |
| 1- RB [*] | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2- RB | 90:10 | 3.43 ± 1.01 | 2.37 ± 0.11 | 7.67 ± 1.57 | 51.93 ± 0.70 | 60.02 ± 2.79 | 78.50 ± 2.57 | 1.51 ± 0.56 |
| 3- RB | 80:20 | 6.01 ± 0.63 | 2.56 ± 0.45 | 6.95 ± 0.86 | 43.82 ± 0.37 | 76.1 ± 2.71 | 78.17 ± 3.05 | 1.58 ± 0.14 |
| 4- RB | 70:30 | 4.65 ± 0.99 | 2.09 ± 0.02 | 8.06 ± 2.43 | 45.39 ± 0.37 | 71.97 ± 2.26 | 88.69 ± 0.74 | 1.25 ± 0.12 |
| 5- RB | 60:40 | 3.92 ± 1.15 | 2.60 ± 0.36 | 5.59 ± 0.55 | 31.95 ± 0.71 | 97.08 ± 2.54 | 81.99 ± 2.23 | 1.39 ± 0.18 |
| 1- NRL [*] | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 8.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2- NRL | 90:10 | 7.44 ± 0.24 | 5.89 ± 1.06 | 27.62 ± 2.75 | 58.58 ± 0.75 | 16.49 ± 0.22 | 78.17 ± 2.57 | 4.03 ± 0.01 |
| 3- NRL | 80:20 | 5.26 ± 0.30 | 4.49 ± 0.45 | 22.56 ± 1.26 | 64.43 ± 0.36 | 36.94 ± 3.49 | 74.04 ± 2.20 | 3.29 ± 0.38 |
| 4- NRL | 70:30 | 6.50 ± 0.70 | 5.59 ± 0.04 | 21.56 ± 4.40 | 73.82 ± 0.38 | 17.96 ± 1.57 | 77.70 ± 2.18 | 3.76 ± 0.07 |
| 5- NRL | 60:40 | 6.33 ± 1.52 | 5.84 ± 0.01 | 15.39 ± 4.64 | 50.89 ± 0.82 | 20.39 ± 1.74 | 73.26 ± 2.40 | 3.44 ± 0.09 |

^{*} RB (Resin binder); NRL (Natural rubber latex).

Table 2
Mechanical properties of FLS -H fiber composite sheets.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|------------|-----------|------------------------|-------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| HIBISCUS | | | | | | | | |
| 1- RB | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2- RB | 90:10 | 9.21 ± 0.04 | 2.92 ± 0.14 | 12.34 ± 0.63 | 77.21 ± 0.34 | 58.74 ± 0.64 | 99.62 ± 0.32 | 3.01 ± 0.14 |
| 3- RB | 80:20 | 5.77 ± 0.66 | 2.60 ± 0.27 | 8.90 ± 2.04 | 76.77 ± 0.29 | 63.65 ± 3.32 | 74.74 ± 2.47 | 1.37 ± 0.37 |
| 4- RB | 70:30 | 7.84 ± 1.58 | 2.54 ± 0.01 | 11.17 ± 0.86 | 55.07 ± 0.38 | 73.72 ± 0.37 | 74.33 ± 3.54 | 1.38 ± 0.57 |
| 5- RB | 60:40 | 7.26 ± 0.33 | 2.40 ± 0.03 | 8.67 ± 0.63 | 53.68 ± 0.37 | 66.69 ± 1.07 | 84.17 ± 1.81 | 2.05 ± 0.19 |
| 1- NRL | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 3.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2- NRL | 90:10 | 7.69 ± 1.70 | 6.49 ± 0.18 | 18.51 ± 7.15 | 84.61 ± 0.37 | 26.23 ± 1.30 | 100.17 ± 0.19 | 3.33 ± 0.03 |
| 3- NRL | 80:20 | 7.11 ± 0.78 | 4.85 ± 0.57 | 18.06 ± 1.18 | 50.95 ± 0.43 | 27.85 ± 0.85 | 89.96 ± 0.46 | 3.38 ± 0.08 |
| 4- NRL | 70:30 | 6.87 ± 0.23 | 5.87 ± 0.74 | 13.06 ± 0.40 | 77.59 ± 0.23 | 23.80 ± 1.38 | 82.84 ± 2.93 | 3.23 ± 0.16 |
| 5- NRL | 60:40 | 5.83 ± 1.67 | 5.75 ± 0.23 | 9.34 ± 3.15 | 57.93 ± 1.07 | 39.89 ± 0.80 | 79.53 ± 0.28 | 2.22 ± 0.57 |

posite sheets prepared using NRL showed better value (18.51 ± 7.15%) in sample 2 (10% PF). The stitch tear strength values of all composite sheets prepared using RB have lower values than those of control (89.40 ± 0.55 N/mm) this means the plant fibers are not contributing to stitch tear strength, however all composite sheets satisfy the required standard for industrial use with the minimum values of (53.68 ± 0.37 N/mm). Except sample 3 (20% PF) having its value of (50.95 ± 0.43 N/mm), all composite sheets made using NRL exhibited higher values than those of control. According to the recommendation of CLRI-SDDC, the minimum requirements are (70 N/mm) for industrial and high quality footwear; (60 N/mm) for fashion and comfort footwear; and (50 N/mm) for light use footwear as per the SASTRA TM5: 2000 test method. The water absorption and desorption requirements for insole board are minimum of 35 and 40% respectively. In this respect, all sheets prepared using RB meet the required standard value but in case of NRL except sample 5 (40% PF) with its water absorption value of (39.89 ± 0.80%), all including the control sheets didn't meet the required standard value for water absorption. The flexing indexes for insole boards according to CLRI-SDDC are 3.70% for industrial and high quality footwear; 3.20% for fashion and comfort footwear; and 2.70% for light use footwear as per the SATRA TM3:1999 test method. The flexing index values for composite sheets made using RB and NRL are 3.80 ± 0.00% and 3.71 ± 0.01% respectively. In the composite sheets all compositions have lower values than those of their respective controls. Only sample 2 (10% PF) made using RB exhibit the required standard value for light use footwear. In NRL except sample 5 (40% PF), all the composite sheets meet the required standard for fashion and comfort footwear.

Table 3 represents data of FLS-J composite sheets. As presented in the Table all tensile strength values of composite sheets prepared using NRL except sample 4 (30% PF) and 5 (40% PF) in the

dry state, are below their respective control values. All of the composite sheets made using RB, have no suitable values in the wet condition ranging (1.78 ± 0.94–2.66 ± 0.39 MPa) but those sheets made using NRL binder, meet the required standard values ranging from (4.06 ± 0.28–8.12 ± 0.31 MPa) in the wet condition. Except, in sample 4 (30% PF), with its elongation at break value of (16.40 ± 1.49%), all composite sheets made using NRL do have lower values than their controls. In the case of stitch tear strength values, all composite sheets made using NRL, except sample 2 (10% of PF) do possess lower values than their respective controls. However, from quality measurement point of view, all composite sheets meet the required standard set for footwear. From water absorption perspective, all composite sheets prepared using RB meet the required standard (minimum 35% as per SATRA TM9:1993) with the optimum values of (71.79 ± 0.08%) but in composite sheets made using NRL, sample 2 (10% PF) and 3 (20% PF) sheets meet the requirement with 20% PF being optimum (51.34 ± 0.28%). The water desorption property of all the composite sheets in both binders meet the standard value (minimum 40% as per SATRA TM9:1993). Flexing strength values of all the composite sheets are below their respective controls. All samples of composite sheets made using RB and all except sample 4 (30% PF) of the sheets made using NRL didn't meet the required standard set (2.7–3.7%) as per SASTRA TM3: 1999 test method.

Table 4 represents the mechanical property values of FLS-P composite sheets. As shown in the table, sample 2 (10% PF) in the sheets made using RB has optimum tensile strength value of (8.30 ± 0.06 MPa in dry and 3.66 ± 0.88 MPa) in wet conditions. All composites except sample 2 (10% PF) (8.21 ± 0.59 MPa) and 3 (20% PF) (8.30 ± 0.06 MPa) in this test showed lower values than those of their control (7.94 ± 1.15 MPa). In the NRL composite sheets, all compositions do possess lower value than the control (9.43 ± 2.74 MPa) in dry condition. In wet condition, composite

Table 3
Mechanical properties of FLS-J fiber composite sheets.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|------------|-----------|------------------------|-------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| JUTE | | | | | | | | |
| 1- RB | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2- RB | 90:10 | 7.43 ± 1.41 | 2.66 ± 0.39 | 11.23 ± 2.99 | 70.22 ± 0.71 | 42.50 ± 1.60 | 75.24 ± 3.53 | 2.45 ± 0.34 |
| 3- RB | 80:20 | 6.07 ± 0.20 | 1.78 ± 0.94 | 8.95 ± 0.86 | 65.92 ± 0.23 | 64.88 ± 1.54 | 70.80 ± 1.46 | 1.26 ± 0.15 |
| 4- RB | 70:30 | 5.06 ± 0.85 | 2.13 ± 0.16 | 8.50 ± 0.71 | 48.92 ± 0.62 | 71.79 ± 0.08 | 77.43 ± 2.43 | 2.82 ± 0.28 |
| 5- RB | 60:40 | 6.23 ± 0.90 | 2.50 ± 0.18 | 8.95 ± 2.12 | 58.21 ± 0.68 | 68.43 ± 2.16 | 98.76 ± 0.21 | 2.15 ± 0.29 |
| 1- NRL | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 8.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2- NRL | 90:10 | 5.29 ± 1.17 | 4.06 ± 0.28 | 11.06 ± 4.79 | 63.90 ± 0.68 | 36.24 ± 2.19 | 85.85 ± 1.32 | 2.05 ± 0.60 |
| 3- NRL | 80:20 | 4.40 ± 0.33 | 4.69 ± 0.63 | 4.95 ± 0.08 | 47.37 ± 0.78 | 51.34 ± 0.28 | 72.02 ± 1.70 | 1.72 ± 0.26 |
| 4- NRL | 70:30 | 9.82 ± 0.17 | 8.12 ± 0.31 | 16.40 ± 1.49 | 77.06 ± 0.25 | 20.79 ± 0.23 | 77.83 ± 0.78 | 3.55 ± 0.15 |
| 5- NRL | 60:40 | 9.44 ± 1.48 | 7.53 ± 1.92 | 11.01 ± 0.63 | 74.82 ± 0.64 | 25.59 ± 0.14 | 95.38 ± 0.21 | 2.36 ± 0.28 |

Table 4
Mechanical properties of FLS-P fiber composite sheets.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|------------|-----------|------------------------|-------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| PALM | | | | | | | | |
| 1- RB | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2- RB | 90:10 | 8.21 ± 0.59 | 3.60 ± 0.03 | 14.56 ± 0.47 | 66.60 ± 0.38 | 51.15 ± 0.60 | 55.60 ± 3.73 | 3.69 ± 0.26 |
| 3- RB | 80:20 | 8.30 ± 0.06 | 3.66 ± 0.88 | 16.56 ± 0.78 | 58.57 ± 0.49 | 65.10 ± 2.45 | 80.06 ± 3.38 | 3.75 ± 0.03 |
| 4- RB | 70:30 | 5.82 ± 0.47 | 1.97 ± 0.55 | 10.89 ± 2.83 | 52.51 ± 0.71 | 87.43 ± 2.60 | 74.40 ± 2.77 | 1.90 ± 0.25 |
| 5- RB | 60:40 | 6.11 ± 0.00 | 2.37 ± 0.56 | 8.00 ± 0.00 | 51.12 ± 1.22 | 79.94 ± 1.44 | 79.78 ± 3.81 | 2.03 ± 0.25 |
| 1- NRL | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 8.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2- NRL | 90:10 | 6.44 ± 0.51 | 4.63 ± 0.84 | 24.34 ± 3.77 | 75.46 ± 0.53 | 16.11 ± 0.06 | 83.71 ± 3.04 | 3.71 ± 0.12 |
| 3- NRL | 80:20 | 8.62 ± 0.29 | 6.21 ± 0.72 | 26.56 ± 1.41 | 66.94 ± 0.22 | 18.98 ± 1.06 | 66.08 ± 2.82 | 3.65 ± 0.02 |
| 4- NRL | 70:30 | 4.87 ± 0.57 | 2.96 ± 0.09 | 13.98 ± 4.55 | 65.09 ± 0.36 | 46.73 ± 1.43 | 64.49 ± 1.68 | 2.55 ± 0.28 |
| 5- NRL | 60:40 | 6.80 ± 0.35 | 3.46 ± 0.33 | 22.67 ± 0.78 | 51.67 ± 1.56 | 42.87 ± 1.32 | 75.50 ± 1.88 | 3.08 ± 0.08 |

sheets made using RB didn't meet the standard requirement set by CLRI-SDDC for footwear (insole) but in case of composite sheets prepared using NRL all of them meet the standard requirements even though they are all lower than their control (8.65 ± 0.64 MPa). Therefore, in these sheets, even though both binders do show reasonable values in the dry condition, only NRL is suitable for preparing the footwear accessory products (insole). Concerning the elongation at break property of composite sheets, sample 3 (20% PF) prepared using MRB do possess ($16.56 \pm 0.78\%$). In the sheets made using NRL all except sample 4 (30% PF) ($13.98 \pm 4.55\%$) do have better values than those of their respective controls. The stitch tear strengths values of all composite sheets meet the required standard for footwear. In the composite sheets made using RB, the results are lower than their respective control (89.40 ± 0.55 N/mm) but in those sheets prepared using NRL, all except sample 5 (40% PF) (51.67 ± 1.56 N/mm) do have better values than their respective control (62.88 ± 0.21 N/mm). Water absorption of all composite sheets prepared using RB showed better values than their control and satisfies the requirement set by CLRI-SDDC (35% minimum) for insole board preparation. However, sheets prepared using NRL except sample 4 (30% PF) ($46.73 \pm 1.43\%$) and 5 (40% PF) ($42.87 \pm 1.32\%$), including the control did not meet the set standard requirement. Water desorption properties of all composite sheets made using both binders meet the standard requirement set by CLRI-SDDC (minimum 40%). Composite sheets prepared using MRB showed optimum Water desorption value of ($80.06 \pm 3.38\%$) and is above the control at sample 3 (20% PF), whereas in NRL optimum value ($83.71 \pm 3.04\%$), which is above the control is registered in sample 2 (10% PF). All flexing strength values of composite sheets in both binders are lower than their controls. Only Samples 2 (10% PF) and 3 (20% PF) made using RB meet the flexing strength requirement. All the composite sheets prepared using NRL, except sample 4 (30% PF) (2.55 ± 0.28 MPa)

meet the required flexing strength value for footwear insole board manufacturing.

As shown in table 5, optimum tensile strength value of FLS-S composite sheets prepared using RB is obtained in sample 5 (40% PF) in the dry state and this result (10.23 ± 1.42 MPa) is better than that of control (7.94 ± 1.15 MPa). All composite sheets prepared using NRL showed lower tensile strength values than the control (9.43 ± 2.74 MPa), the optimum value (9.02 ± 0.16 MPa) is seen in sample 4 (30% PF). In the wet condition, composite sheets prepared using MRB showed optimum tensile strength value (7.81 ± 1.17 MPa), in sample 2 (10% PF) and this meets the desired requirement. All tensile strength values of composite sheets prepared using NRL meet the required standard for all levels of footwear. The optimum value (10.23 ± 1.42 MPa) is recorded in sample 2 (10% PF) and is better than its control (8.65 ± 0.64 MPa). Elongation at break of the sheets prepared using RB showed lower values than their respective control ($14.78 \pm 2.98\%$) with the optimum value of ($10.17 \pm 0.86\%$) being in sample 5 (40% of PF). In case of the composite sheets prepared using NRL, all but sample 5 (40% of PF) have better values than their respective control ($15.17 \pm 3.56\%$). The stitch tear strength values of control are better than those of all the composite boards using RB. However, all the composite sheets prepared using NRL exhibit better results compared to those of control, with sample 3 (20% PF) showing optimum stitch tear strength value of (77.95 ± 0.05 N/mm). Water absorption values of composite sheets prepared using RB do have better values than their respective control and all meet the required standard for shank/insole board making. Among the composite sheets prepared using NRL, only sample 4 (30% PF) satisfy the standard requirement needed for manufacturing of insole board (35% minimum), however sample 1 (control), sample 2 (10% PF), sample 3 (20% PF) and sample 5 (40% PF) didn't meet the standard requirement. In case of water

Table 5
Mechanical properties of FLS -S fiber composite sheets.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|------------|-----------|------------------------|--------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| SISAL | | | | | | | | |
| 1- RB | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2- RB | 90:10 | 4.62 ± 0.00 | 7.81 ± 1.17 | 8.67 ± 0.47 | 45.58 ± 0.06 | 72.06 ± 1.58 | 78.26 ± 0.32 | 0.80 ± 0.24 |
| 3- RB | 80:20 | 3.28 ± 0.35 | 1.34 ± 0.14 | 5.67 ± 1.10 | 33.97 ± 0.07 | 76.32 ± 2.33 | 91.17 ± 1.52 | 0.77 ± 0.37 |
| 4- RB | 70:30 | 6.32 ± 1.02 | 1.46 ± 0.86 | 8.00 ± 0.31 | 44.02 ± 0.73 | 85.87 ± 0.40 | 83.34 ± 0.34 | 2.83 ± 0.20 |
| 5- RB | 60:40 | 10.23 ± 1.42 | 3.04 ± 0.40 | 10.17 ± 0.86 | 50.77 ± 0.40 | 74.32 ± 3.37 | 94.97 ± 3.66 | 2.20 ± 0.68 |
| JUTE | | | | | | | | |
| 1- NRL | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 3.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2- NRL | 90:10 | 5.39 ± 0.66 | 10.23 ± 1.42 | 33.23 ± 6.13 | 70.14 ± 0.04 | 17.76 ± 3.61 | 156.01 ± 7.11 | 3.46 ± 0.09 |
| 3- NRL | 80:20 | 6.02 ± 0.23 | 5.05 ± 0.10 | 24.23 ± 1.73 | 77.95 ± 0.05 | 29.69 ± 2.48 | 78.41 ± 3.11 | 3.42 ± 0.12 |
| 4- NRL | 70:30 | 9.02 ± 0.16 | 5.64 ± 0.09 | 26.01 ± 0.78 | 74.87 ± 0.66 | 37.23 ± 0.38 | 86.78 ± 2.97 | 3.72 ± 0.03 |
| 5- NRL | 60:40 | 7.81 ± 1.17 | 5.05 ± 0.59 | 13.28 ± 2.43 | 74.83 ± 0.21 | 31.04 ± 0.45 | 91.19 ± 3.77 | 3.41 ± 0.06 |

desorption property all prepared samples meet the standard requirement (40% minimum). Concerning the flexing strength aspect, all composite sheets prepared using RB do possess lower flexing and didn't meet the required (2.7–3.7%) standard value except sample 4 (30% PF) that showed flexing strength of (2.83 ± 0.20 MPa) which is suitable for light use footwear insole manufacturing.

Table 6 shows the pooled data of optimum plant fiber composite sheets. As indicated in the above table, by observing the optimum values of the composite sheets from each plant and binder, the tensile strength value in dry condition of FLS-S composite sheet made using RB ranked first with its value of (10.23 ± 1.42 MPa) at its (40% PF) and this value is better than the value of its control (7.94 ± 1.15 MPa) followed by jute (9.82 ± 0.17 MPa) prepared using NRL at its (30% PF). However, in wet condition Composites prepared using NRL and jute ranked first with its tensile strength value of (8.12 ± 0.31 MPa) at (30% PF) followed by hibiscus (6.49 ± 0.18 MPa) at its 10% PF. The values of the present study are much better than values of previous studies done by (Sekar et al., 2009) from chrome shaving boards (2.96 ± 0.06 MPa) and that of (Senthil et al., 2014) from regenerated leather boards (5.88 ± 0.09 MPa). All composite sheets prepared using NRL have shown very good tensile strength values in the wet condition and all meet the requirement needed for insole board making. In its elongation at break values, enset ranked first (27.62 ± 2.75%) at its (10% PF) followed by palm (26.56 ± 1.41 MPa) at its (20% PF) and sisal (26.01 ± 0.78 MPa) at its (30% PF). All of these results

are above their respective controls indicating that the plant fibers are contributing to elongation property of the composite sheets. As seen from the pooled data the optimum values of plant fiber may vary depending on the type of binder used and ratio of the plant. The stitch tear strength of all the composite sheets except 20% enset (43.82 ± 0.37 N/mm) prepared using RB fulfills the required standard (70–50 N/mm) set by CLRI-SDDC; however, all have stitch strength values below their respective control. The stitch tear strength values of composite sheets made using NRL all except 20% of enset (58.58 ± 0.75 N/mm) have values above their control and all including the 20% of enset meet the required standard set by CLRI-SDDC for insole board making as per the SATRA TM5: 2000 test method. The water absorption values of composite sheets prepared using RB are better than their control and meet the required standard for insole board making. However, the results of composite sheets prepared using NRL all except the 20% of sisal don't meet the required standard set by CLRI-SDDC as per the SATRA TM 9: 1993 test method. In water desorption study, all composite sheets prepared using two binders meet the required standard. The flexing strength values of 10% enset (4.03 ± 0.01%) and 20% palm (3.75 ± 0.03%) prepared using NRL showed better values than their respective control.

Fig. 2 exhibits products prepared using the composite boards prepared in the study. The pictures show raw composite sheet Fig. 2 (A), the finished composite sheet Fig. 2 (B) and the final products prepared from these composite sheets 2 (C). As can be seen from these pictures, the different products prepared from these

Table 6
Comparison of plant fiber having optimum values pooled from all tables.

| Sample No. | LF/PF (%) | Tensile strength (MPa) | | Elongation at break (%) | Stitch tear strength (N/mm) | Water absorption (%) | Water desorption (%) | Flexing index (%) |
|-------------|-----------|------------------------|-------------|-------------------------|-----------------------------|----------------------|----------------------|-------------------|
| | | Dry | Wet | | | | | |
| 1. CONTROL | | | | | | | | |
| 1.RB | 100:00 | 7.94 ± 1.15 | 3.94 ± 0.15 | 14.78 ± 2.98 | 89.40 ± 0.55 | 47.23 ± 4.88 | 79.56 ± 5.62 | 3.80 ± 0.00 |
| 2.NRL | 100:00 | 9.43 ± 2.74 | 8.65 ± 0.64 | 15.17 ± 3.56 | 62.88 ± 0.21 | 21.27 ± 0.76 | 77.39 ± 0.40 | 3.71 ± 0.01 |
| 2. ENSET | | | | | | | | |
| 1.RB | 80:20 | 6.01 ± 0.63 | 2.56 ± 0.45 | 6.95 ± 0.86 | 43.82 ± 0.37 | 76.1 ± 2.71 | 78.17 ± 3.05 | 1.58 ± 0.14 |
| 2.NRL | 90:10 | 7.44 ± 0.24 | 5.89 ± 1.06 | 27.62 ± 2.75 | 58.58 ± 0.75 | 16.49 ± 0.22 | 78.17 ± 2.57 | 4.03 ± 0.01 |
| 3. HIBISCUS | | | | | | | | |
| 1.RB | 90:10 | 9.21 ± 0.04 | 2.92 ± 0.14 | 12.34 ± 0.63 | 77.21 ± 0.34 | 58.74 ± 0.64 | 99.62 ± 0.32 | 3.01 ± 0.14 |
| 2.NRL | 90:10 | 7.69 ± 1.70 | 6.49 ± 0.18 | 18.51 ± 7.15 | 84.61 ± 0.37 | 26.23 ± 1.30 | 100.17 ± 0.19 | 3.33 ± 0.03 |
| 4. JUTE | | | | | | | | |
| 1.RB | 90:10 | 7.43 ± 1.41 | 2.66 ± 0.39 | 11.23 ± 2.99 | 70.22 ± 0.71 | 42.50 ± 1.60 | 75.24 ± 3.53 | 2.45 ± 0.34 |
| 2.NRL | 70:30 | 9.82 ± 0.17 | 8.12 ± 0.31 | 16.40 ± 1.49 | 77.06 ± 0.25 | 20.79 ± 0.23 | 77.83 ± 0.78 | 3.55 ± 0.15 |
| 5. PALM | | | | | | | | |
| 1.RB | 80:20 | 8.30 ± 0.06 | 3.66 ± 0.88 | 16.56 ± 0.78 | 58.57 ± 0.49 | 65.10 ± 2.45 | 80.06 ± 3.38 | 3.75 ± 0.03 |
| 2.NR L | 80:20 | 8.62 ± 0.29 | 6.21 ± 0.72 | 26.56 ± 1.41 | 66.94 ± 0.22 | 18.98 ± 1.06 | 66.08 ± 2.82 | 3.65 ± 0.02 |
| 6. SISAL | | | | | | | | |
| 1.RB | 60:40 | 10.23 ± 1.42 | 3.04 ± 0.40 | 10.17 ± 0.86 | 50.77 ± 0.40 | 74.32 ± 3.37 | 94.97 ± 3.66 | 2.20 ± 0.68 |
| 2.NRL | 70:30 | 9.02 ± 0.16 | 5.64 ± 0.09 | 26.01 ± 0.78 | 74.87 ± 0.66 | 37.23 ± 0.38 | 86.78 ± 2.97 | 3.72 ± 0.03 |

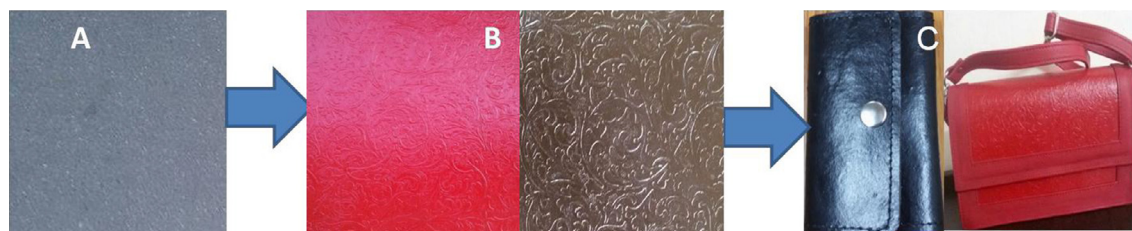


Fig. 2. (A) Raw composite sheet, (B) finished composite sheets & (C) final products.

composite sheets made of the leather fiber and plant fibers in combination with binders have smooth feel, attractive look and are suitable for consumer service.

4.2. Surface morphology of composites

Scanning electron microscope (SEM) images of the sampled composite sheets are shown in Fig. 3. Fig. 3(A) shows the SEM image of the finished leather scrap (FLS) sheet as control. In this image the network of leather fiber adhering with binder is clearly seen. This confirms that the composite nature of the leather fiber. The diameter of individual fibers is more or less same. The SEM image of FLS-E shown in Fig. 3(B) reveals the binding nature of the binder with leather and enset fibers. The width of enset fiber ($82\ \mu\text{m}$) seems to be more than that of the control sheet ($48\ \mu\text{m}$). The composite nature of this sample is evident. SEM image of FLS-H, as shown in Fig. 3(C), the fiber width of ($52\ \mu\text{m}$) is clearly seen. This shows that the combination of leather and hibiscus fiber with NRL binder is obvious. As seen in Fig. 3(D), width of the FLS-J is ($56\ \mu\text{m}$). In the FLS-P of Fig. 3(E) SEM image, it looks that the fiber is coated with binder. In FLS-S image of Fig. 3(F), it is observed that the fiber is well embedded with the binder and it appears less porosity in the composite. All composite sheets prepared in this experiment exhibited an intermingling of fibers along with the binder with no significant difference among the samples in their SEM images revealing that they have composite nature. The SEM images

in this study are comparable to those of composite boards made in the earlier study (Sekar et al., 2007).

4.3. Fourier transform infrared studies

Fourier transform infrared (FTIR) is an easy way to identify the presence of certain functional groups in a molecule. One can also use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. The Fourier transform infrared (FTIR) spectra of the samples prepared in this study are shown in Fig. 4.

The FTIR spectrum of the control sheet as shown in Fig. 4(A) indicates the amide bonds of collagen fibers at $1636\ \text{cm}^{-1}$, $1536\ \text{cm}^{-1}$ and $1241\ \text{cm}^{-1}$ representing amide I, II and III respectively (Ramnath et al., 2012). Strong absorption bands are seen between $3600\text{--}3200\ \text{cm}^{-1}$ region resulting from superimposed —OH and NH_3^+ stretching bands. Sharp peak is observed at $2905\ \text{cm}^{-1}$ representing C—H of the rubber latex and a broad peak around $1080\text{--}1000\ \text{cm}^{-1}$ showing bonded —OH groups in the sample.

FTIR spectra of FLS-E composite sample Fig. 4(B) shows broad peak from $1010\text{--}1638\ \text{cm}^{-1}$ representing C—O—C and C—O stretch (primary and secondary hydroxide group) and bonds belonging to the glucoside linkage and possibly due to lignin (Sekar et al., 2009). The peak at $1445\ \text{cm}^{-1}$ in this spectrum represents H—CH and O—CH in plane bending vibration. The peak at $1234\ \text{cm}^{-1}$ represents —C—H bending at C-6 in the cellulose molecular structure.

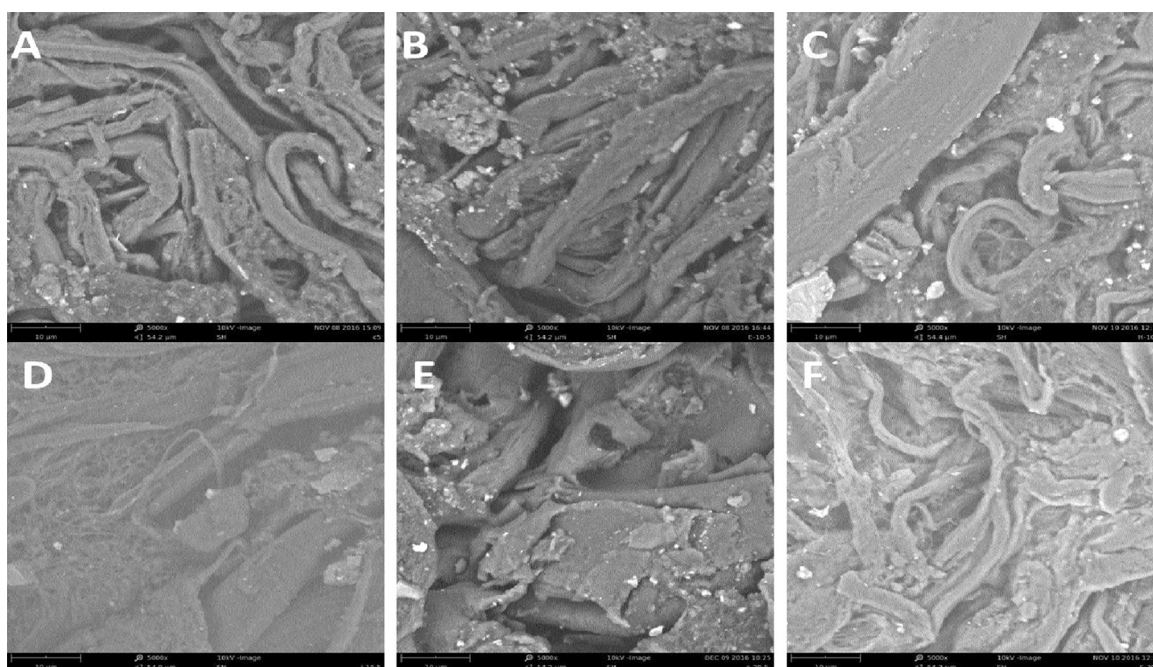


Fig. 3. Scanned Electron Microscope Images of A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S.

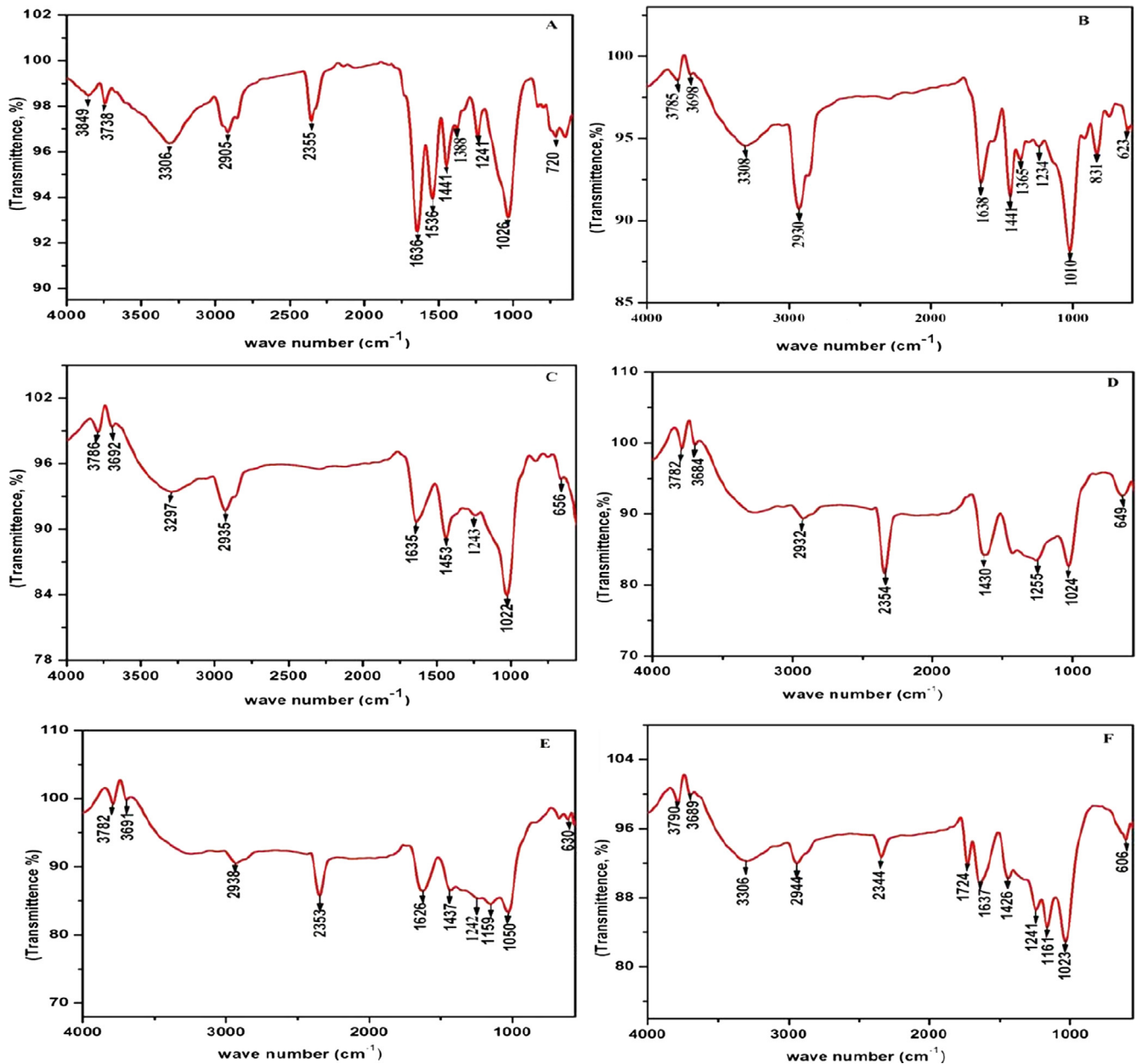


Fig. 4. FTIR results of Leather-plant fibers composite sheets A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S.

The FTIR spectrum of FLS -H composite sample Fig. 4(C) is similar to FLS-E composite. However, we can see in-plane CH bending at 1453 cm^{-1} (Sekar et al., 2009); in the spectra of FLS-J; FLS-P; and FLS-S Fig. 4(D, E & F), more or less similar pattern is observed. The reason for this similarity might be due to the similar nature of cellulose in all the samples representing collagen and cellulose.

4.4. Thermo gravimetric analysis studies of composites

As shown in Fig. 5, the thermo gravimetric analysis (TGA) study revealed weight loss of materials with increase in temperature. In this study, samples of control and composite sheets were subjected to TGA from $32\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$. In the control sheet Fig. 5(A), a three step weight loss was observed. The first weight loss (13%) was due to the loss of free and bound water up to $231\text{ }^{\circ}\text{C}$. The second major weight loss (42%) up to $400\text{ }^{\circ}\text{C}$ was due to collagen degradation in the samples. The final weight loss (38%) was due to decomposition of degraded products. Around 7.7% residue was observed at about

$800\text{ }^{\circ}\text{C}$. In the case of FLS-E Fig. 5(B), three step weight losses have been occurred. The initial weight loss (21%) up to $347\text{ }^{\circ}\text{C}$ is due to the loss of water molecules in the sample. The second major weight loss (57%) that has occurred up to $471\text{ }^{\circ}\text{C}$ is due to protein and cellulose degradation. The third weight loss (9%) which occurred up to $800\text{ }^{\circ}\text{C}$ may be due to the decomposition of the degraded products. Residue of 12% was also registered in this sample. In composite samples of FLS-H, FLS-J and FLS-S as seen in Fig. 5 (C, D, & F), exhibited more or less the same thermogravimetric pattern. However, residues of 17.23% and 17.04% were observed in FLS-H and FLS-J respectively. This higher value might be due lignin content present in these plant fibers or mineral fraction. In FLS-P Fig. 5(E), four step weight loss was observed. First weight loss (11%) that has occurred up to $222\text{ }^{\circ}\text{C}$ was due to loss of water molecules in the sample. Second weight loss (47%) which has occurred up to $392\text{ }^{\circ}\text{C}$ may be due to protein and cellulose degradation. Third weight loss (40%) up to $589\text{ }^{\circ}\text{C}$ and fourth weight loss (0.47%) up to $800\text{ }^{\circ}\text{C}$ might be due to decomposition of degraded

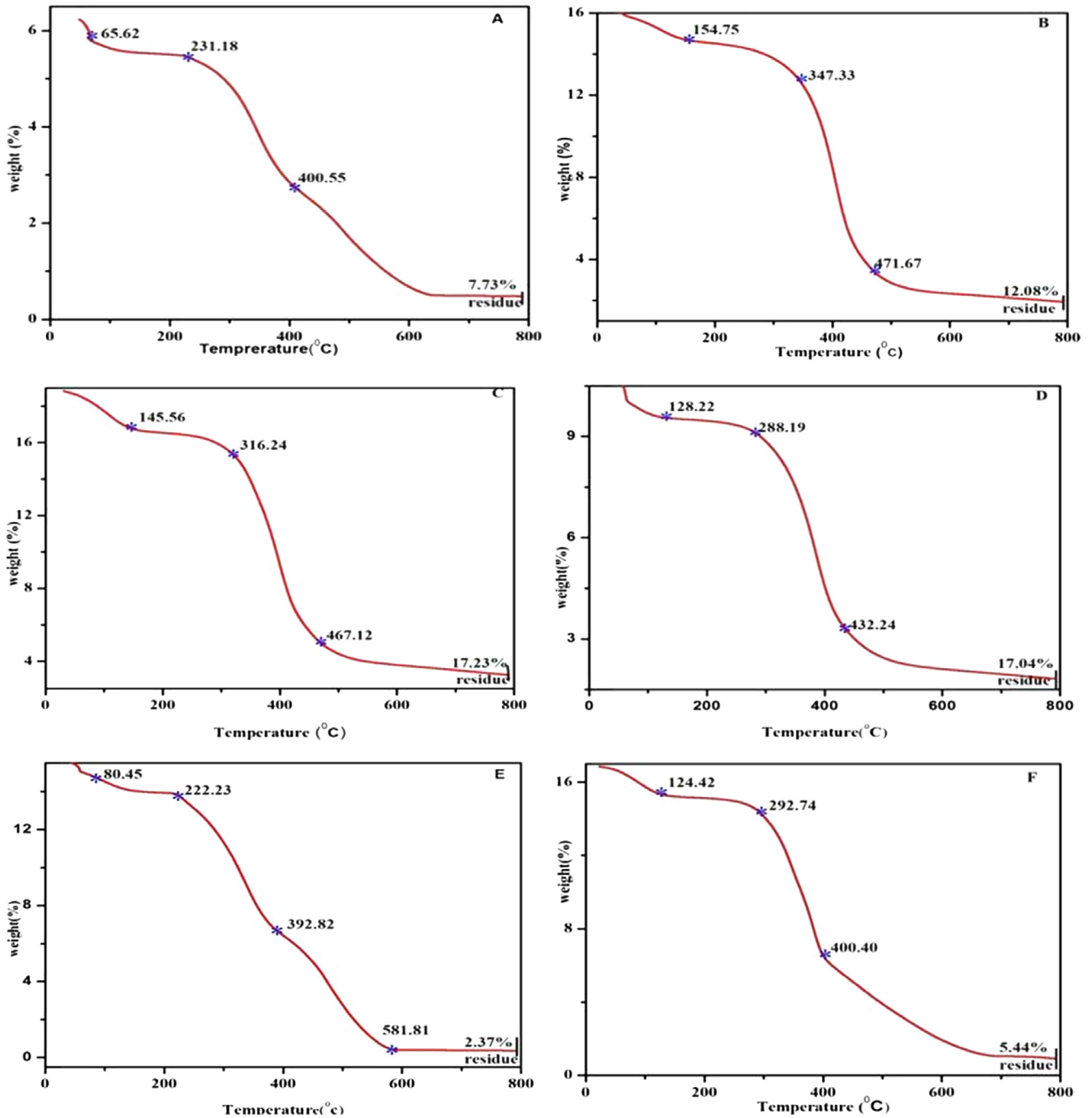


Fig. 5. Thermo gravimetric analysis of composite samples A. Control; B. FLS-E; C. FLS-H; D. FLS-J; E. FLS-P; and F. FLS-S.

products. Residue of 2.37%, the least residue of all samples was also seen in this sample.

4.5. Differential scanning calorimeter studies of composites

Differential scanning calorimeter (DSC) is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as function of temperature. The DSC thermogram of the control sample Fig. 6(A) exhibited melting temperature (T_m) at 94.14 °C. This T_m peak is lower than the other leather-plant composite sheets peak temperatures 100.68 °C for Fig. 6(B), 118.87 °C for Fig. 6 (C), 101.53 °C for Fig. 6(D), 114.33 °C for Fig. 6(E) and 110.35 for

Fig. 6(F). All of the leather-plant composite samples showed higher endothermic temperature (T_m) than their respective control. This could be due to the fact that all the fibers were well dispersed in the leather matrix, so that their melting phase has shifted to higher temperature.

5. Conclusion and recommendation

In conclusion, among the different composite sheets, FLS-J (30% PF) prepared using NRL; FLS-H (10% PF), FLS-P (20% PF) and FLS-S (40% PF) prepared using RB exhibited better mechanical properties than their respective controls. FLS-H (30% PF) prepared using RB

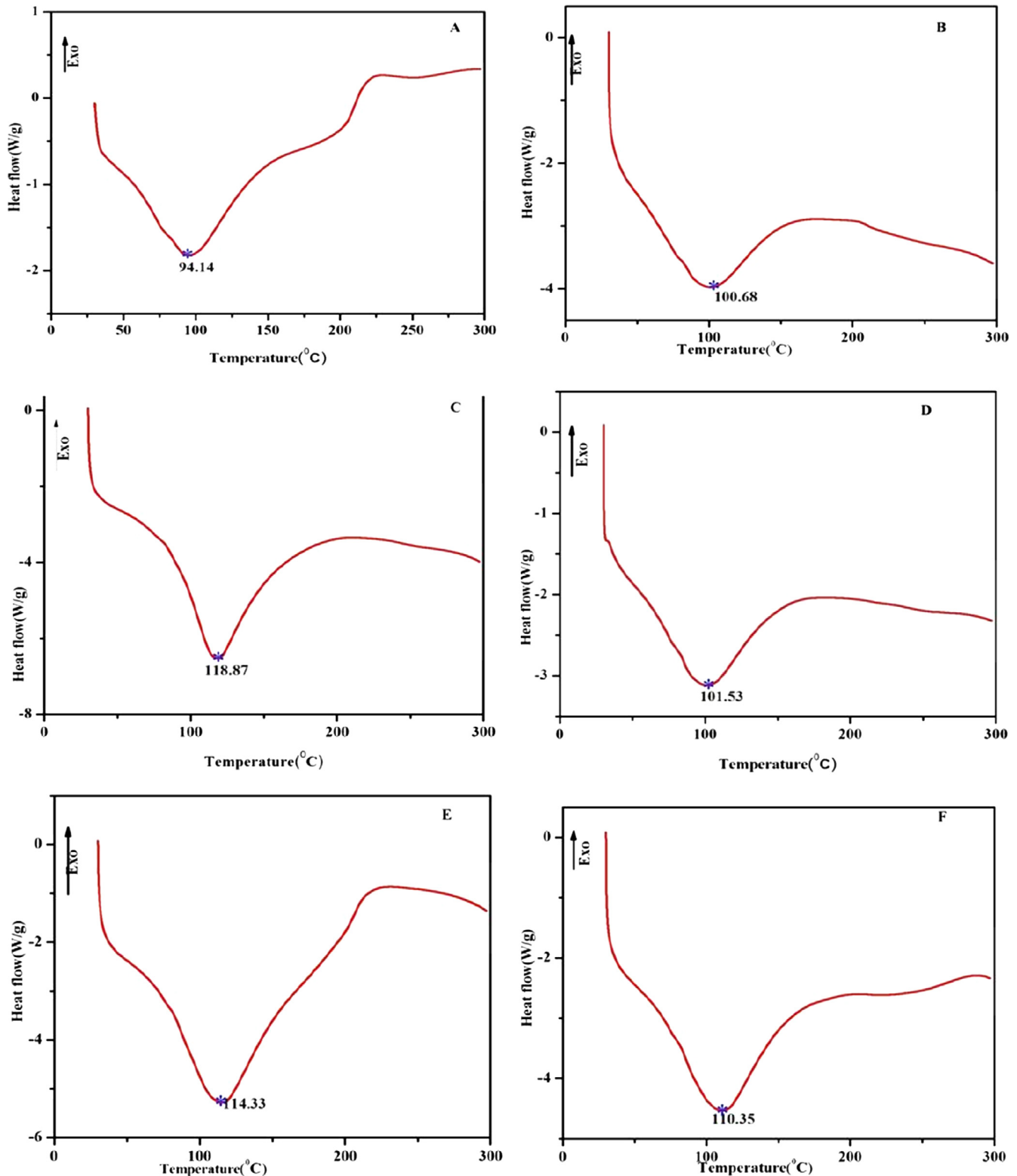


Fig. 6. DSC thermograms of leather-plant composite sheets A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S.

and all composite samples prepared using NRL showed better elongation at break. Particularly for insole board preparation in wet condition, sheets prepared using NRL meet most of the requirements. The smooth surface, better tensile strength, flexibility, reasonable water absorption as well as excellent desorption values of the composite sheets find potential application not only for foot-

wear but also in the preparation of value added consumer products such as stiff hand bag, ladies hand bag, wallet, keychain, chappal upper, false roofing, interior decorations and wall cover. SEM studies have shown the composite nature of all sheets prepared. FTIR, TGA and DSC studies have confirmed the composite nature of the sheets.

As a recommendation, future work should be done on choosing better binder that will enable to produce better quality products and also in improving some of the parameters like the water absorption and flexural characteristics of sheets prepared using NRL.

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Conflict of interest

The authors declare that there is no conflict of interest.

References

- EFDRE (Embassy of the Federal Democratic Republic of Ethiopia), 2015. Investment Opportunity in Leather and Leather Products Industry in Ethiopia, New Delhi, India.
- FAO (Food and Agricultural Organization), 2013. World Statistical Compendium for raw hides and skins, leather and leather footwear 1993–2012; Market and Policy Analyses of Raw Materials, Horticulture and Tropical Products Team, FAO, 2013.
- FAO (Food and Agricultural Organization), 2015. World statistical compendium for raw hides and skins, leather and leather footwear 1998–2014.
- HMIP (Her Majesty's Inspectorate of Pollution), 1995. Chief Inspectors' Guidance to Inspectors-Processing of Animal Hides and Skins, Process Guidance, Her Majesty's Inspectorate of Pollution, UK.
- John, A., 2007. Industry Assessment and Benchmarking: Ethiopian Leather Sector, Commissioned by ecgp, study report, Addis Ababa, Ethiopia.
- Khan, M.A., Islam, J., Rahman, M.M., Arifur, M., Khan, R.A., Islam, T., 2010. Study on the effect of urea on the mechanical and morphological properties of jute/gelatin composites. *P.P. Tech. Engg.* 49 (9), 885–891.
- Lang, Maier F., Kolozmik, K., Sukop, S., Dekm, Mla, 1999. Products of enzymatic decomposition of chrome-tanned leather waste. *JSLTC* 83 (4), 187.
- Ozgunay, H., Colak, S., Mutlu, M.M., Akyuz, F., 2007. Characterization of leather industry wastes. *Polish J. Environ. Stud.* 16 (6), 867–873.
- Ramnath, V., Sekar, S., Sankar, S., Sankaranarayanan, C., Sastry, T.P., 2012. Preparation and evaluation of bio-composites as wound dressing material. *J. Mater. Sci. Mater. Med.* 23 (12), 3083–3095.
- Satyanarayana, K.C., Sukumaran, K., Mukherjee, P.S., Pavithran, C., Pillai, S.G.K., 1990. Natural fibre-polymer composites. *Cem. Concr. Compos.* 12 (2), 117–136.
- Sekar, S., Mohan, R., Ramasastry, M., Das, B.N., Sastry, T.P., 2007. Preparation and particle characterization of composite boards using chrome shavings and various binders. *Leather Age* 19, 86–92.
- Sekar, S., Mohan, R., Ramasastry, M., Das, B.N., Sastry, T.P., 2009. Preparation and characterization of composite boards using chrome shavings and plant fibers. *J. Ind. Leather Technol. Assoc.* 10, 765–770.
- Senthil, R., Hemalatha, T., Kumar, B.S., Uma, T.S., Das, B.N., Sastry, T.P., 2014. Recycling of finished leather wastes: a novel approach. *Clean Technol. Environ. Policy*. <http://dx.doi.org/10.1007/s10098-014-0776-x>.
- Taj, S., Munawar, M.A., Khan, S.U., 2007. Review: natural fiber-reinforced polymer composite. *Proc. Pak. Acad. Sci.* 44 (2), 129–144.
- Taylor, M.M., Cabeza, L.F., Dimaio, G.L., Brown, E.M., Marmer, W.N., Carrio, R., Celma, P.J., Cot, J., 1998. Processing of leather waste: pilot scale studies on chrome shavings. Part I. Isolation and characterization of protein products and separation of chrome cake. *JAL CA* 93 (3), 61.
- Thomson, R.S., 1985. Chrome tanning in the nineteenth century. *JSLTC* 69, 93–98.
- Wikipedia, home page, accessed on Dec 2010 <http://en.wikipedia.org>.
- Zhang, Z., Li, G., Shi, B., 2006. Physicochemical properties of collagen, gelatin and collagen hydrolysate derived from bovine limed split wastes. *J. Soc. Leather Technol. Chem.* 9023.