Re-utilization of Finished Leather Waste (scraps) Blended with Different Plant Fibers Using Polymer Resins: A Waste to Wealth Approach, of the Ethiopian Case

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Abstract

In the process of tanning significant amount of solid, liquid and gaseous wastes are generated. The waste generated from the tanning industry then causes negative health effects on the environment which in turn leads to health issue of the local community. The present then study is focused on making of leather composites using solid leather waste, different plant fibers namely enset *(Ensete ventricosum)*, hibiscus *(Hibiscus cannabinus)*, jute *(Corchorus trilocularis* L*)*, palm *(Phoenix dactylifera)* and sisal *(Agave sisalana)* and two polymer resins i.e., Resin Binder (RB) and Poly Urethane Binder (PUB) in various proportions. Composites containing leather fiber incorporated with hibiscus, sisal and palm fibers along with resin binder exhibited better tensile strength values than their respective controls. This shows the compatibility of the resin binder with plant fibers and leather fibers. Composites prepared using sisal fibers gave better tensile strength values compared to others prepared in this study.

SEM pictures of the products in this study showed composite nature. FTIR studies have shown the functional groups of collagen protein, cellulose and binders. In the DSC study, the composite sheets of jute (LF-JS), palm (LF-PS) and sisal (LF-SS) exhibited higher melting points than the control, however, enset (LF-ES) and hibiscus (LF-HS) samples showed lower melting temperature than their respective controls. Based on these results, all composite sheets that meet the set standard can be used for preparation of products such as light hand bags, false roofing coverage, mouse pads, key chains, wallets, components of furniture and other interior decorations.

Keywords: Leather; Binder; Plant; Fiber; Waste

Nomenclature: LF: Leather Fiber; JS: Jute Sheet; PS: Palm Sheet; SS: Sisal Sheet; ES: Enset Sheet; HS: Hibiscus Sheet

Introduction

In search of a covering material for himself, his hut and food, early man turned either to large leaves from plants or to the skins of the animals he killed. The skins were chosen for clothing as they were bigger, stronger and warmer. However, they soon putrefy if left in a damp condition. Dried skins/hides on the other hand lost flexibility and softness becoming very hard and brittle leading to cracking which is unsuitable for clothing and other uses. To stop all these, early man discovered tanning technology which converts hides and skins into leather that do not putrefy even after drying and wetting back [1]. Leather is obtained by tanning skins and hides by any one of several methods. By convention, the term 'hide' generally refers to the skin-covering of larger animals (cows, steers, horses, buffaloes), and the term 'skins', to those of smaller animals (calves, sheep, goats, pigs, etc.). Although the physical properties of these different skins vary, their basic chemical, physical, and histological characteristics are similar [2].

The leather industry, though it is the well-known in world leather trade, is held responsible for its negative environmental externality. It is highly environment polluting sector by generating organic and inorganic pollutants that pose a major challenge to the surroundings and bionetwork [3]. The environment is under increasing pressure from solid and liquid wastes emanating from this industry. Waste generation is an inevitable by-product of the leather manufacturing process and causes significant pollution unless treated in some ways prior to discharge [4]. The solid wastes generated during leather processing are significant since leather industry makes uses of only 20

-25 percent of the raw material in the finished leather, 75 -80 percent end up as wastes in the environment [5]. Many conventional disposal methods exist in practice for the management of solid waste generated in leather processing industries, which mainly comprise of land co-disposal, thermal incineration and anaerobic digestion. These disposal/treatment methods normally possess one or more demerits like vast use of land fill sites, large man power handling which provokes unhygienic conditions and a possibility for the conversion of trivalent chromium (nontoxic) to hexavalent chromium (toxic) during thermal incineration. The trivalent chromium in environment will have its own toxic effects, when the living organism comes in contact. However, it would not create any adverse health effects up to a concentration of 10 mg/person/day according to UK Expert group on vitamins and minerals (EVM) [6].

Though environmental pollution is an alarming issue of the time in most parts of the world including Ethiopia, Leather industries in general provide less attention to solid waste management and it is common to see heaps of illegitimately dumped wastes around rivers,

tannery compounds and other open places. Burning of solid waste is also a common happening in many areas. There is no sorting of the solid wastes based on their properties and mixed solid wastes are disposed in open dumping sites and this confirms that negligible focus is given to the waste at this moment [7]. In the leather goods and footwear manufacturing industries, huge amount of leather is discarded as waste, and presently it is basic to make an effort to utilize this waste in Ethiopia because it is untapped resource [8]. The nature of the tanning industry and the negative effect of the waste as well as the careless attention given to the utilization practice and/or disposal methods of the waste at this time calls for scholarly work to be done in Ethiopia. The objective of this study therefore is to prepare composite sheets, which can be used for consumer applications, by utilizing solid leather waste, plant fibers and synthetic polymers in appropriate proportions.

Materials and Methods

Materials

Finished leather scrap was collected from ELICO (Ethiopian Leather Industry Corporation). Resin binder (RB), polyurethane binder (PUB), Polyethylene glycol (PEG) and $Al_2(SO_4)$ 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. The work was carried out at CSIR-CLRI (Council of Scientific and Industrial Research-Central Leather Research Institute), India.

Methods

Preparation of leather fiber (LF) and plant fibers (PFs): Finished leather scrap was cut into small pieces (length 5-10 cm and width 2-3 cm) using Swing ARM Clicker machine (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 [9,10].

Optimization of binders: Composite sheets were prepared using the leather fiber and two different synthetic binders namely resin binder (RB) and Poly urethane binder (PUB) at different levels of (30, 60, 90, 120 and 150 ml (weight of the leather fiber) and tested for their tensile strength to take the optimum result as reference for the binders.

Preparation of leather sheets using resin binder: About 130 g of fiberized leather fiber was soaked in 1000 ml of water for 12 hours, minced in meat mincing machine (La Minerva C/E 680N) (minced three times to reduce the particle size) and made into fine paste. To this paste 90 ml of RB, 10 ml of PEG and 4 percent 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 in to the sheet making machine of (30 cm x 30 cm) and wet sheet was pressed using hydraulic press (polyhydron 4DL10SGS-10) at a pressure of 1500 PSI for 10 seconds. The pressed sheet was air dried for at least three days and plated using hydraulic press at a pressure of 2,000 PSI at 80 0C for 10 seconds.

Preparation of leather sheets using PUB: The process was same

as above (RB-Lb preparation) the change is only binder, Instead of RB, PUB was used.

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 percent, 20 percent, 30 percent and 40 percent (weight of the leather fiber) 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:

- Composite sheet made from leather fiber and binders served as control labeled as " LF-CS"

- Composite sheet made from leather fiber and enset fiber labeled as "LF-ES"

- Composite sheet made from leather fiber and hibiscus fiber labeled" LF-HS"

- Composite sheet made from leather fiber and jute fiber labeled "LF-JS "

- Composite sheet made from leather fiber and palm fiber labeled "LF-PS"

- Composite sheet made from leather fiber and sisal fiber labeled "LF-SS"

Characterization of control and composite sheets

All the composite sheets (CBs) were characterized for their physicochemical properties such as mechanical studies, thermal stability (TGA), formation and changes in the functional groups (FT-IR) and surface morphology (SEM).

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 (percent) 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 (percent) capacities of the different control leather and composite sheets were determined according to Sekar et al. [11]. Flexing endurance strength was also assessed using SATRA fiber sheet flexing (TER 74) machine according to (STM 129) test method.

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 4,000–600 cm^{-1} using Nicolet 360 FTIR Spectrometer. Thermo gravimetric analysis (TGA) and differential scanning calorimeter (DSC) 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°C–800°C at a heating rate of 10°C/min. under nitrogen atmosphere at flow rate of 60 ml/min. Surface morphology of the samples was visualized by scanning electron microscope (SEM Model LEICA stereo scan 440 instruments).

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.

Results and Discussion

The mechanical studies of composite sheets are very important characteristics because the products made have to bear the mechanical stress exerted when used by the consumer. Products with good mechanical properties last long and are commercially viable in the market. Keeping these truths in mind, mechanical properties of the composite sheets prepared in this study were examined. The mechanical properties such as tensile strength, elongation at break, stitch tear strength, flexing strength were examined. Apart from these water absorption and desorption properties of the composites prepared were also determined.

As presented in Figure 1, optimum values in tensile strength (TS) of both binders i.e., resin binder (RB) and poly urethane binder (PUB) were obtained at the levels of 90 and 120 ml (in weight/volume ratio) respectively, and these values were taken as reference to prepare controls as well as other composite sheets.

As presented in Table 1, composite sheets of LF-H were prepared using two different synthetic binders (RB and PUB) with their optimum respective tensile strength values of (8.25 ± 1.48 and 5.41 ± 0.30 MPa). All composite sheets prepared using RB showed better tensile strength values than their respective controls, however, sample 2 (8.25 ± 1.48 MPa) has shown optimum values. But, composite sheets prepared using PUB showed lower tensile values than their respective control, sample 5 (20 percent PF) (5.41 ± 0.30 MPa) has shown better values in this group. This observation implies that PUB might not be contributing much to the tensile strength of composite sheets, however in RB treated composite sheets the polymer seems to be more compatible and adhesive in nature to both PF and LF. The tensile strength values in most of these composite sheets prepared in this study did meet the required standard set by Central Leather Research Institute shoe design and development center (CLRI-SDDC) (4.0-7.0 MPa) for the insole/shank sheet of footwear as per the SATRA TM2: 1995 test method because their value is in the range of (4.66 ± 0.03–8.25 ± 1.48 MPa) except in the 10 percent plant fiber of PUB which has a tensile strength value of (3.77 ± 0.42 MPa). Elongation at break of composite sheets prepared using RB showed better values than their respective control

but in those prepared using PUB showed lower values their respective controls. The stitch tear strength of composite sheets prepared using RB have higher values than their controls in sample 3 (20 percent PF) (53.59 ± 0.67 N/mm) and sample 5 (40 percent PF) (90.43 ± 0.36 N/mm) with the optimum result being at sample 5 (40 percent PF), where as in composite sheets prepared using PUB all except sample 3 (20 percent PF) (37.46 ± 0.35 N/mm) do have higher values than their respective controls with the optimum result being at sample 4 (30 percent PF) (58.62 ± 0.37 N/mm). All water absorption values of composite sheets prepared using RB are lower than their respective controls, however in composite sheets prepared using PUB all results are above their respective controls with the optimum value being at sample 3 (20 percent PF). Water desorption properties of composite sheets prepared using RB have higher values in sample 2 (10 percent PF) and sample 3 (20 percent PF) than their respective controls but in those composite sheets prepared using PUB all have lower values than their respective controls. The results of flexing index in all except sample 2 (10 percent PF) (3.02 ± 2.08) of those prepared using RB are lower than their respective controls and did not meet the required standard for foot wear insole manufacturing, this low value might be due to the nature of the binders.

As presented in Table 2, LF-S composite sheets were prepared using the two synthetic binders (RB and PUB). In the composite sheets prepared using RB sample 4 (30 percent PF) and sample 5 (40 percent PF) with their respective values of (8.57 ± 0.85 and 9.08 ± 0.91 MPa) do have better tensile strength values than their respective controls with their optimum value (9.08 ± 0.91 MPa) seen in sample 5 (40 percent PF). In the composite sheets prepared using PUB sample 4 (30 percent PF) and sample 5 (40 percent PF) with their respective values of (6.45 ± 0.78 and 8.02 ± 1.62 MPa) do show better tensile strength than their controls. This indicates that the plant fibers are contributing to the strength of sheets. Elongation at break of composite sheets prepared using RB showed better values than their respective controls with their optimum value being in sample 2 (10 percent PF), however in those composite sheets prepared using PUB, all samples exhibited lower values of elongation at break. This difference might be seen due to the difference in the nature of the binders. Stitch tear strength of composite sheets prepared using RB all except sample 2 (10 percent PF) do possess higher values than their respective controls. In the composite sheets prepared using PUB only sample 2 (10 percent PF) and sample 5 (40 percent PF) do have higher value whereas sample 2 has shown optimum value at (10 percent PF). Water absorption properties of all composite sheets prepared using RB do have lower values whereas in those composite sheets prepared using PUB all do have better water absorption properties with the optimum result being in sample 5 (40 percent PF). Water desorption properties of all composite sheets prepared using RB do have better value than their respective controls with the optimum being in sample 2 (10 percent PF). In those composite sheets prepared using PUB all except sample 4 (30 percent PF) do have better water desorption properties, however, optimum value was observed in sample 2 (10 percent PF). Flexing index value of all composite sheets prepared using RB do have better values than their controls but in those composite sheets prepared using PUB all except sample 5 (40 percent PF) do have lower values of flexing index than their respective controls.

Composite sheets of LF-E are prepared using RB and PUB. In all of the sheets prepared the tensile strength values of the composites are lower than their respective controls (Table 3), with the optimum value for RB being in sample 4 (30 percent PF) and for PUB in sample 3(20 percent PF). The elongation at break values of composite sheets
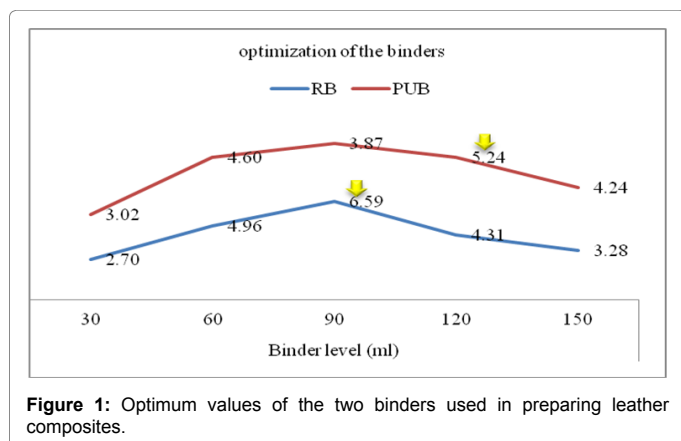
Figure 1: Optimum values of the two binders used in preparing leather composites.

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			Hibiscus				
1. RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
2. RB	90:10:00	8.25 ± 1.48	8.33 ± 0.33	49.82 ± 0.02	65.16 ± 1.06	74.62 ± 0.57	3.02 ± 2.08
3. RB	80:20:00	7.00 ± 0.04	9.12 ± 1.10	53.59 ± 0.67	78.27 ± 0.22	82.28 ± 0.99	0.15 ± 0.00
4. RB	70:30:00	6.14 ± 0.71	7.40 ± 0.08	46.99 ± 0.14	92.17 ± 0.98	72.03 ± 3.09	0.83 ± 0.68
5. RB	60:40:00	8.08 ± 0.21	8.06 ± 1.65	90.43 ± 0.36	76.50 ± 1.52	70.05 ± 3.31	0.68 ± 0.32
1. PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
2. PUB	90:10:00	3.77 ± 0.42	2.84 ± 0.23	51.37 ± 0.69	86.43 ± 3.81	76.62 ± 3.35	0.61 ± 0.06
3. PUB	80:20:00	4.91 ± 1.39	4.45 ± 0.63	37.46 ± 0.35	105.82 ± 3.23	76.25 ± 2.69	0.9 ± 0.08
4. PUB	70:30:00	4.66 ± 0.03	4.02 ± 0.46	58.62 ± 0.37	96.79 ± 2.80	70.11 ± 2.15	0.15 ± 0.06
5. PUB	60:40:00	5.41 ± 0.30	3.95 ± 0.08	47.59 ± 0.29	95.61 ± 2.53	77.13 ± 0.89	0.25 ± 0.11

* RB=Resin binder *PUB=Polyurethane binder

Table 1: Mechanical properties of LF-H composite sheets.

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			Sisal				
1. RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
2. RB	90:10:00	4.61 ± 0.68	7.78 ± 0.95	39.87 ± 0.49	92.07 ± 3.19	94.51 ± 2.53	0.44 ± 0.13
3. RB	80:20:00	5.33 ± 0.95	6.34 ± 0.94	56.35 ± 0.04	92.31 ± 386	82.14 ± 2.19	0.52 ± 0.20
4. RB	70:30:00	8.57 ± 0.85	7.84 ± 0.08	61.92 ± 0.19	97.04 ± 0.71	81.34 ± 0.65	1.08 ± 0.09
5. RB	60:40:00	9.08 ± 0.91	7.73 ± 1.34	57.69 ± 0.25	99.44 ± 2.45	90.97 ± 0.12	1.94 ± 0.44
1. PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
2. PUB	90:10:00	3.71 ± 0.91	4.50 ± 0.71	62.51 ± 0.10	77.32 ± 1.28	117.19 ± 2.76	0.23 ± 0.07
3. PUB	80:20:00	4.59 ± 0.70	4.06 ± 0.40	37.11 ± 0.04	129.30 ± 0.88	87.96 ± 2.96	0.34 ± 0.16
4. PUB	70:30:00	6.45 ± 0.78	3.95 ± 0.71	43.02 ± 0.28	106.24 ± 3.54	85.05 ± 1.49	1.03 ± 0.06
5. PUB	60:40:00	8.02 ± 1.62	4.19 ± 0.58	46.36 ± 0.21	138.67 ± 4.93	88.43 ± 2.45	1.65 ± 0.40

Table 2: Mechanical properties of LF-S composite sheets.

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			Enset				
1. RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
2. RB	90:10:00	3.68 ± 0.38	6.67 ± 1.57	32.73 ± 0.72	80.02 ± 2.49	82.34 ± 2.10	0.69 ± 0.04
3. RB	80:20:00	4.24 ± 2.14	5.39 ± 2.43	41.66 ± 0.70	88.61 ± 3.32	89.24 ± 2.40	1.22 ± 0.24
4. RB	70:30:00	5.92 ± 0.23	7.45 ± 0.64	39.92 ± 0.69	93.51 ± 0.25	79.64 ± 1.87	1.46 ± 0.14
5. RB	60:40:00	5.43 ± 0.36	5.84 ± 0.54	48.28 ± 0.36	106.25 ± 0.80	90.44 ± 3.62	1.35 ± 0.15
1. PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
2. PUB	90:10:00	2.98 ± 0.01	4.45 ± 0.35	24.16 ± 0.42	134.77 ± 0.20	84.21 ± 2.56	0.93 ± 0.05
3. PUB	80:20:00	4.24 ± 2.14	5.39 ± 2.43	26.80 ± 1.08	85.89 ± 0.03	83.79 ± 3.06	2.58 ± 1.43
4. PUB	70:30:00	1.84 ± 0.58	2.06 ± 0.23	33.91 ± 0.20	103.36 ± 2.52	81.93 ± 1.50	1.27 ± 0.25
5. PUB	60:40:00	3.71 ± 0.57	2.67 ± 0.78	44.11 ± 0.71	105.72 ± 2.18	82.28 ± 2.74	1.38 ± 0.17

Table 3: Mechanical properties of LF-E composite sheets.

prepared using RB are better than their respective controls except in sample 3 (20 percent PF) with sample no 4 (30 percent PF) exhibiting the optimum value. In composite sheets prepared using PUB all do have lower values of elongation at break than their respective controls, sample 3 (20 percent PF) has shown optimum value. Stitch tear strength values of all composite sheets prepared using RB do have lower values than their respective controls and all except sample 5 (40 percent PF) of those prepared using PUB also do have lower values than their respective controls. Concerning the water absorption properties of the composites all except sample 5 (40 percent PF) of those prepared using RB do have lower values than their respective controls but in composites prepared using PUB all do have better water absorption values than their controls. The waster desorption properties of composites prepared using RB do have better values than their respective controls

but in those composites prepared using PUB all do have lower values than their respective controls. Flexing is another characteristic taken in to consideration. So, in all composite samples prepared using RB they do have better flexing values than their respective controls, however in those composite samples prepared using PUB all except sample 3 (20 percent PF) exhibited lower values than their controls. In all the composites whether control or other composites, the flexing properties don't meet the required standard for insole making this might be due to the nature of the plant fibers is compatible with the that of PF used in this experiment.

As shown in Table 4, LF-J composite sheets are prepared using RB and PUB like the others. In these composites all the experimental samples have shown lower values of tensile strength than their

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			Jute				
1. RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
2. RB	90:10:00	5.82 ± 0.69	6.34 ± 1.25	73.86 ± 0.25	60.29 ± 1.06	88.87 ± 3.30	1.32 ± 0.60
3. RB	80:20:00	5.98 ± 1.26	8.28 ± 0.71	55.73 ± 0.36	78.80 ± 34	75.62 ± 0.40	1.60 ± 0.19
4. RB	70:30:00	5.37 ± 0.10	7.06 ± 0.40	45.08 ± 0.16	90.78 ± 1.04	73.92 ± 0.90	1.79 ± 0.24
5. RB	60:40:00	5.21 ± 0.76	5.28 ± 0.40	54.97 ± 0.76	82.12 ± 2.15	67.98 ± 1.24	1.65 ± 0.22
1. PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
2. PUB	90:10:00	5.17 ± 0.28	4.23 ± 0.16	51.38 ± 0.70	104.81 ± 1.82	68.76 ± 1.17	1.15 ± 0.13
3. PUB	80:20:00	4.15 ± 0.37	3.84 ± 0.08	50.94 ± 1.56	102.99 ± 0.33	70.09 ± 2.67	1.08 ± 0.11
4. PUB	70:30:00	4.98 ± 0.87	5.06 ± 0.08	38.17 ± 1.08	100.65 ± 2.75	74.26 ± 0.62	1.56 ± 0.30
5. PUB	60:40:00	4.45 ± 0.25	4.17 ± 0.08	56.35 ± 0.86	85.51 ± 1.04	96.00 ± 2.28	1.15 ± 0.13

Table 4: Mechanical properties of LF-J composite sheets.

respective controls with the optimum value of being (5.98 ± 1.26 MPa) in sample 3 (20 percent PF) for RB and (5.17±0.28 MPa) in sample 2 (10 percent PF) for PUB. Concerning the elongation at break composite sheets prepared using RB all except sample 5 (40 percent PF) exhibited better values than their respective controls. The stitch tear strength of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better value. Composite sheets prepared using PUB have also shown better values except in sample 4 (30 percent PF). All composite sheets made using RB do have lower values of water absorption than their respective controls whereas those composite sheets prepared using PUB do have better values than their respective controls this difference might arise due to binder difference. The water desorption properties of the composite sheets prepared using RB all except sample 5 (40 percent PF) do possess better values than their respective controls however in those composite sheets prepared using PUB all except sample 5 (40percent PF) do possess lower values than their controls. Flexing index of composite sheets prepared using RB have higher values than their respective controls, but in those composite sheets prepared using PUB all do have lower values than their respective controls.

Composite sheets of LF-P were prepared using RB and PUB (Table 5). Among the composite sheets prepared using RB only sample 2 (10 percent PF) and sample 3 (20 percent PF) have showed better tensile strength than their respective control whereas those sheets prepared using PUB have exhibited lower values of tensile strength than their respective controls. Elongation at break of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better values however, in those composite sheets prepared using PUB all samples possess lower values than their controls with the optimum value of (7.56 ± 1.34 MPa) being at sample 4 (30 percent PF). The stitch tear strength properties of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better values than their respective controls but in those composite sheets prepared using PUB all except sample 4 (30 percent PF) do possess lower value than their respective controls. Concerning water absorption properties all of the composite sheets prepared using RB do possess lower values than their respective control however in those composite prepared using PUB all do have better values than their respective controls in both cases all meet the requirement set by CLRI-SDDC to prepare industrial and high quality foot wear (minimum of 35 percent) as per the test method of SASTRA TM9:1993. The water desorption properties of composite sheets prepared using RB sample 2 (10 percent PF) and sample 3 (20 percent PF) do have better values than their respective controls but in those composite sheet prepared using PUB all do have lower values than their respective controls. The flexing strength of composite sheets prepared

using RB all do have better values than their respective control and only sample 3 (20 percent PF) meet the requirement needed to prepare light use footwear set by CLRI-SDDC as per the test method of (SASTRA TM3: 1999).

As can be seen from the pooled data Table 6 the tensile strength values of the composite sheets are above their respective controls in Hibiscus using RB, in sisal using both binders and in palm using RB whereas the rest do have lower results than their respective controls which implies that the plant fibers are not contributing to the strength of the products. Among all of the plant fibers sisal performed better than the others in tensile strength. This indicates that it is contributing better to the tensile strength as compared to the other plants.

As presented in Figure 2, the pictures exhibited the raw materials used for the manufacturing process and products prepared i.e. the different fibers used Figure 2A-D, raw composite sheet Figure 1E the finished composite sheet Figure 2F and the final products prepared from these composite sheets as major raw material Figure 2G. As can be seen from these pictures, the different products (composite sheets) were prepared from leather and plant fiber in combination with the synthetic binders have attractive look and are suitable for consumer use.

Scanning electron microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution of materials having micro (1 micron = 10^{-6} m) and nanoscale (1 nanometer = 10^{-9} m). Specimens can be observed in high vacuum in conventional SEM, or in low vacuum or wet conditions in variable pressure or environmental SEM and at a wide range of cryogenic or elevated temperatures with specialized instruments [12]. SEM represents a high performance method used to investigate the structure of the materials. It is defined by: easiness to prepare samples to be tested, large diversity of information reached, good resolution associated with high field depth, large and continuous range of magnifying, etc. The examination of microstructures with SEM offers two benefits as compared to optical microscopy (OM): much more resolution and magnification, as well as very large field depth giving the impression that images obtained are outstanding [13].

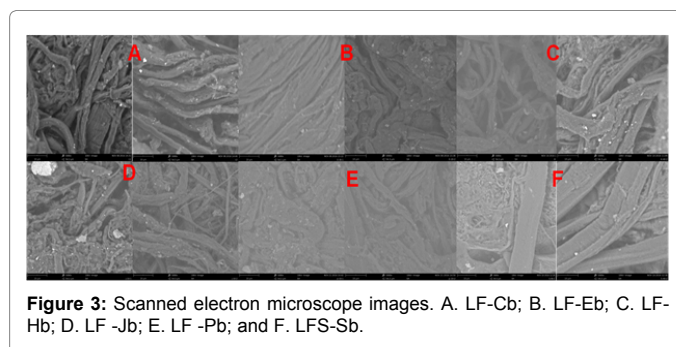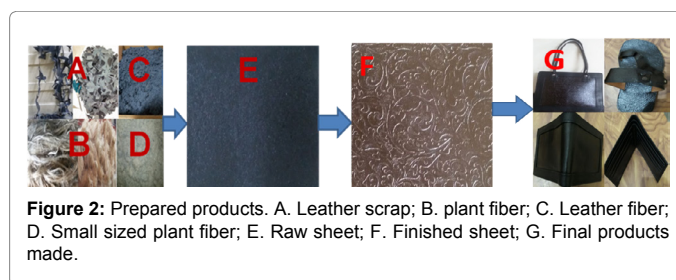| Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			Palm				
1. RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
2. RB	90:10:00	8.08 ± 1.43	10.45 ± 1.73	71.06 ± 0.17	68.80 ± 0.35	82.75 ± 3.41	2.13 ± 0.33
3. RB	80:20:00	7.46 ± 0.76	10.01 ± 0.78	62.01 ± 0.36	83.96 ± 1.81	83.24 ± 0.91	3.00 ± 0.31
4. RB	70:30:00	3.24 ± 0.52	4.12 ± 0.47	30.72 ± 1.03	103 ± 1.28	56.85 ± 0.26	1.21 ± 0.11
5. RB	60:40:00	4.95 ± 1.02	7.67 ± 1.57	52.93 ± 0.62	102.55 ± 2.65	52.64 ± 2.17	1.92 ± 0.11
1. PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
2. PUB	90:10:00	3.91 ± 0.24	3.89 ± 0.47	30.95 ± 0.86	100.56 ± 3.43	85.89 ± 1.44	1.36 ± 0.17
3. PUB	80:20:00	4.31 ± 0.23	3.73 ± 0.54	32.78 ± 0.35	130.72 ± 1.08	69.42 ± 2.60	1.17 ± 0.15
4. PUB	70:30:00	5.87 ± 1.34	7.56 ± 1.34	49.92 ± 0.86	107.45 ± 1.09	62.20 ± 2.22	1.69 ± 0.01
5. PUB	60:40:00	4.24 ± 0.01	3.78 ± 0.62	35.22 ± 0.70	157.18 ± 2.35	59.36 ± 1.15	1.30 ± 0.14

Table 5: Mechanical properties of LF-P composite sheets.

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
			controls				
RB	100:00:00	6.05 ± 0.57	5.73 ± 0.23	52.63 ± 0.89	103.37 ± 1.56	73.65 ± 2.34	0.15 ± 0.00
PUB	100:00:00	6.25 ± 0.24	12.34 ± 0.16	43.82 ± 0.35	71.44 ± 4.74	86.10 ± 1.65	1.61 ± 0.17
			Hibiscus				
RB	90:10:00	8.25 ± 1.48	8.33 ± 0.33	49.82 ± 0.02	65.16 ± 1.06	74.62 ± 0.57	3.02 ± 2.08
PUB	60:40:00	5.41 ± 0.30	3.95 ± 0.08	47.59 ± 0.29	95.61 ± 2.53	77.13 ± 0.89	0.25 ± 0.11
			Sisal				
RB	60:40:00	9.08 ± 0.91	7.73 ± 1.34	57.69 ± 0.25	99.44 ± 2.45	90.97 ± 0.12	1.94 ± 0.44
PUB	60:40:00	8.02 ± 1.62	4.19 ± 0.58	46.36 ± 0.21	138.67 ± 4.93	88.43 ± 2.45	1.65 ± 0.40
			Enset				
RB	70:30:00	5.92 ± 0.23	7.45 ± 0.64	39.92 ± 0.69	93.51 ± 0.25	79.64 ± 1.87	1.46 ± 0.14
PUB	80:20:00	4.24 ± 2.14	5.39 ± 2.43	26.80 ± 1.08	85.89 ± 0.03	83.79 ± 3.06	2.58 ± 1.43
			Jute				
RB	80:20:00	5.98 ± 1.26	8.28 ± 0.71	55.73 ± 0.36	78.80 ± 34	75.62 ± 0.40	1.60 ± 0.19
PUB	90:10:00	5.17 ± 0.28	4.23 ± 0.16	51.38 ± 0.70	104.81 ± 1.82	68.76 ± 1.17	1.15 ± 0.13
			Palm				
RB	90:10:00	8.08 ± 1.43	10.45 ± 1.73	7.106 ± 0.17	68.80 ± 0.35	82.75 ± 3.41	2.13 ± 0.33
PUB	70:30:00	5.87 ± 1.34	7.56 ± 1.34	49.92 ± 0.86	107.45 ± 1.09	62.20 ± 2.22	1.69 ± 0.01

Table 6: Mechanical properties of the pooled data of composite sheets.

The SEM images of sampled composite sheets are shown in Figure 3A indicates the SEM image of the sheet made from leather fiber as control (LF-Cb) (112 μm). 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 LF-Eb shown in Figure 3B reveals the binding nature of the binder with leather and enset fibers. The width of enset fiber (129 μm) seems to be more than that of the control (112 μm). The composite nature of this sample is evident. In SEM image of LF-Hb as shown in Figure 3C, with its fiber width of (120 μm) is clearly seen. This shows that the combination of leather and hibiscus fiber with binder is obvious. As seen in Figure 3D, width of the LF-Jb is (139 μm). In the LF-Pb of Figure 3E SEM image, it looks that the fiber is well-established in the binder with its width of (129 μm). In LF-Sb image of Figure 3F, it is observed that the fiber is well embedded with the binder and it seems less porosity of the composite. All composite sheets prepared in this experiment exhibited an assortment of fibers along with the binder having 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 sheets made in the earlier study of Sekar et al. and Teklay et al. [8,11].

Fourier transform infrared studies

Figure 2: Prepared products. A. Leather scrap; B. plant fiber; C. Leather fiber; D. Small sized plant fiber; E. Raw sheet; F. Finished sheet; G. Final products made.

Figure 3: Scanned electron microscope images. A. LF-Cb; B. LF-Eb; C. LF-Hb; D. LF -Jb; E. LF -Pb; and F. LFS-Sb.

Infrared (IR) or Fourier transform infrared (FTIR) spectroscopy has a large application range, from the analysis of small molecules or molecular complexes to the analysis of cells or tissues. The imaging of tissues is one of the recent developments of infrared spectroscopy, taking advantage of infrared microscopy and of the use of synchrotron IR radiation. It is used for the mapping of cellular components (carbohydrates, lipids, proteins) to identify abnormal cells [14,15]. FTIR spectroscopy has also been increasingly applied to the study of proteins. This concerns the analysis of protein conformation, protein folding, and of molecular details from protein active sites during enzyme reactions using reaction-induced FTIR difference spectroscopy [16]. 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 Figure 4. The FTIR spectrum of the control sheet as shown in Figure 4A indicates the amide bands of collagen fibers at 1644 cm^{-1}, 1536 cm^{-1} and 1427 Cm^{-1} representing amide I, II and III respectively [17].

FTIR spectra of LF-Eb composite sample Figure 4B showed abroad peak from 1031-1727 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 [18]. The peak at 1443 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1242 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of LF-Hb composite sample Figure 4C shows similar trend to LF-Eb composite. However we can see in the plane C=O stretch bending at 1632 cm^{-1} [18], in the spectra of LF-Jb; LF-Pb; and LF-Sb Figure 3D-F, showed more or less similar pattern. The reason for this similarity might be due to the similar nature of cellulose in all the samples representing collagen and cellulose.

Thermo gravimetric analysis studies

As shown in Figure 5, the thermo gravimetric analysis (TGA) study revealed weight loss of materials with increase in temperature is inevitable. In this study, samples of control and composite sheets were subjected to TGA from 32⁰C to 800⁰C. In the control sheet Figure 5A, a three step weight loss was observed. The first weight loss (21.29 percent) was due to the loss of free and bound water up to 301.22⁰C. The second major weight loss (37.15 percent) up to 414.42⁰C was due to collagen degradation in the samples. The final major weight loss (11.68 percent) up to 789.17⁰C was due to decomposition of degraded products.

In the case of LF–Eb Figure 5B, three step weight losses have been occurred. The initial weight loss (12.02 percent) up to 179.50⁰C is due to the loss of water molecules in the sample. The second major weight loss (60.75 percent) that has occurred up to 464.17⁰C is due to protein and cellulose degradation. The third weight loss (16.38 percent) which occurred up to 786.85⁰C may be due to the decomposition of the degraded products. In composite samples of LF-Hb, LF-Jb and LF-Sb as seen in Figure 5C-F, exhibited more or less the same thermogravimeteric pattern.

Differential scanning calorimeter studies

Differential scanning calorimetry (DSC) is one of the thermo-analytical techniques. A calorimeter measures the heat into or out of a sample. A differential calorimeter measures the heat of sample relative to a reference. A differential scanning calorimeter does all of the above and heats the sample with a linear temperature ramp [19]. 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. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. Only a few mg of material are required to run the analysis. DSC is the most often used thermal analysis method, primarily because of its speed, simplicity, and availability [20]. It is mostly used for quantitative analysis [21].

The DSC thermogram of the control sample in this study as seen in Figure 6A exhibited its peak or melting temperature(Tm) at 96.29⁰C. This Tm peak is higher than the peaks of composite sheets of B (enset) and C (Hibiscus) peak which do have 95⁰C each Figure 6B and C. But
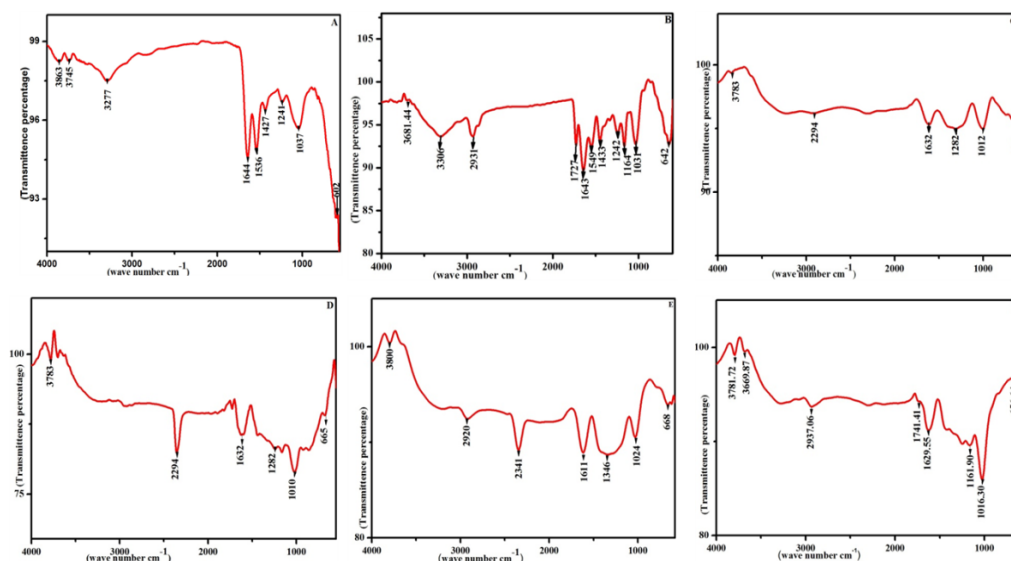

Figure 4: FTIR results of Leather-plant fibers composite sheets using the two synthetic binders. A. control; B. Enset; C. Hibiscus; D. Jute; E. Palm and F. Sisal.
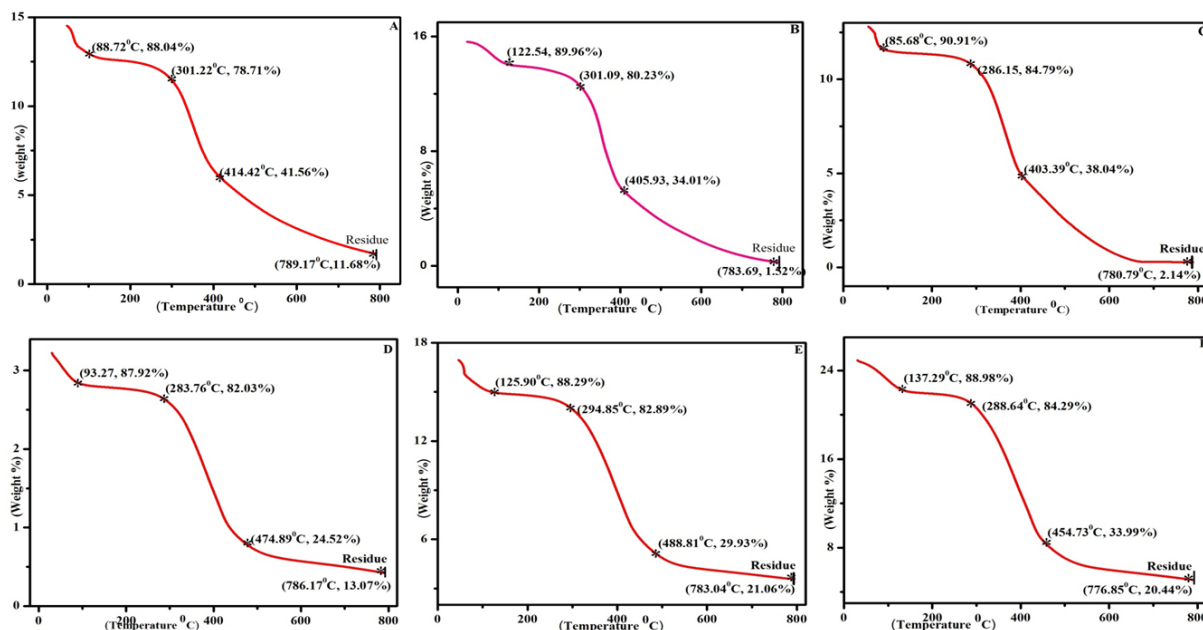
Figure 5: Thermo gravimetric analysis of composite samples A. Control; B. LF-E; C. LF-H; D. LF-J; E. LF-P; and F. LF-S.
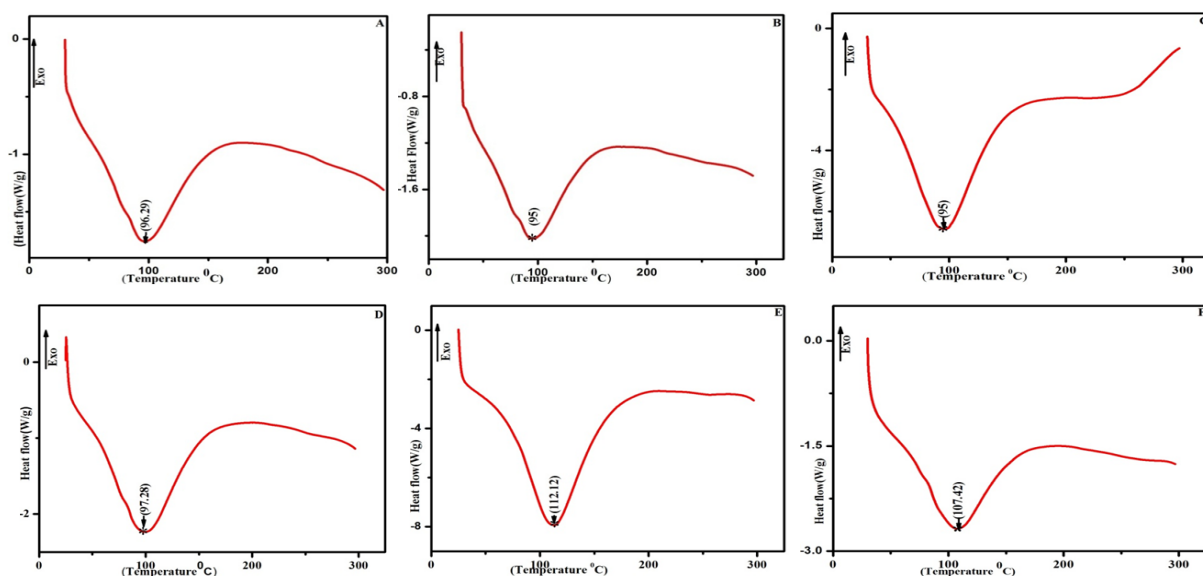

Figure 6: DSC thermograms of RGL composite sheets A. Control; B. LF-Eb; C. LF-Hb; D. LF-Jb; E. LF-Pb; and F. LF-Sb.

lower than D (Jute), E (Palm) and F (Sisal) each having 97.29, 112.12 and 107.42^{0}C respectively Figure 6D-F. The better melting temperature (Tm) for these samples than their respective control 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.

Conclusion and Recommendation

The optimum tensile strength values of composite sheets (8.25 ± 1.48 MPa in LF-Hb at 10 percent of the PF; 9.08 ± 0.91 MPa in LF-Sb at 40 percent of the PF; 5.43 ± 0.36 MPa in LF-Eb at 40 percent of the PF; 5.98 ± 0.69 MPa in LF-Jb at 10 percent of the PF; 8.08 ± 1.43 MPa in LF-Pb at 10 percent of the PF) prepared using RB as a binder met the required standard for insole/shank sheet making (4.0-7.0 MPa). However, since the tensile strength value of the control is (6.05 ± 0.57 MPa), sheets of LF-Hb, LF-Sb and LF-Pb are preferred. In composite sheets prepared using PUB, only optimum value of LF-Sb (8.02 ± 1.62 MPa) at 40 percent of the PF is preferred as it is above the value of the control (6.25 ± 0.24 MPa). SEM studies of the products prepared have shown their composite nature. FTIR, TGA and DSC studies have confirmed the composite nature of the sheets made from waste raw materials. The above composite sheets which have suitable mechanical properties, appealing surface, higher tensile strength value, reasonable flexibility, water absorption and desorption values may be used as raw materials for the production of components of footwear, preparation

of value added consumer products such as stiff hand bag, ladies hand bag, wallet, keychain, false roofing, interior decorations and wall matt etc.

Acknowledgement

Conflict of Interest

The authors declare that there is no conflict of interest.

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