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Preparation of Shoe Soling Material from Leather Waste

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Abstract- The footwear industry is an exciting blend of fashion, craft, technology & science. Footwear is a man made outer covering of foot. It is generally made out of leather and polymers. It can also be defined as wearing apparel for the feet. Polymers plays vital role in the production of footwear and some important polymeric materials used in footwear fabrication is last and soles. Soles are bottom components of footwear and some common soling materials used in footwear making are Leather (sole leather), Rubber (NBR, SBR, Isoprene, Microcellular rubber& crepe rubber), PVC (Poly vinyl chloride), TPR (Thermoplastic rubber), PU (Poly urethane). In our research soling materials were prepared using chrome shaving (tannery solid waste), EPDM and isoprene rubber. In this study strap cutting machine, two roll mill and compression moulding machine used for making composite. The soling material made was characterised using IR-S and SEM and tested for mechanical properties. The aim of this research is to reduce the solid waste generated by leather industry by utilising them as a shoe soling material.

1. INTRODUCTION

Leather manufacturing is one of the industrial activities that are considered to be highly polluting. The three forms of pollutants generated from leather industries are

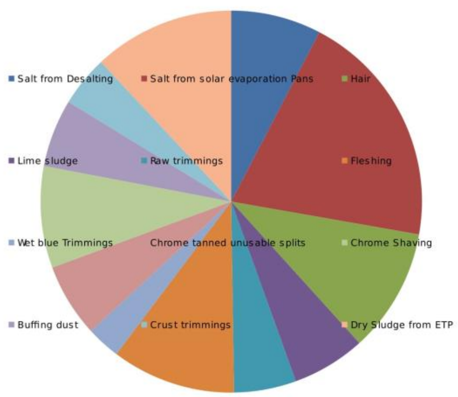
1. Solid waste
2. Liquid waste
3. Gaseous waste

According to the regulation and norms of the pollution control board tanneries need to reduce those wastes to meet all the discharge standards. The utilization of waste as a raw material /feed stock would be important aspect of environmental management. Moreover this strategy has multiple advantages including reduction in waste generation ,waste treatment facility, area of land required for disposal, cost inbuilt in the waste management and revenue generation from the conversion of waste in to value added product.

Solid wastes from the tanning industry are unavoidable. This is because leather processing primarily associated with purification of a muti-component skin to obtain a single protein,collagen.The intrinsic nature of the leather processing steps and the nature of chemicals employed are also responsible for the generation of certain quantum of solid wastes starts at the first operation namely, desalting the raw hides/skis and prolongs through almost all unit processes and operations till end of the process sequence , namely shaving and buffing operations based on the nature of solid waste generated from the leather processing, they can be categorized into chemical and protein based solid waste.

In India according to the estimated production of hides and skins by CLRI more than 24 million pieces of cattle hides, 22 million of buffalo hides, 106 million of goat skins and 37 million of sheep skins are processed in about 1600 tanneries. Approximately 2 lakhs tonnes of solid waste are generated annually from leather industry.

Quantum of solid wastes produced from processing 1-metric ton of raw material is



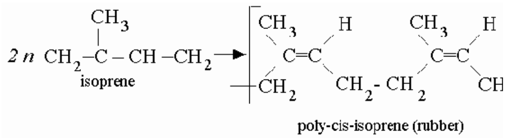
Tonnes of chrome tanned leather wastes are generated every month by the leather and apparel industries. Currently, in several countries, these kinds of waste are burned, or are buried in suburban fields. About 30% of leather substance processed in tanneries is rejected, mainly after the shaving process, in the form of protein wastes containing 3–5% of chromium (III). These wastes are partly utilized, but mainly they are deposited in storage yards, posing a hazard to the environment.

1.1. Materials

The raw materials used for development of shoe soling material from Leather waste (Chrome shaving) – Polymer composites such as Isoprene rubber, EPDM and other ingredients used for laboratory grade.

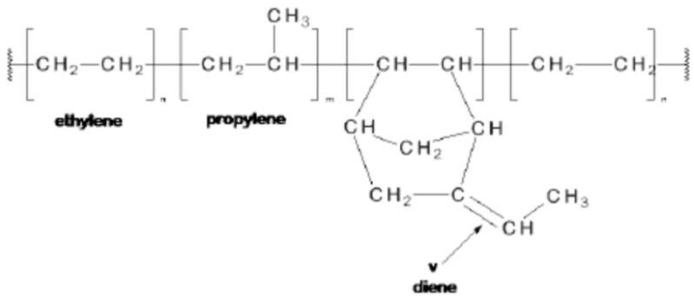
1.1.1. Isoprene Rubber

Polyisoprene (IR/NR) is a cost effective and widely used commercial rubber. It is either harvested in the form of latex from rubber trees (NR) or synthetically produced by polymerization of 1-methyl-1,3-butadiene (IR). Natural rubber is also known as India rubber. It is the only non-synthetic rubber and has been in commercial use since the beginning of the 20th century. Natural and synthetic polyisoprene have good fatigue resistance and are, therefore, an excellent choice for dynamic applications at low and ambient temperatures. It's elasticity, compression set, creep and abrasion resistance is excellent over its working temperature range of approximately -50°C to +100°C (-60°F to 215°F). However, like most other polydiene elastomers, rubber has poor resistance to ozone, gasoline and many organic solvents. Due to its outstanding mechanical properties and low cost, isoprene rubber is the preferred material for many engineering applications. Typical uses include anti-vibration mounts, drive couplings, tires, springs, bearings, soles and adhesives. The largest portion of produced IR and NR is used for tires. The structure of isoprene is mentioned below



1.1.2. EPDM Rubber

EPDM stands for Ethylene Propylene Diene Monomers and it's a type of high density synthetic rubber. It's not as heat resistant as silicone but is able to withstand high temperatures up to 130°C. Because of that it's used as a component within a wide variety of industries including industrial, construction and automotive. In lower temperatures, EPDM will reach brittle point at -40°C.EPDM is also popular as an outdoor rubber as it's resistant to weathering including acid and alkali resistance. As such, you'll typically find it being used for things such as window and door seals or waterproofing sheets.EPDM also has good abrasion, cut growth and tear resistance. The structure of EPDM rubber is mentioned below



1.1.3. Chrome shavings

Chrome shavings are small, thin of leather formed during shaving operation, which is being done to achieve the desired thickness of the leather. Chrome shavings come under the hazardous waste category. Trimmings and chrome shavings alone contribute approximately 35% of the total tannery waste generated. In India every year about 20000 tones of chrome shavings are generated. Chrome shavings alone constitute to an extent of 10% of the quantum of raw Hides/Skins processed amounting to 0.8 million tonnes of chrome shavings generated across the world.

2. PRE TREATMENT OF CHROME SHAVINGS

Waste chrome leather shavings, collected from a local tannery, contains Chromium 2.5 % and Nitrogen 11.21 %. The untreated leather fibres were dried at 100 °C for 15 minutes in an air oven and after cooling to ambient temperature, they were shredded into fine particles. The untreated leather particles were acidic in nature which would interfere with the vulcanization of rubber compound. To overcome the acidic nature, 1% solution of urea, aqueous ammonia and sodium bicarbonate were used separately as neutralizing agents. After neutralization, the leather particles were separated by filtration and the excess water was removed. The resultant cake was dried in sunlight for 2 days followed by drying in a hot air oven at 100 °C for 15 minutes. The treated chrome shavings were passed in to strap cutting machine to reduce the fibre length and then chrome shavings were tested in CLRI laboratory for various characterisation.

3. CHEMICAL CHARACTERIZATION OF CHROME SHAVINGS

Tests	Values
Humidity (wt %)	7.92 ± 0.22
Greases and Oils (wt %)	1.97 ± 0.36
Ash (wt %)	12.86 ± 0.20
Chrome Oxide (wt %)	3.41 ± 0.10
PH in water Extract (wt %)	4.15 ± 0.20
Nitrogen (wt %)	9.71 ± 1.41
Protein (wt %)	54.58 ± 3.80
Decomposition Temperature (°C)	323.0 ± 10.0
Diameter Average (μm)	4.52 ± 0.03
Length Average (μm)	258.5 ± 2.50

4. MACHINERY

A. Strap cutting machine(for chrome shaving fibre length reduction)

B. Two roll mill(Santosh Model, Mumbai) with roller dimension *D*=220mm and *L* = 450 mm

C. Compression moulding machine

5. EXPERIMENTS

Rubber mixes were prepared by using a laboratory scale two roll rubber mixing mill. The temperature of the rolls was 303–312K and the front roll speed *V*o = 16 rpm. The prepared mixes were used to draw out sheets with a thickness of 6–8mm that were then stored at 275–312 K. As per the base formulation given as follows:

5.1. Trail A- (TA) (Control)

Isoprene rubber (RSS Grade) - 100 phr, Silica-50 phr, Zinc oxide – 10 phr, Stearic acid - 4 phr, dibenzothiazyl disulphide (MBTS) - 3 phr, Tetra methyl thiuram disulphide (TMTD)- 2 phr and N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) – 2 phr, aromatic process oil- 20 phr and Sulphur- 5 phr were used for compounding. Oil was added followed by the addition of antioxidant, zinc oxide and stearic acid. After complete mixing and band formation were ensured, accelerators and sulphur were added finally. Appropriate nip gaps were maintained and 3/4th cuts were made during the mixing process in order to get uniform compound quality.

5.2. Trail B- (TB)

Isoprene rubber (RSS Grade) - 100 phr, Chrome shaving-50phr, Zinc oxide – 10 phr, Stearic acid - 4 phr, dibenzothiazyl disulphide (MBTS) - 3 phr, Tetra methyl thiuram disulphide (TMTD)- 2 phr and N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) – 2 phr, aromatic process oil- 20 phr and Sulphur- 5 phr were used for compounding. Oil was added followed by the addition of antioxidant, zinc oxide and stearic acid. After complete mixing and band formation were ensured, accelerators and sulphur were added finally. Appropriate nip gaps were maintained and 3/4th cuts were made during the mixing process in order to get uniform compound quality.

5.3. Trail C- (TC)

EPDM rubber - 100 phr, Chrome shaving-50phr, Zinc oxide – 10 phr, Stearic acid - 4 phr, dibenzothiazyl disulphide (MBTS) - 3 phr, Tetra methyl thiuram disulphide (TMTD)- 2 phr and N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) – 2 phr, aromatic process oil- 20 phr and Sulphur- 5 phr were used for compounding. Oil was added followed by the addition of antioxidant, zinc oxide and stearic acid. After complete mixing and band formation were ensured, accelerators and sulphur were added finally. Appropriate nip gaps were maintained and 3/4th cuts were made during the mixing process in order to get uniform compound quality.

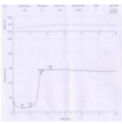
5.4. Trail D- (TD)

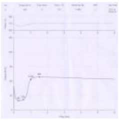
Isoprene rubber – 50phr,EPDM rubber - 50 phr, Chrome shaving-50phr, Zinc oxide – 10 phr, Stearic acid - 4 phr, dibenzothiazyl disulphide (MBTS) - 3 phr, Tetra methyl thiuram disulphide (TMTD)- 2 phr and N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) – 2 phr, aromatic process oil- 20 phr and Sulphur- 5 phr were used for compounding. Oil was added followed by the addition of antioxidant, zinc oxide and stearic acid. After complete mixing and band formation were ensured, accelerators and sulphur were added finally. Appropriate nip gaps were maintained and 3/4th cuts were made during the mixing process in order to get uniform compound quality.

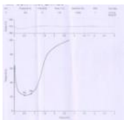
6. CURING

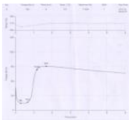
The polymer composite sheet is cured in pre – heated M.S mould maintained at 140°C - 160ºC for 3 to 10 minutes to get cured sample by compression moulding process. Compression moulding is widely used for making composites from prepress such as sheet moulding compounds (SMC), bulk moulding compound (BMC), or glass mat reinforced thermoplastic(GMT). This process uses matching male and female mould halves. A pre-weighed charge cut to the size is placed inside the mould. Which is then closed, and suitable pressure and temperature are applied using a hot press. The applied temperature and pressure force the material to fill the mould cavity and facilitate polymerization (or cross-linking) and consolidation of composite material.

The curing time and temperature of these samples were calculated by using. The images are shown below


F1.Isoprene-Control(TA)


F2.Isoprene+ Cr.Shavings(TB)


F3.EPDM+ Cr.Shavings(TC)


F4.Isoprene+ EPDM+Cr.Sha.(TD)

7. CHARACTERISATION

7.1. Physical testing

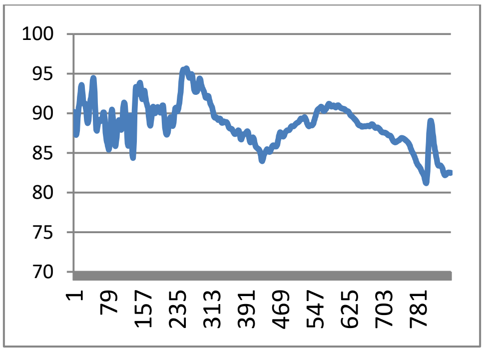
Required test specimens were punched out from the prepared soling material using die. Mechanical properties such as tensile strength, percentage of elongation at break, abrasion resistance, sole flexing endurance and hardness were measured in CLRI laboratory. The results are shown in the below Table. Each reported value is an average of three samples

S.No	Composite	Tensile strength (kg/cm2)	Percentage of Elongation (%)	Flexing endurance (mm^3)	Density (gm/cc)	Abrasion Resistance (flexes)	Hardness (Shore A)
1	Isoprene(Control)-(TA)	50	125	295	1.1608	150000	45
2	Isoprene+Cr.Shavings-(TB)	45	121	297	1.1607	150000	75
3	EPDM+Cr.Shavings-(TC)	36.30	106.60	294	1.1016	78000	85
4	Isoprene+EPDM+Cr.Shv.-(TD)	32.50	56.60	344	1.1836	150000	80

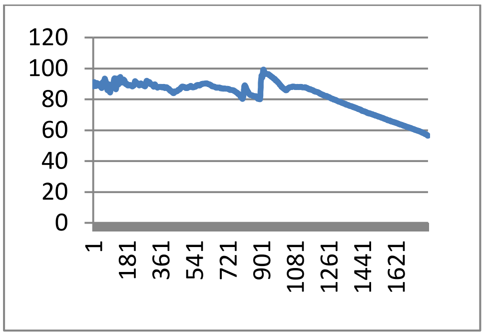
Table 1

7.2. IR-Spectroscopy

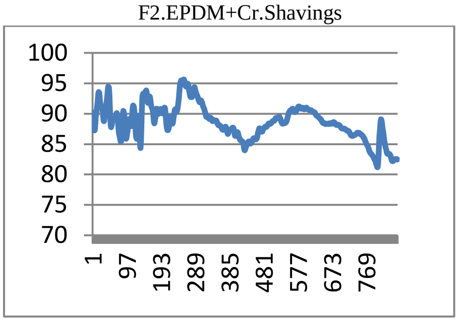
KBR pellets (500mg) each containing 2-6mg of the sample, were prepared for IR spectroscopy. The IR spectra of the sample were then taken using a Nicolet impact 400 FTIR spectroscope. The results are shown in the below Figure



F1.Isoprene+Cr.Shavings



F2.EPDM+Cr.Shavings

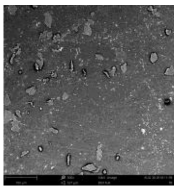


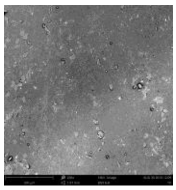
F3.Isoprene+EPDM+Cr.Sha.

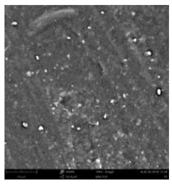
7.3. Scanning Electron Microscopy (SEM)

The SEM Micrographs (500X) of the fractured surfaces of the tensile tested specimens were taken using S150 stereo scan model. In order to provide visual data, to support the physico mechanical behaviour of the four polymeric compositions tensile fractured surfaces of the specimens Isoprene /Cr. Shaving; EPDM/Cr. Shaving; Isoprene/EPDM/Cr. Shaving; were subjected to SEM Micrograph study.

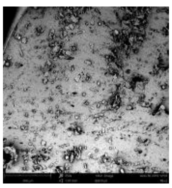
Surface Morphology

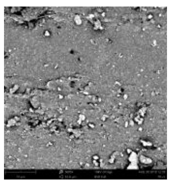

F1.Isoprene+ Cr.Shavings

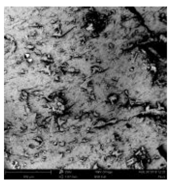

F2.EPDM+ Cr.Shavings


F3.Isoprene+EPD M +Cr.Sha.

Cross sectional Morphology







F1.Isoprene+ Cr.Shavings	F2.EPDM+ Cr.Shavings	F3.Isoprene+EPDM +Cr.Sha.

8.RESULTS AND DISCUSSION

8.1. Mechanical properties

8.1.1 Effect of composition and Tensile strength & Elongation at break

It is clear that good compatibility between Isoprene and Cr. Shaving dust, there is a gradual increase in Tensile strength and Elongation at break. Which obtain a peak at NR/Cr. Shaving and Isoprene/EPDM/Cr.Shaving composition. Then there is a gradual decrease in these properties in EPDM/Cr. Shaving composition. It shows that NBR/Cr. Shaving being a good Tensile strength, Elongation at break, Flexibility, Lower density.

8.1.2 Effect of composition on Density

From the Table It is clear that there is a gradual increase in density from 1.162 to 1.186 which shows that effective composites of Isoprene and EPDM with Cr. Shaving enables weight improving of the composites.

8.1.3 Effect of composition on Flexural Endurance

Table show that Isoprene/Cr.Shaving &Isoprene/EPDM/Cr.Shaving enables good flexural endurance beyond 150000 flexes.

8.1.4 Effect of composition on Abrasion Resistance

Abrasion resistance is reasonably good for all three composites.

8.2. IR Spectroscopy

The infrared spectra of the samples TB, TC&TD are shown in the above figures. All the samples show the amide absorption band around 1680 cm^{-1}.Asorbtion band at 1025 cm^{-1},1120 cm^{-1} and 1130 cm^{-1} represent OH group in the samples. The spectra show multiple bands between 3250 cm^{-1} to 2530 cm^{-1}.Thus the IR spectra reveal the presence of leather fiber in the composite.

8.3. Scanning Electron Microscopy

The SEM images of the sample are shown in the above figure. While individual SEM image of sample TB and sample TC shows individual fibres of chrome shavings without much aggregation. The SEM image of sample TD shows aggregation of fiber due to blending of Isoprene and EPDM with chrome shavings. The SEM image reveals that in all three samples chrome shavings are intermingled with polymers and also can see that in all the three samples chrome shavings are closely knitted.

9.CONCLUSION

9.1. Isoprene / Cr. Shaving

Due to good mutual compatibility between Isoprene and leather fiber the composites are well in terms of all the physic-mechanical behaviours like flexural endurance, elongation at break, hardness, density and tensile strength. The abrasion resistance which is good in the case of Isoprene/Cr. Shaving composition.

9.2. EPDM / Cr. Shaving

Due to good mutual compatibility between EPDM and leather fiber the composites are moderate in terms of all the physic-mechanical behaviours like flexural endurance, elongation at break, hardness, density and tensile strength.

9.3. Isoprene /EPDM / S. Cr. Shaving

Due to good mutual compatibility between Isoprene/EPDM/ leather fiber the composites are well in terms of all the physic-mechanical behaviours like flexural endurance, elongation at break, hardness, density, tensile strength and the abrasion resistance also good in this composition.

The mechanical Properties of the soling materials are given in the table 1.It can be seen from Table 1 that soling materials prepared using Isoprene/EPDM / Chrome shavings exhibits moderate tensile strength and percentage of elongation. All other samples exhibits comparable results.Therefore,it may be concluded that taking all other parameters consideration, the sole made using Isoprene and EPDM is almost meet out control properties.

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