Sustainable Value Creation from Leather Solid Wastes: Preparation of Shoe Soling Material using Nano Fillers

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Abstract. This research aims at recycling of the leather industry solid waste, chrome shaving, into shoe components, such as outsole and insole material. Chrome shaving waste from the leather industry was used for making shoe soles by mixing with rubber and inorganic nanoparticles. Isoprene and Ethylene propylene monomer (EPDM) rubbers were used for this purpose. Various combinations of rubber, nanoparticle and chrome shaving waste were studied to get the desired characteristics of soling material. The prepared shoe soles were characterized for physico-mechanical behaviours like hardness, density, abrasion resistance and tensile strength, and compared with those of the rubber-based soling material available commercially. The shoe sole prepared using a combination of the isoprene and EPDM (1:1) rubber along with chrome shaving waste and kaolinite/silica nanoparticles showed physico-mechanical characteristics very close to the commercial soling material with higher value of percentage elongation. Hence, an efficient use of the fibrous chrome shaving and trimming wastes from leather industry in sole making would avoid the environmental problem, and could be a source of sustainable value-creation.

1 Introduction

Leather processing contains discharge of enormous amounts of liquid and solid wastes. Though there has been noticeable progress in recycling and in-plant controls of liquid effluent, methods or practices to manage solid waste in sustainable way still put the leather manufacturers in decision making dilemma. Wastes generated from the various unit operations are namely, desalting salts, raw trimmings, hairs, fleshing waste, shaving and buffing waste & finished leather trimmings. An easy choice to dispose solid wastes like chrome shavings and trimmings is land filling, which is subjected to strict environmental protocols due to the presence of chromium in these solid wastes. In India, more than 2.4 crores pieces of cattle hides, 2.2 crores of buffalo hides, 10.6 crores of goat skins and 3.7 crores of sheep skins are processed in about 1600 tanneries of leather industry. This generates around 0.2 million tons of solid wastes annually (CLRI, 2015). Chrome shavings are considered as a hazardous waste owing to the chrome present in it, also there is a certain risk that chromium may be washed off and it may contaminate the ground water if dumped carelessly. Hence, the safe disposal/application of chrome shavings should be addressed.

Considerable efforts have been made to recycle the chromium containing wastes by using recycling methods such as incineration, pyrolysis and alkaline or enzyme hydrolysis; these methods, however, are seldom complete without adding onto the environmental problems. Unfortunately, in such recycling processes, the inherent fibrous structure of these materials gets totally destroyed. Presently, chrome shavings are utilized as several low value applications such as –

- Preparation of regenerated leather using natural and synthetic blend polymer [1].
- Composite board made from chrome shavings and various binders [2].

- Using chrome shaving as a filler of Butadiene-acrylonitrile rubber [3].
- Production of parchment like materials [4].
- Value added composite from leather and non-leather fibers [5].
- Chemical sand [6].
- Bio Gas Production [7].

However, most of these applications have not been commercialized. Conventional leather boards have also been made that are used as insoles and packing materials etc.

Applications based on the fibrous nature of the shavings and trimmings are presently limited, but various possibilities are being explored even today. An efficient way of using these fibrous waste materials may be to combine them in a suitable form with synthetic polymers to give composite materials. Short fiber reinforcement of polymers is an important area in polymer composites, where both synthetic and natural fibers are effectively used.

The present communication describes the making of rubber soles using chrome shaving waste as the filler. Besides, three inorganic nanomaterials were also used as filler along with the chrome shaving waste. The influence of chrome shaving waste and inorganic nanomaterials on the physico-mechanical properties of the soles were studied and compared with those properties of a commercial rubber sole.

2 Materials and Methods

2.1 Materials

Isoprene rubber, EPDM rubber were used for preparation of soling materials, Zinc oxide and Stearic Acid as an activator & Pilcure CBS, Pilcure MBTS & Pilcure TMT as an accelerator and other chemicals like sulphur used is laboratory grade. Bentonite (BNT), Kaolinite (KLN) and silica (SI) nanoparticle were procured form Sigma Aldrich. Chrome shaving waste was collected from the leather industry.

2.2 Pre-treatment of the Chrome shavings

Normally chrome shavings are acidic in nature. To remove the acidity, the chrome shaving wastes collected from the leather industry were treated with aqueous ammonia, 1% solution of urea and sodium bicarbonate followed by washing with water and drying under sunlight for 24 hours. The dried chrome shaving fibers were turned into fine particles by using strap cutting machine and stored for further use.

2.3 Preparation of soles

Rubber soles of six different compositions were made using isoprene and/or EPDM rubber along with the treated chrome shaving as filler. The detail compositions are presented in Table 1 and Table 2. Table 1 presents the three different compositions of rubber soles, TA, TB and TC. Table 2 presents the sole compositions similar that of TC but the $CaCO_3$ has been replaced with bentonite (BNT) / kaolinite (KLN) / silica (SI) nanoparticles.

Table 1. Trial with Isoprene & EPDM Rubber and chrome shavings

Composition of the different Trials			Role of the material	Quantity (Phr)
Trial-A (TA)	Trial-B (TB)	Trial-C (TC)		
Isoprene rubber	EPDM Rubber	Isoprene + EPDM rubber	Base polymer	100
Chrome shaving	Chrome shaving	Chrome shaving	Solid waste / filler	50
Zinc oxide	Zinc oxide	Zinc oxide	Activator	10
Stearic acid	Stearic acid	Stearic acid	Activator	4
CBS	CBS	CBS	Accelerator	1
MBTS	MBTS	MBTS	Accelerator	1
TMT	TMT	TMT	Accelerator	0.5
Sulphur	Sulphur	Sulphur	Vulcanising Agent	5
$CaCO_3$	$CaCO_3$	$CaCO_3$	Filler	50

Table 2. Trial with Isoprene & EPDM Rubber and chrome shavings

Composition of the different Trials			Role of the material	Quantity (Phr)
TC-BNT	**TC-KLN**	**TC-SI**		
Isoprene rubber	Isoprene rubber	Isoprene rubber	Base polymer	50
EPDM Rubber	EPDM Rubber	EPDM Rubber	Base polymer	50
Chrome shaving	Chrome shaving	Chrome shaving	Solid waste / filler	50
Zinc oxide	Zinc oxide	Zinc oxide	Activator	10
Stearic acid	Stearic acid	Stearic acid	Activator	4
CBS	CBS	CBS	Accelerator	1
MBTS	MBTS	MBTS	Accelerator	1
TMT	TMT	TMT	Accelerator	0.5
Sulphur	Sulphur	Sulphur	Vulcanising Agent	5
BNT	**KLN**	**SI**	**Nano-Filler**	**10**

To prepare the sole samples, accurately weighed quantities of the ingredients were fed to a two roll rubber mixing mill (with roller dimension D=220mm and L = 450 mm) maintained at a temperature of 47-67 °C and rolling at a speed of 15 rpm. Rubber soles of 6–8 mm thickness were made and stored at room temperature.

The above experiments were carried out in the curing temperature around 140–160 ºC and curing time around 5 to 12 minutes in the compression moulding machine. Corresponding female and male mould halves were used in this process. A pre-weighed charge cut were placed inside the mould. To facilitate polymerization (or cross-linking) and consolidation of composite material an appropriate pressure force were maintained. During this compounding process proper nip cap and cuts were maintained in order to get the uniform compounding.

Soles of different compositions, TA, TB, TC, TC-BNT, TC-KLN and TC-SI were made following the above mentioned procedure.

2.3 Characterization techniques

The morphology of the prepared sole materials was characterized using scanning electron microscopy (SEM make: Phenom world, model: phenom Pro). Physico-mechanical properties of the sole materials were studied using Universal Test Machine (INSTRON, model: 3369/J7257), Bata Flexing Resistance (SATRA, Model: STM 612) and Leather Sole Abrasion Tester (SATRA, Model: STM 140).

3 Results and Discussions

3.1 Scanning Electron Microscopic (SEM) Study

The SEM Micrographs of the fractured surfaces of the tensile tested specimens of TA, TB and TC are presented in figure 1. Figure 1 also shows the SEM images of cross-sectional surfaces of the nano-filler incorporated soles, TC-BNT, TC-KLN and TC-SI.

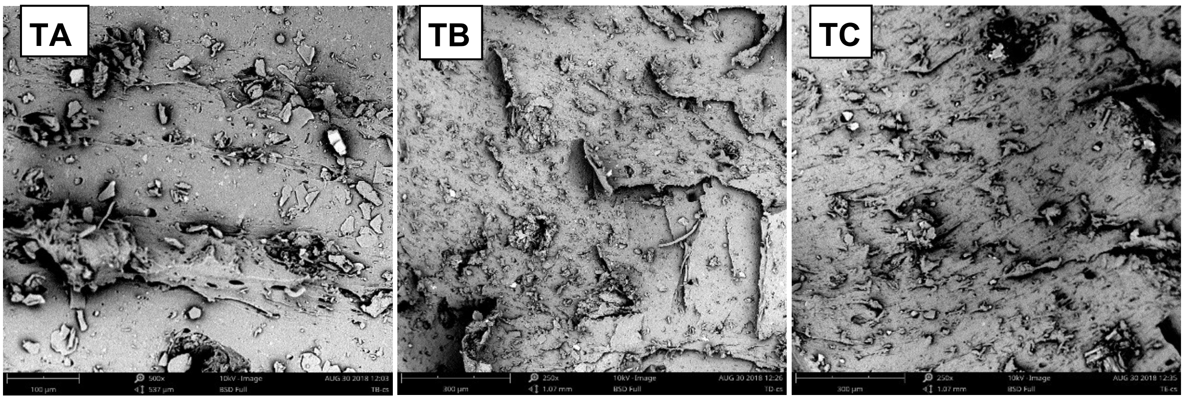

Figure 1. SEM images of the fractured surfaces of TA, TB, TC, and cross sectional view of TC-BNT, TC-KLN and TC-SI sole samples.

The SEM images of the experiment I and experiment II are shown in the above Fig. 5 to 8. The SEM images of sample TA, TB and TC show aggregation of fibre 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 be seen that in all the six samples chrome shavings are closely knitted.

3.2 Physico-mechanical properties

The prepared soling materials were subjected to physic-mechanical testing to study the properties like, abrasion resistance, tensile strength, percentage of elongation at break, hardness, density and flexing endurance. The values obtained for these properties were compared with those properties of the control sole sample. The control sole sample is a commercial rubber sole obtained from AGGU Soles Pvt Ltd, Ranipet, Tamilnadu, India. The physico-mechanical properties of the control sole material are tabulated below:

Table 3. Values of physico-mechanical parameters of the control sole sample.

S.No	Mechanical Properties	Values
1.	Tensile strength	8.0 MPa
2.	Percentage of Elongation	300 %
3.	Flexing endurance	150000 flexes
4.	Density	1.25 gm/cc
5.	Abrasion Resistance	150 mm^3
6.	Hardness	70 (Shore A)
7.	Thickness	0.8 mm

The physico-mechanical characteristics of the rubber soles made using isoprene and/or EPDM rubber along with chrome shaving waste (as per the composition listed in table 1) are presented in table 4. The same characteristics of the rubber soles made using mixture of isoprene and EPDM rubber along with chrome shaving waste and inorganic nanomaterials as filler (as per the compositions in table 2) are presented in table 5.

Table 4. Values of physico-mechanical parameters of the rubber sole samples prepared using chrome shaving waste as filler.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	8.0	300	150000	1.25	150	70
TA	4.5	121	150000	1.161	297.98	73
TB	3.6	46.60	78000	1.102	293.97	70
TC	3.2	106.60	150000	1.184	335.25	84

The values presented in table 4 show that the properties like, sole flexing (except TB), density, and hardness, of the sole samples prepared by using chrome shaving waste as filler (TA, TB and TC) are comparable with those of the control sole sample. The abrasion resistance values of these soles are much higher than that of the control sample. However, the values of tensile strength are lower (almost half) than that of the control sample.

Based on the physico-mechanical properties of the sole samples TA, TB and TC, the sole composition of TC was selected for further study by incorporation of inorganic nanoparticles as filler in place of $CaCO_3$.

Table 5. Values of Physico-mechanical parameters of the rubber sole samples prepared using chrome shaving waste along with inorganic nanomaterials as filler.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	8.0	300	150000	1.25	150	80
TC-BNT	5.6	450	150000	0.989	127	82
TC-KLN	11.1	350	150000	0.979	144	85
TC-SI	7.5	450	150000	0.984	145	83

The values of physic-mechanical characteristics presented in table 5 clearly show that incorporation of nanoparticle along with the chrome shaving waste improves all the sole characteristics (except density). The marginal decrease in density of the soles might be due to the replacement of $CaCO_3$. All the sole samples with nanoparticle showed either similar or higher tensile strength than that of the control sole. Among the three inorganic nanoparticles, kaolinite and silica showed excellent soling characteristics when compared with the control sole sample.

The physic-mechanical characteristics exhibited by the prepared sole samples from rubber and chrome shaving waste proves good mutual compatibility. Hence, the composition of TC-KLN and TC-SI can be considered for further development.

4. Practical Implications

Comparison between conventional and proposed method of leather solid waste management indicates that negative externalities caused by incineration, pyrolysis and alkaline or enzyme hydrolysis and land filling could be eliminated with the use of fibrous content of solid waste in shoe sole manufacturing.

5. Conclusion

Sole samples were successfully made using the chrome shaving waste with rubber and with/ without inorganic nanoparticles. The SEM images showed that the chrome shaving waste showed good compatibility with both isoprene and EPDM rubber. The sole samples without the nanoparticles showed good physico-mechanical characteristics except the tensile strength. However, incorporation of kaolinite and silica nanoparticle along with the chrome shaving waste improved the tensile strength of the sole samples. Therefore, the isoprene + EPDM + chrome shaving + inorganic nanoparticles composite can be considered for further development, which in turn could be a sustainable way of making use of the hazardous solid waste generated by the leather industry. Hence, it may be concluded that efficient use of the fibrous nature of chrome shavings and trimmings would avoid the environmental problem, and could be a source of sustainable value-creation from these solid wastes.

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