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PREPARATION OF LOW COST SHOE SOLING MATERIAL FROM LEATHER WASTE

S.Ponsubbiah[1]&Dr.Sanjeev Gupta[2]
[1] *Institute of Leather Technology &* [2]*CSIR-CLRI*

Abstract: Sole is the bottom component of footwear and it protects our feet from heat and other sharp objects. The roles of polymers are very important in the production of footwear. Abrasion résistance, sole flexing, hardness, Tensile strength, density & Thermal stability are the important properties required for soling materials. Some common soling materials used in footwear making are

1. Leather (sole leather)
2. Rubber (NBR, SBR, Isoprene, Microcellular rubber& crepe rubber)
3. PVC (Poly vinyl chloride)
4. TPR (Thermoplastic rubber)
5. PU (Poly urethane)

In our research in the previous study soling materials were prepared using chrome shaving (tannery solid waste), EPDM, isoprene rubber with three different types of commercial nano fillers namely SI, KLN, BNT .Out of these three trial soling material made using KLN (clay based) nano fillers exhibits good Physical and Mechanical properties. In this study the soling materials were prepared using EPDM, isoprene rubber, KLN nano filler with different proposition(50 Phr to 100 Phr) of pre treated chrome shaving (tannery solid waste). This research fully focus on reduce the solid waste generated by leather industry by utilising them as a low cost shoe soling material.

1. INTRODUCTION

Leather processing involves discharge of enormous quantities of liquid and solid wastes. While efficient recycling methods and in-plant controls have considerably reduced the discharge of obnoxious liquid streams, satisfactory methods to the solid waste management still elude the leather manufacturers. Land-filling is an easy option for the disposal of solid wastes like chrome shavings and trimmings, but is subjected to stringent environmental regulations because of the presence of chromium in these materials. Considerable efforts have been made to recycle the chrome containing wastes by methods such as incineration, pyrolysis and alkaline or enzyme hydrolysis. These recycling processes, however, are seldom complete without further environmental problems. Unfortunately, in such recycling processes the inherent fibrous structure of these materials gets completely destroyed.

Applications based on the fibrous nature of the shavings and trimmings are presently limited but various possibilities are being explored continuously. An efficient way of utilization of these fibrous waste materials may be to combine them in a suitable form with synthetic polymers to give composite materials. Short fiber reinforcement of polymersis an important area in polymer composites where both synthetic and natural fibers are effectively used. Such applications based on the fibrous nature of the chrome shavings and trimmings would circumvent the environmental problem as well as evolve value added products based on these waste materials.

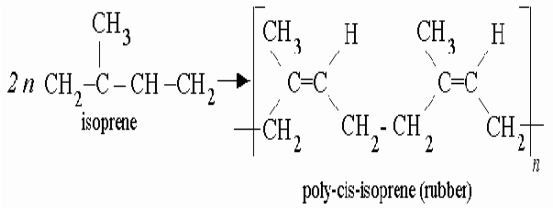
1.1. Materials

The following materials were used for development of shoe soling material from Leather waste (Chrome shaving).

Name of the material	Role of the material
Isoprene rubber	Base polymer
Chrome shaving	Solid waste/filler
Zinc oxide	Activator
Stearic acid	Activator
CBS	Accelerator
MBTS	Accelerator
TMT	Accelerator
SULPHUR	Vulcanising Agent
KLN	Nano filler

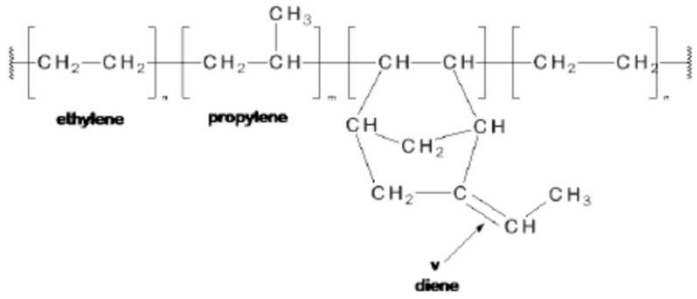
1.1.1. Isoprene Rubber

Isoprene (C_5H_8) is a widely-used polar rubber and economical commercial rubber. We can harvest isoprene from rubber trees (NR) as latex and also we can produce it synthetically by polymerization. Natural rubber comes under the category of non-synthetic rubber. In the beginning of the 20th century it has been commercialised. The structure of isoprene is mentioned below



1.1.2. EPDM Rubber (Ethylene Propylene Diene Monomers)

EPDM is also a synthetic polar rubber with high density and able to withstand high temperatures up to 130°C. As such, we can used for things such as window and door seals or waterproofing sheets.It has good scrape, cut growth and tear resistance. The structure of EPDM rubber is shown below



1.1.3. Chrome shavings

Chrome shavings are derived when the wet blue leathers are subjected in shaving operation in order to reduce thickness desirable thickness Chrome shavings are tiny, thin and fibre protein material This is harmful waste category and across the country about 35% of the total tannery waste are generated during leather processing as trimmings and chrome shavings. Every year about 20000 tones of chrome shavings are generated in india. Chrome shavings alone constitute to an extent of 10% of the total weight of raw Hides/Skins.

1.1.4. KLN Nano fillers

Fillers are the materials that are added to a polymer formulation to lower the compound cost or to improve properties. They can be in the form of solid, liquid or gas. Suitable selection of these materials can improve not only the economics but also the other properties such as processing and mechanical behaviour. The fillers also require a balance of formulation for optimum processing properties. In this research clay based nano filler are used and also it is commercially available (manufactured by alpha chemist India Ltd) in the market.

2. PRETREATMENT OF CHROME SHAVINGS

The shavings were collected from Viralli Enterprises, Chennai-44 and it was subjected to pre-treatment. Normally chrome tanned leathers are acidic in nature and in order to neutralisation it was treated with 2 % of Ammonia Solution and 2% of Alkaline salt (Sodium bi carbonate).After the pre treatment the shavings were dried in sun light for 48 hours and then it was passed in the strap cutting machine to reduce the length.

3. CHARACTERIZATION OF CHROME SHAVINGS

The pre-treated chrome shavings were tested for various characterisations as mentioned below.

Tests	Values
PH in water Extract (wt %)	4.15 ± 0.20
Chrome Oxide (wt %)	3.41 ± 0.10
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. Two roll mill(roller dimension D=220mm and Length L = 450 mm)
B. Strap cutting machine(for chrome shaving fibre length reduction)
C. Compression moulding machine

5. EXPERIMENTS

The homogeneous rubber mixes were prepared by using a two roll mill. The following parameters were considered at the time of compounding process

1. Temperature of the rolls 303–312K.
2. Roll speed Vo = 16 rpm.
3. Pressure 160 kg/cm^2
4. Height of the die 8 mm

Then it was stored at temperature 275–312 K.

5.1. Control

Commercially available vulcanised rubber materials are used as a control in this research. (manufactured by Shalimar soles Pvt Ltd.)

5.2. Trial 1- (T1) -Control

The following compounding materials were used in this trial

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	50 Phr
Zinc oxide	10 Phr
Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

5.3. Trial 2- (T2)

The following compounding materials were used in this experiment

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	60 Phr
Zinc oxide	10 Phr

Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

5.4. Trial 3- (T3)

The following compounding materials were used in this experiment

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	70 Phr
Zinc oxide	10 Phr
Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

5.5. Trial 4- (T4)

The following compounding materials were used in this experiment

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	80 Phr
Zinc oxide	10 Phr
Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

5.6. Trial 5- (T5)

The following compounding materials were used in this experiment

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	90 Phr
Zinc oxide	10 Phr
Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

5.7. Trial 6- (T6)

The following compounding materials were used in this experiment

Name of the material	Quantity
Isoprene rubber	50 Phr
EPDM Rubber	50 Phr
Chrome shaving	100 Phr
Zinc oxide	10 Phr
Stearic acid	4 Phr
CBS	1 Phr
MBTS	1 Phr
TMT	0.5 Phr
SULPHUR	5 Phr
Nano Filler KLN	10 Phr

During this compounding process in order to get the uniform compounding proper nip cap and cuts were maintained

6. CURING

Pre – heated mould which maintained at 140°C - 160ºC for 5 to 12 minutes to get cured sample by compression moulding machine. Matching male and female mould halves were used in this process. A pre-weighed charge cut to the size is placed inside the mould.. 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 and noted.

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 Table.

S.No	Composite	strength Tensile	on Percentage of	durance Flexing	(gm/cc) Density	stance Abrasion	ore A) Hardness
1	Control	8.0	300	150000	1.25	150	80
2	Isoprene+EPDM+ Cr.Shavings(50 Phr) +KLN(T1)	11.1	350	150000	0.9795	144	85
3	Isoprene+EPDM+ Cr.Shavings(60 Phr) +KLN	9.2	320	150000	0.9825	140	82
4	Isoprene+EPDM+ Cr.Shavings(70 Phr) +KLN	8.5	300	150000	0.9922	135	80
5	Isoprene+EPDM+ Cr.Shavings(80 Phr)+ KLN	7.2	250	75000	1.115	120	65
6	Isoprene+EPDM+ Cr.Shavings(90 Phr)+ KLN	6.8	200	45000	1.0682	90	62
7	Isoprene+EPDM+ Cr.Shavings(100 Phr)+KLN	5.8	150	30000	1.0704	80	60

Table 1

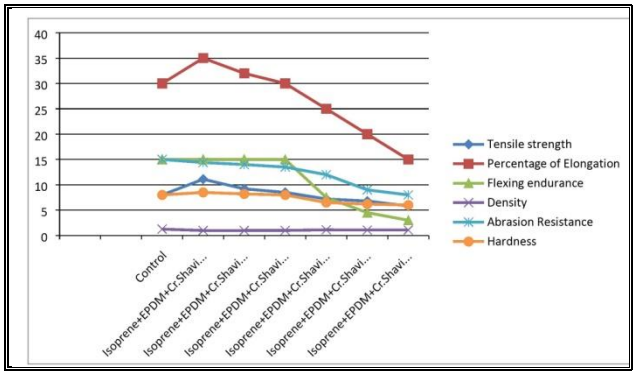


Chart 1

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 following condition were followed and the results are shown in the below Figures

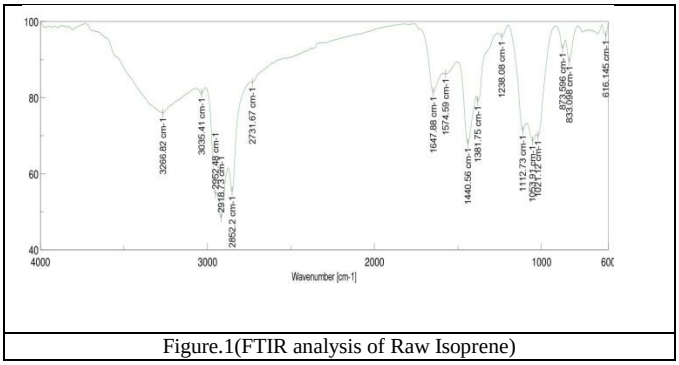


Figure.1(FTIR analysis of Raw Isoprene)

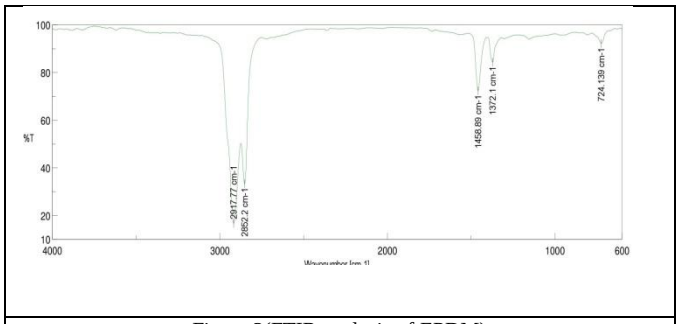


Figure.2(FTIR analysis of EPDM)

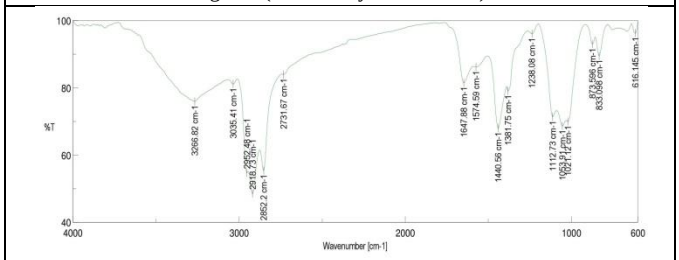


Figure.3(FTIR analysis of KLN nano filler)

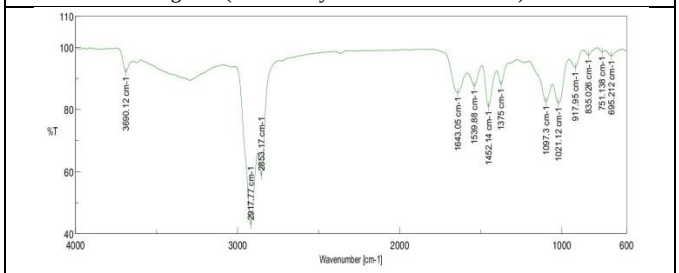


Figure4 (FTIR analysis of Isoprene +EPDM+KLN +90 Phr of Cr. Shav.)

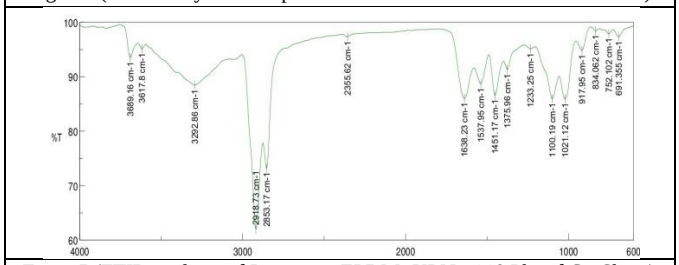


Figure5 (FTIR analysis of Isoprene +EPDM+KLN +110 Phr of Cr. Shav.)

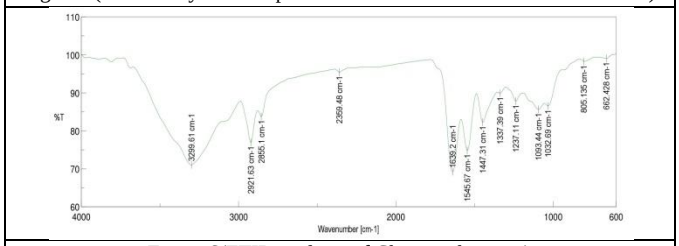
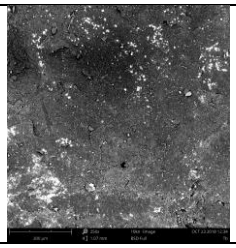
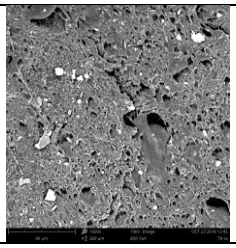
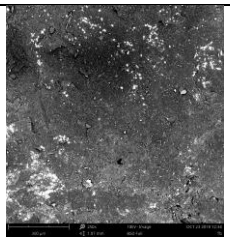
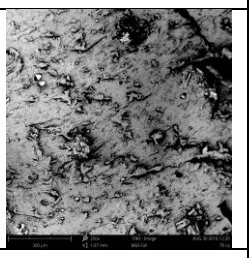
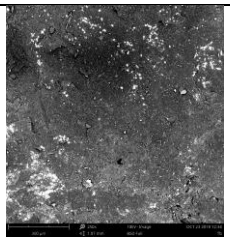
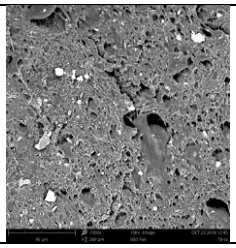
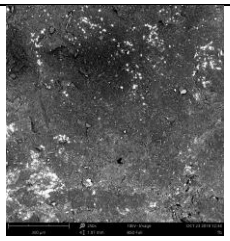
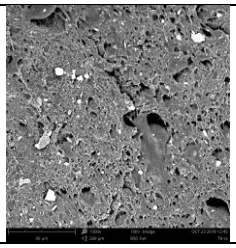
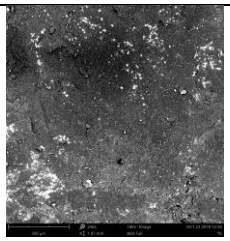
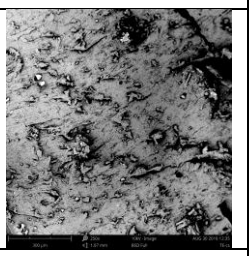
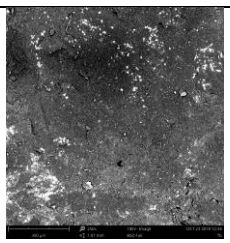
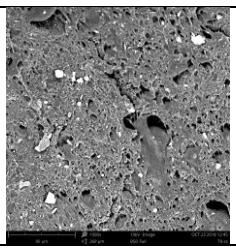


Figure.6(FTIR analysis of Chrome shavings)

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	Cross Section
	
T1	T1
	
T2	T2
	
T3	T3
	
T4	T4
	
T5	T5
	
T6	T6

8. RESULTS AND DISCUSSION

8.1. Mechanical Properties

In our trials it is clear that good compatibility between Isoprene, EPDM, Chrome shavings and KLN nano filler, while adding different proportion of chrome shaving (70Phr to 100 Phr) there is a gradual decrease in mechanical properties such as tensile strength, Elongation to break and flexing endurance . But any have it is almost meet the control parameters while adding chrome shavings up to 70 Phr. The density and abrasion resistance of all composite is reasonably good.

8.2. IR Spectroscopy

The infrared spectra of the samples are shown in the above figures. Fig4 & Fig5 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 T1,T2&T3 shows individual fibres of chrome shavings without much aggregation. The SEM image of sample T5 and T6 shows aggregation of fiber due to blending of Isoprene and EPDM with 100Phr of 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

It is very clear that the properties such as Tensile strength , Elongation at break , hardness, Sole flexing & Abrasion Resistance of the trial are gradually decreased as compare to commercial control sample when we mix more than 70 PHR of chrome shavings in the composite. The Trial containing 50PHR to 70PHR of chrome shavings in the composite have meets the control parameters. So it is evident that for optimum property we can mix chrome shavings up to 70 PHR in the composite

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