International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-9 Issue-2, December, 2019

Characterisation of Shoe Soling Material Prepared by using Rubber and Leather Solid Waste

S. Ponsubbiah, Sanjeev Gupta

Abstract: ***The ultimate aim of this research is to develop footwear soling materials from solid waste generated from leather industry. The Chrome shaving from the leather sector is used as a solid waste in this study. Styrene butadiene, Nitryl, Ethylene propylene monomer (EPDM) and Isoprene elastomers were used for this research. The rubber and chrome shavings mixes were prepared by using industrial two roll mill. Various propositions of rubbers, chrome shavings and nano fillers were characterised in this research. The developed soling materials were tested for physical testing like hardness, abrasion resistance, tensile strength, density and elongation at break and compared with compared with commercially available soling material. In this research four different experiments has been conducted among the four experiments the soling material prepared using a isoprene rubber-70 Phr and EPDM rubber - 30Phr with chrome shavings -50 Phr and KLN(Silica based) nano fillers- 7 Phr meets the required parameters of commercial soling material. Hence, it is concluded that chrome shaving wastes from tannery in soling material preparation is one of the best remedy for the environmental issues.***

; Key words

- ***Phr – Parts per hundred parts of rubber***
- ***EPDM-Ethylene propylene Diene Monomer***
- ***NBR-Nitryl Rubber***
- ***SBR-Styrene butadiene Rubber***
- ***SEM-Scanning Electron Microscope***

I. INTRODUCTION

Leather industry plays a vital role in Indian economy in terms of export earnings and employment. The solid and liquid waste generated in the various unit operations of leather processing is unavoidable. For sustainable development, leather industries need to reduce those wastes to meet all the vindicate standards. Certain solid wastes are generated because of the chemicals involved in leather processing. Raw trimmings, desalting salts, fleshing, hairs, Chrome shaving and snuffing /buffing dust & leather trimmings are the wastes generated from the various unit operations in leather processing. In India, according to the survey conducted by the Central leather research institute around 2.2 crore of buffalos, 2.4 crore of cattle's, 3.7 crore of sheeps and 10.6 crore of goats hides and skins are available live stock for leather processing in the various tanneries in India. Around 0.2 million tonnes of solid waste generated per year (CLRI, 2015) and Chrome shaving waste are consider to be a hazardous waste since chrome (VI) present in the shavings.

Revised Manuscript Received on December 30, 2019.

* Correspondence Author

S.Ponsubbiah, Lecturer, Institute of Leather Technology, Tharamani, Chennai (Tamil Nadu) India. 113. ponsubbiah@gmail.com

Dr.Sanjeev Gupta, Chief Scientist, CSIR- CLRI, Adyar,Chennai(Tamil Nadu) India.-20. sgupta1281@gmail.com

The safe disposal of chrome shavings to be addressed to avoid environmental issues. Currently, chrome solid wastes are utilized as–

- Composites made from chrome shavings and natural fibers using rubber solution (US Patent)(Parrini et. al. 1979)
- Preparation of leather like materials using synthetic and natural blend polymer (US Patent)(Parrini et.al. 1979)
- Value added composite from leather and no-leather fibers (US Patent) (Parrini et. al. 1979)
- Sustainable Landfill (Indian Patent No.125DEL 2006)
- Production of parchment like materials (Indian Patent No.300DEL 1999)

However, the above applications have not been commercialised on industry level. Other utilities do not find much use due to cost constrains and feasibility. The below figure 1 elaborated the research methodology of this research.

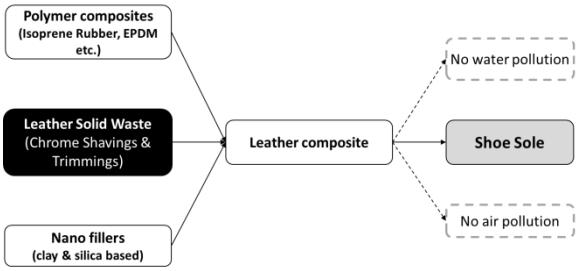


Figure 1. Methodology of this research

II. MATERIALS

In this trial to prepare of soling materials EPDM rubber, Nitryl rubber, Styrene butadiene rubber and Isoprene rubber were used. The activator used in this study is Zinc oxide and Stearic Acid & the accelerator used in this study is MBTS, CBS & TMT and sulphur and other chemicals used is laboratory grade. KLN, SI and BNT nano fillers were sourced from Sigma Aldrich Ltd. Chrome solid waste (shavings) were obtained from the local tannery in Chennai. Chromium and Nitrogen is the major constituent of chrome shaving. Normally chrome shavings are acidic in nature; this causes interruption during the vulcanisation process. In order to conquer the acidic nature, the shavings were treated with 1% solution of urea, aqueous ammonia and alkaline salts. Then chrome shavings were tested in CLRI laboratory for various characterisations. The tested chrome shaving fibres were dried in sun light for 24 hours and after, the particles size of the chrome shavings were reduced by strap cutting machine.

Table 1: Material used in this research

Name of Compounding material	Role of Compounding material	Sourcing
Isoprene rubbers	Elastomer	Riddhi Polymers, Chennai
Styrene Butadiene Rubber	Elastomer	Riddhi Polymers, Chennai
Nitryl Rubber	Elastomer	Riddhi Polymers, Chennai
EPDM	Elastomer	Riddhi Polymers, Chennai
Chrome shaving	Solid waste/filler	Viralli Enterprises,Chennai-44
Zinc oxide	Activator	Nocil Ltd,Mumbai
Stearic acid	Activator	Nocil Ltd,Mumbai
CBS	Accelerator	Nocil Ltd,Mumbai
MBTS	Accelerator	Nocil Ltd,Mumbai
TMT	Accelerator	Nocil Ltd,Mumbai
SULPHUR	Vulcanising Agent	Nocil Ltd,Mumbai
Calcium carbonate	Filler	Nocil Ltd,Mumbai
BNT,KLN & SI	Nano fillers	Sigma Aldrich,USA

2.1 Machinery used

The following equipment /machineries were used to conduct the experiments:

- Two roll mill (with roller dimension D=220mm and L = 450 mm)
- Compression moulding machine
- Strap cutting machine(for chrome shaving fibre length reduction)

III. PREPARATION OF FOOTWEAR COMPONENTS

To prepare rubber compounding mixes two roll mill were used. In two roll mill the roll speed were maintained at $\mathbf{V}_0$ = 15 rpm and temperature was maintained at 320–340K. The elastomers and other ingredient were passed into the two roll mill with a thickness of 6–8mm and then stored at 270–310 K. The commercially available soling materials were as control in this experiment. In order to develop footwear components four different experiments has been conducted using different elastomers and leather solid waste.

3.1 Experiment I

In this experiment seven different compositions of rubber mixes were prepared by using Isoprene, Styrene butadiene, Nitryl & EPDM rubbers along with pre treated chrome shaving and caco3 filler. The various composition of this experiments are shown in the below Table 2.

Table 2: Trial with Isoprene, Nitryl, Styrene butadiene and EPDM Rubbers

Trial 1(A1)	Trial 2(A2)	Trial 3(A3)	Trial 4(A4)	Trial 5(A5)	Trial 6(A6)	Trial 7(A7)	Qty (Phr)
Isoprene	SBR	NBR	EPDM	Isoprene + EPDM	SBR+ EPDM	NBR+ EPDM	100
Chrome shaving	Chrome shaving	Chrome shaving	Chrome shaving	Chrome shaving	Chrome shaving	Chrome shaving	50
Zinc oxide	Zinc oxide	Zinc oxide	Zinc oxide	Zinc oxide	Zinc oxide	Zinc oxide	10
Stearic acid	Stearic acid	Stearic acid	Stearic acid	Stearic acid	Stearic acid	Stearic acid	4
CBS	CBS	CBS	CBS	CBS	CBS	CBS	1
MBTS	MBTS	MBTS	MBTS	MBTS	MBTS	MBTS	1
TMT	TMT	TMT	TMT	TMT	TMT	TMT	0.5
Sulphur	Sulphur	Sulphur	Sulphur	Sulphur	Sulphur	Sulphur	5
$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	50

3.2 Experiment II

In this experiment four different compositions of rubber mixes were prepared by using different proposition of Isoprene, EPDM rubbers along with pre treated chrome shaving and caco3 filler. The various composition of this experiments are shown in the below Table 3.

Table 3: Trial with different proposition of Isoprene and EPDM Rubbers

Trial 1(B1)	Qty (Phr)	Trial 2(B2)	Qty(Phr)	Trial 3(B3)	Qty(Phr)	Trial 4(B4)	Qty(Phr)
Isoprene + EPDM	60/40	Isoprene+ EPDM	70/30	Isoprene + EPDM	80/20	NBR+ EPDM	90/10
Chrome shaving	50	Chrome shaving	50	Chrome shaving	50	Chrome shaving	50
Zinc oxide	10	Zinc oxide	10	Zinc oxide	10	Zinc oxide	10
Stearic acid	4	Stearic acid	4	Stearic acid	4	Stearic acid	4
CBS	1	CBS	1	CBS	1	CBS	1
MBTS	1	MBTS	1	MBTS	1	MBTS	1
TMT	0.5	TMT	0.5	TMT	0.5	TMT	0.5
Sulphur	5	Sulphur	5	Sulphur	5	Sulphur	5
$CaCO_3$	50	$CaCO_3$	50	$CaCO_3$	50	$CaCO_3$	50

3.3 Experiment III

In this experiment three different compositions of rubber mixes were prepared by using Isoprene-70 Phr, EPDM -30 Phr and pre treated chrome shaving-50 Phr along with three different types of nanoparticle. The various composition of this experiments are shown in the below Table 4.

Table 4: Trial with Isoprene and EPDM Rubber with different nanoparticle

Trial 1(C1)	Trial 2(C2)	Trial 3(C3)	Qty(Phr)
Isoprene+ EPDM	Isoprene+ EPDM	Isoprene+ EPDM	70/30
Chrome shaving	Chrome shaving	Chrome shaving	50
Zinc oxide	Zinc oxide	Zinc oxide	10
Stearic acid	Stearic acid	Stearic acid	4
CBS	CBS	CBS	1
MBTS	MBTS	MBTS	1
TMT	TMT	TMT	0.5
Sulphur	Sulphur	Sulphur	5
BNT	KLN	SI	5

3.4 Experiment IV

In this experiment six different compositions of rubber mixes were prepared by using Isoprene-70 Phr, EPDM -30 Phr and pre treated chrome shaving-50 Phr along with various quantity of KLN nanoparticle. The various composition of this experiments are shown in the below Table 5.

Table 5: Trial with Isoprene and EPDM Rubber with different quantity of KLN nanoparticle

Composition	Trial 1(D1)	Trial 2(D2)	Trial 3(D3)	Trial 4(D4)	Trial 5(D5)	Trial 6(D6)
Isoprene+ EPDM	70/30	70/30	70/30	70/30	70/30	70/30
Chrome shaving	50	50	50	50	50	50
Zinc oxide	10	10	10	10	10	10
Stearic acid	4	4	4	4	4	4
CBS	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
TMT	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	5	5	5	5	5	5
KLN	1	3	5	7	9	11

3.5 Curing

The various trails were carried out in this research and the following parameters were maintained in the curing process

Table 6: Curing Parameters

S.No	Parameters	Values
1.	Temperature	140^0C-160^0C
2.	Pressure	250 Kg/cm^2
3.	Time of curing	5-12 minutes

Appropriate male and female moulds were used in this study and pre-weighed rubber mixes were placed inside the mould.

3.6. Characterisation

The surface and cross-sectional morphology of shoe soling materials were studied by Scanning Electron Microscopy - SEM (model: Phenom Pro & make: Phenom world,). Physical properties of the developed shoe soling materials were studied using

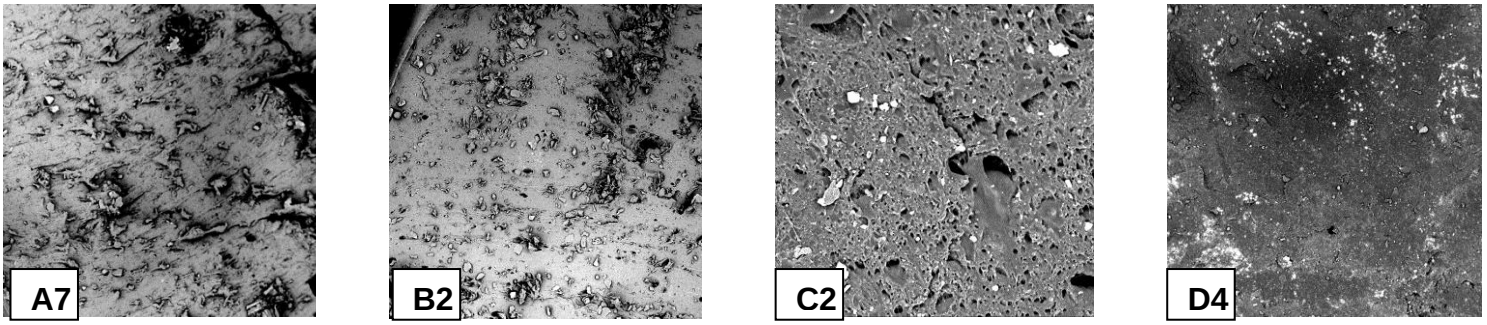
1. Universal Test Machine (model: 3369/J7257-INSTRON)
2. Bata Flexing Resistance (Model: STM 612-SATRA)
3. Leather Sole Abrasion Tester (Model: STM 140-SATRA)

IV. RESULTS AND DISCUSSIONS OF THIS STUDY

4.1 SEM-Scanning Electron Microscopic images of soling materials

The Scanning Electron Microscopy images of the tensile tested specimens of all the above four experiments were shown in the below figures

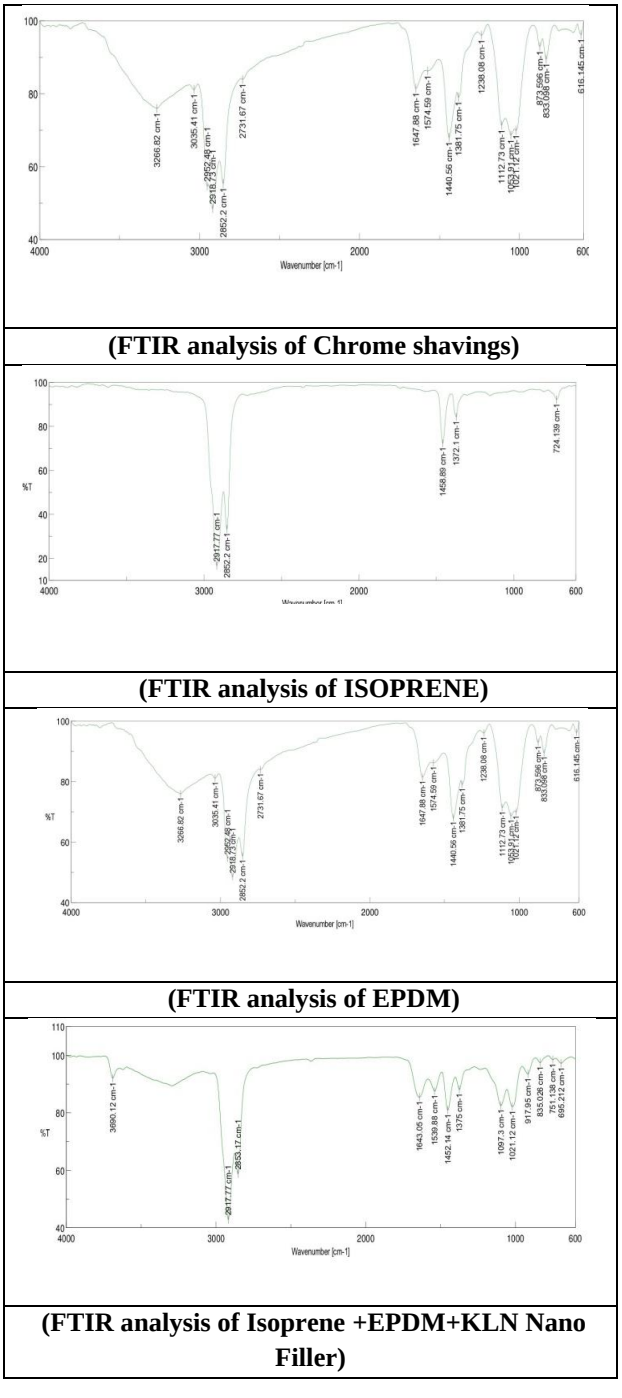
Figure 2: SEM images of the fractured surfaces of samplesA7, B2, C2 and D4.



The Scanning Electron Microscopy images of the trail I, II, III and Trail IV are shown in Fig. 2. The Scanning Electron Microscopy images of shoe soling samples A7, B2, C2 and D4 show aggregation of fibre due to blending of Isoprene and EPDM with chrome shavings. The SEM image reveals that in all four samples chrome shavings are intermingled with polymers and also can be seen that in all the six samples chrome shavings are closely knitted.

4.2 IR Spectroscopy

The IR images of the samples are shown in the below figure 3. The final sample demonstrates the absorption at 1045 cm^{-1}, 1150 cm^{-1} and 1170 cm^{-1}whichreveals that the more functional groups present in the sample. The IR spectrum shows multiple bands between 3450 cm^{-1} to 2630 cm^{-1} and this indicates the presence of leather fibres in the composite.



(FTIR analysis of Chrome shavings)

(FTIR analysis of ISOPRENE)

(FTIR analysis of EPDM)

(FTIR analysis of Isoprene +EPDM+KLN Nano Filler)

Figure 3: FTIR analysis of Isoprene and EPDM rubbers

4.3 Physical testing and their impacts

The prepared soling materials were subjected to the following physical testing

1. Abrasion resistance,
2. Tensile strength,
3. Percentage of elongation at break,
4. Hardness,
5. Density
6. Flexing endurance.

The test results of the soling materials were compared with standard value of the control. The commercial rubber soling material is used as a control in this study and it was purchased from sole unit in Ranipet. The physical properties of the control soling material are listed in the table 7:

Table 7: Values of physical properties of the control soling material

S.No	Physical properties	Test Values
1	Percentage of Elongation	220 %
2	Density	1.25 gm/cc
3	Tensile strength	6.0 MPa
4	Abrasion Resistance	162 mm^3
5	Thickness	8 mm
6	Hardness	65 (Shore A)
7	Flexing endurance	52000 flexes

The physical properties of the soling material prepared by Nitryl rubber, Styrene butadiene rubber, isoprene rubber and EPDM rubber with chrome waste are tabulated in the table 8. The soling material prepared by using different proposition of EPDM rubber and isoprene rubber with chrome waste are tabulated in the table 9. The soling material prepared by mixture of isoprene and EPDM rubber along with chrome waste and nano fillers are tabulated in the table 10. The soling materials prepared by isoprene and EPDM rubber with chrome shaving waste and different quantity of nano fillers are presented in table 11.

Table 8: Physical properties of soling materials prepared by different elatomers and chrome waste.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	6.0	220	52000	1.25	162	65
A1	3.90	320	25200	1.161	135.98	69
A2	2.87	420	24560	1.142	129.45	68

A3	4.23	375	27459	1.171	142.62	68
A4	4.05	175.60	20520	1.102	162.97	75
A5	3.80	186.60	26541	1.174	285.25	70
A6	4.05	198.60	24520	1.169	305.25	71
A7	4.50	185.60	28200	1.184	335.25	70

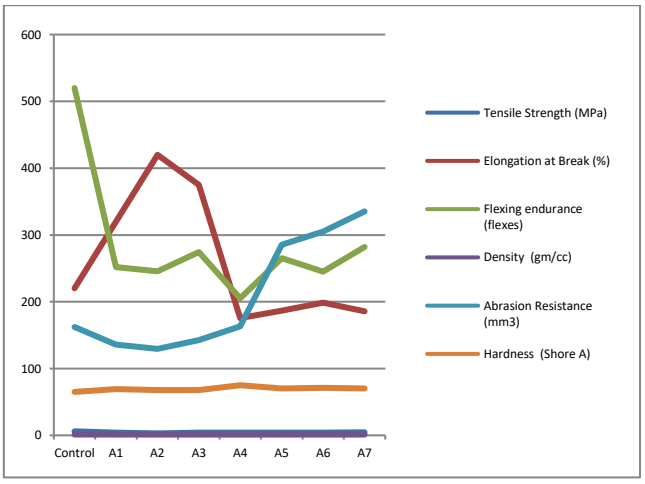


Figure 4: Line diagram of experiment I

The physical properties of soling materials were (by different elastomer and chrome waste) tabulated in table 6 .In this experiment eight different trails were conducted namely A1, A2, A3, A4, A5, A6 and A7.When we adding the EPDM rubber in the mixes the abrasion resistance values are enormously increased than the control sample. However, the tensile strength value and sole flexing values are slightly lesser than the control sample. Based on physical properties value obtained for the various trails A1, A2, A3, A4, A5, A6 and A7, it is concluded that the composition of trail A7 consider for further study.

Table 9: Physical properties of soling materials prepared using chrome shaving waste and different proposition of Isoprene and EPDM Rubber.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	6.0	220	52000	1.25	162	65
B1	4.50	185.60	28200	1.184	355.25	70
B2	4.55	190.25	29525	1.1187	332.4	69
B3	4.62	205.12	30250	1.1443	321.42	68
B4	4.05	200.50	30520	1.1058	292.50	64

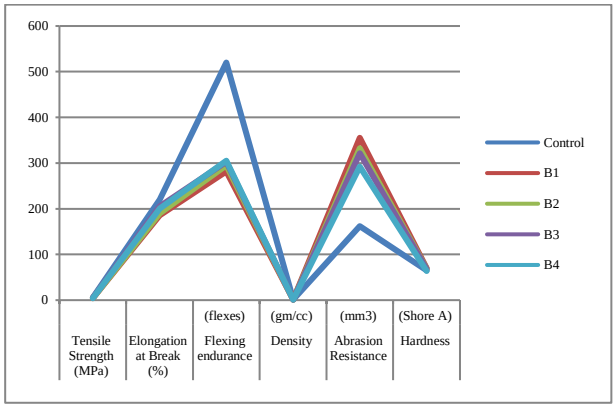


Figure 5: Line diagram of experiment II

The physical testing values of soling materials prepared using chrome shaving waste and different proposition of Isoprene and EPDM Rubber are tabulated in table 7.It is very clear that the marginal increase in tensile and sole flexing while increasing the quantity of Isoprene rubber in the chemical composition. Based on the physical testing value of the sole samples B1, B2, B3 and B4, the trail B2 (Isoprene-70 Phr and EPDM 30 Phr) is very near to the control value. it is concluded that the composition of trail B2 is consider for further study.

Table 10: Physical properties of soling materials prepared using chrome shaving waste and Isoprene and EPDM Rubber with different types of nano fillers.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	6.0	220	52000	1.25	162	65
C1	5.05	185.50	38520	1.1058	292.50	64
C2	5.8	189.20	40500	0.979	284.20	69
C3	5.5	190.40	39635	0.984	285.89	71

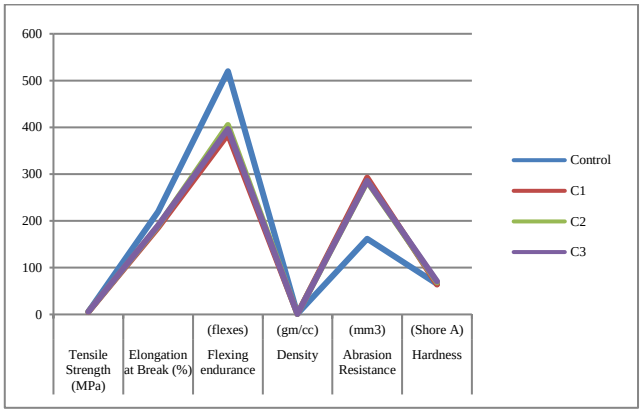


Figure 6: Line diagram of experiment III

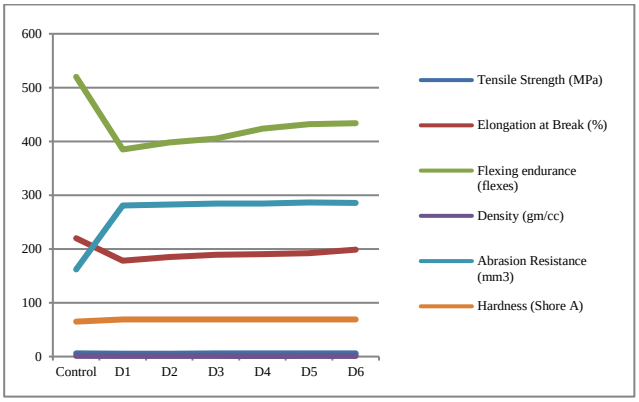


Figure 7: Line diagram of experiment IV

The physical testing values of soling materials prepared using chrome shaving waste and Isoprene and EPDM Rubber with different types of nano fillers (SI,KLN &BNT) tabulated in table 8 .It is clear that the marginal decrease of density of soling material due to the replacement of $CaCO_3$ nano fillers. All the trails with nano fillers showed similar or higher tensile strength than the control soling material. Among the three inorganic nano fillers, KLN nano filler and SI nano filler exhibits good physical properties when compare to control soling materials. The physical properties show the good mutual compactability between rubbers and chrome shaving. Hence, the trail C2 (KLN nano filler) can be consider for further development of soling material.

Table: 11 Physical properties of soling materials prepared using chrome shaving waste and Isoprene and EPDM Rubber with different quantity of KLN nano fillers.

Sole Sample	Tensile Strength (MPa)	Elongation at Break (%)	Flexing endurance (flexes)	Density (gm/cc)	Abrasion Resistance (mm^3)	Hardness (Shore A)
Control	6.0	220	52000	1.25	162	65
D1	5.4	178.20	38500	0.998	281.14	69
D2	5.6	185.28	39800	0.989	282.35	69
D3	5.8	189.20	40500	0.979	284.20	69
D4	5.9	190.52	42360	0.972	284.41	69
D5	5.9	192.34	43200	0.975	286.45	69
D6	5.9	198.56	43383	0.975	285.63	69

Physical properties of soling materials prepared using chrome shaving waste and Isoprene and EPDM Rubber with different quantity of KLN nano fillers are tabulated in table 9 .It is clear that the sole samples with 7-11 Phr of nanoparticle (D4, D5 and D6) showed higher physical properties than that of the control sole. Due to cost constrain the soling material made up of 7 Phr of KLN nano filler can be consider for further development.

V. CONCLUSION

Footwear components were effectively prepared by the rubbers, chrome shaving and inorganic nano fillers. The Scanning Electron Microscopy images showed that the chrome shavings are good compatibility with EPDM rubber and isoprene rubber. The soling material with commercial filler $CaCO_3$ shows good physical properties except the sole flexing and tensile strength. The replacement of KLN nano fillers by $CaCO_3$ in this study improved the tensile strength and sole flexing properties of the soling material. Therefore, the isoprene-70 Phr, EPDM-30 Phr, Chrome shaving -50 Phr and inorganic nanoparticles-7 Phr sample can considered for further development and this will be the effective way to utilize solid waste generated by the leather industries and avoid the environmental issues.

REFERENCES

1. Report of the meeting of the IULTCS Tannery wastes commission (1981).Waalwijk, Holland 9-11 May.
2. Srinivasan T S., M Anendrakumal: Krishnan T S and K.J Scaria(1985)"Chrome Shavings-a tannery waste, current practice and future trends for its utilization "Presented in the 3rd AAP Animal Science Congress,Seoul,Korea.
3. Okamura H &Shirai K, Chrome shavings and its products, J Am Leather ChemAssoc, **71** (1976) 173-179.
4. Cot J &Gratacos E, Chrome shavings treatments, AQEIC Bol.Tech, **26** (1975) 353-376.
5. Suseela K, Parvathi M S &Nandy S C, Chromium containing leather wastes, Leder, **34 (**1983) 82-87.
6. DhanasekaranPrakash and **Sellamuthu N. Jaisankar***, Thermoplastic poly(urethane-thiourethane) triblock copolymers with SWCNTs composite,Diam. Relat. Mater.93, 34-41, **2019**.
7. **Sellamuthu N. Jaisankar**, Donna J. Nelson and Christopher Brammer, Preparation and properties of thermoplastic nanocomposites based on polyurethane ionomers, Proc. of 53rd Pentasectional Meeting of the American Chemical Society, 14, **2008**.

8. Seena Joseph, Tushar S. Ambone, Abhijit V. Salvekar, **S. N. Jaisankar**, P. Saravanan E. Deenadayalan, Processing and characterization of waste leather based polycaprolactonebiocomposites, Polym. Composite (DOI: 10.1002/pc.23891) (In Press **2015**).
9. Rajeswari,N. Malarvizhi, E. Deenadayalan and **Sellamuthu N Jaisankar*** Influences of functionalized nanoclays on morphology and mechanical properties of polyvinyl alcohol based composites by twin-screw extruder, Polym. Plast. Technol. Eng.56, 883-888, 2017
10. Anoop V, SubramaniSankaraiah, **S. N. Jaisankar**, SohiniChakraborty& Mary N.L, Enhanced mechanical, thermal and adhesion properties of polysilsesquioxane spheres reinforced epoxy nanocomposite adhesive, J. Adhes., **2019**, DOI: 10.1080/00218464.2019.162010

AUTHORS PROFILE

S.Ponsubbiah, ponsubbiah@gmail.com
Working as a lecturer in Institute of Leather Technology, Tharamani, Chennai-113.I am the bachelor in Leather Technology and masters in Footwear technology. I have completed my B.Tech and M.Tech in Anna University, Chennai.I have more than 12 years of Teaching experience in the same institution and four years industrial experience. At present I am doing my Ph.D under the supervision of Dr.Sanjeev Gupta in CSIR-CLRI,Adyar,Chennai-20.I have published six research papers relevant to this research.

Dr.Sanjeev Gupta, Chief Scientist,CSIR-CLRI,Adyar,Chennai-20. sgupta1281@gmail.com
He is the eminent scientist in the area of Leather technology and he has published more than 80-research paper.The educational and the research experiences are listed below

Academic /Research Experience/Employment :

Sl.No	From	To	Name	Position Held
1	01.01.2012	Till date	CSIR-Central Leather Research Institute, Chennai, Tamil Nadu	Chief Scientist
2	01.01.2006	31.12.2012	CSIR-Central Leather Research Institute, Chennai, Tamil Nadu	Senior Principal Scientist Gr. IV(5)
3	01.01.2001	31.12.2005	CSIR-Central Leather Research Institute, Chennai, Tamil Nadu	Principal Scientist Gr. IV(4)
4	05.08.1996	31.12.2000	CSIR-Central Leather Research Institute, Chennai, Tamil Nadu	Senior Scientist Gr. IV(3)
5	05.08.1991	04.08.1996	CSIR-Central Leather Research Institute, Chennai, Tamil Nadu	Scientist Gr. IV(2)
6	1987	1991	Harcourt Butler Technological Institute, (H.B.T.I.) Kanpur, Uttar Pradesh	Lecturer
7	1986	1987	Harcourt Butler Technological Institute, (H.B.T.I.) Kanpur, Uttar Pradesh	Senior Research Fellow
8	1985	1986	J. K. Synthetics, Kota, Rajasthan	Chemical Engineer