Composite Materials for Shoe Soles

A thesis submitted towards partial fulfilment of BS-MS Dual Degree Programme

By

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Certificate

This is to certify that this dissertation entitled "**Composite Materials for Shoe Soles**" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research Pune represents original research carried out by **Siddharth Chopra** at **Footwear Design and Development Institute (FDDI), Noida**, under my supervision during the academic year 2013-2014.

Place: Noida

Date: 28th March, 2014

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Declaration

I hereby declare that the matter embodied entitled “**Composite Materials for Shoe Soles**“ are the results of the investigations carried out by me at “**Footwear Design and Development Institute (FDDI)** “, under the supervision of “**Mr. V. B. Parvatikar**“ and the same has not been submitted elsewhere for any other degree.

Date:

Place: Signature

Acknowledgement

I would like to take this opportunity to express my gratitude towards Mr. V. B. Parvatikar for agreeing to supervise and guide me on this project. It would not have been possible if not for his invaluable insights into the footwear industry, growing trends of the materials used and also involving the right people all throughout. The greatest motivation was that even after being so busy, he was always approachable for the minutest thing and made sure I had what I needed. I am highly grateful to Dr. A. K. Mathur for all his guidance on polymer processing and their properties relevant to footwear industry. The project would not have turned out the way it did if not for his continuous assessment of the progress. I would also like to mention Mr. Faisal Mohammad for training me how to carry out the various tests on which the whole project is based.

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Abstract

The worldwide trend towards using inexpensive, nontoxic and durable materials from renewable resources or industrial wastes, which contributes to ecological and sustainable development has already caught mainstream attention. Use of rice straw, wood fibre, vegetal fibres, rice husk, groundnut husk, wheat straw etc. as filling material is on the rise. This study explores the potential use of a few of such industrial and agricultural wastes as a filling material in the conventional shoe sole polymers, with ease of adoption being a priority.

Based on the feasibility of research study, thermoplastic rubber was chosen as the polymer matrix, and the synthesis of thermoplastic rubber granules as the stage of experimentation. Leather dust, rice husk and wheat straw/husk were used in bulk and powder forms and in various percentage loadings to synthesize different composites. Testing of various mechanical properties (hardness, tensile strength, abrasion etc.) was carried out for these composites and compared to that with $CaCO_3$ as the filler. Addition of any filler resulted in an increase in specific gravity, hardness and abrasion and decrease in tensile strength and elongation at break. 15% loading is above the saturation limit of the polymer matrix and 10% is a more optimum loading. Powder forms gave better results than the bulk forms. Rice husk and wheat straw/husk give better resulting properties than $CaCO_3$ filled composite, and offer a cost advantage over the original compound with no filler loading. This may contribute to an easier and quicker shift towards sustainability in the near future.

Chapter 1
INTRODUCTION: Shoe Soles

The choice of material for the shoe sole varies according to the application required as well as on the geography and country of use around the world, for example, most of the countries have different regulations and compliance requirements regarding materials and the extent to which they can be used in the products intended for sale inside their boundaries. This chapter gives a basic idea of shoe sole materials. Section 1.1 points out the ideal qualities of shoe soles. Section 1.2 briefly describes a few of the most commonly used polymeric materials in shoe soles. Section 1.3 gives an idea about the shift towards sustainability and ecological manufacturing.

1.1 Ideal Qualities of Shoe Soles

- Adequate durability
- Good flexing properties
- Light weight
- Non-slip
- Uniformity
- Waterproof
- Comfortable
- Environmental stability
- Colour stability and colourability
- Good adhesion ability to the upper materials

1.2 Common Polymeric materials used in footwear industry

A few of the most commonly used materials in manufacturing of the shoe soles are as following

1.2.1 Polyvinyl Chloride (PVC)[1]

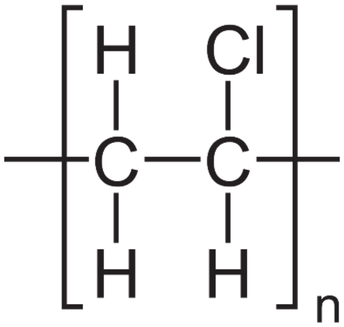


Figure 1: Structure of Polyvinyl Chloride

Polyvinyl Chloride (PVC) is a versatile thermoplastic with an extensive range of applications in virtually all areas of human activity. These varied applications require processing and conditioning of the PVC with various materials like plasticisers, of which phthalates are the most common. Due to its carcinogenic nature, it is in the direction of being phased out, but due to its very low cost, it is still the most widely used material for making shoe soles.

Processing

The components are first weighed out and then the following sequence of operation is followed

- Cold premixing
- Hot mixing
- Milling
- Extrusion
- Pelletizing
- Injection moulding of the compound

Advantages

- It has the lowest unit cost of all man made soling currently available.
- It is very versatile as it can be blended with a wide range of plasticizers and other polymeric materials.
- The wear resistance is satisfactory provided the compound is not too hard.
- Smooth surfaces are easy to obtain.
- It has flame retardant properties.

Disadvantages

- PVC produces toxic corrosive fumes of hydrogen chloride when it is hot.
- Slip resistance of PVC sole can be poor especially in wet conditions.
- PVC hardens as the temperature falls.
- Its oil and solvent resistance is poor.
- When excess of plasticizer is used, sole adhesion problem can arise.
- It has relatively higher density.

1.2.2 Rubber[2]

Rubber occurs in both natural and synthetic forms. Raw rubber is mixed with a variety of compounding ingredients to modify its characteristics. Rubber in its various forms account for a major portion of the specialized shoe sole market.

General properties of rubber are as follows:

- It combines high strength with outstanding resistance to fatigue.
- It has excellent tack, which means that it has the ability to stick to itself and to other materials.
- It is moderately resistant to environmental damage.
- It has high resistance to cutting, chipping and tearing.

The various types of rubbers used in sole manufacturing are:

- Natural Rubber
- SBR – Styrene Butadiene Rubber
- CR – Chloroprene Rubber
- NBR – Nitrile Rubber

Processing

The production of rubber soles involves two basic operations – compounding and curing.

- Mastication – In other words, it means polymer breakdown. It is necessary for compounds containing a blend of polymers to provide a uniform mixture prior to further compounding.
- Master-batching – It means incorporation of the other compounding ingredients into the rubber, except the curing system.
- Remilling – In case of inadequate dispersion, it is required to prepare it for the next step.
- Finish Mixing – This step incorporates the curing system.
- Extruding - It is used in both compounding operations and to form articles for vulcanization.
- Calendaring – In case of sheet formation.
- Vulcanization – It may be accomplished by a number of methods, depending on the compound in process, and the size, shape and overall structure of the finished article. Sulphur is the most commonly used curing agent.

1.2.3 Thermoplastic Rubber (TPR)[2,3]

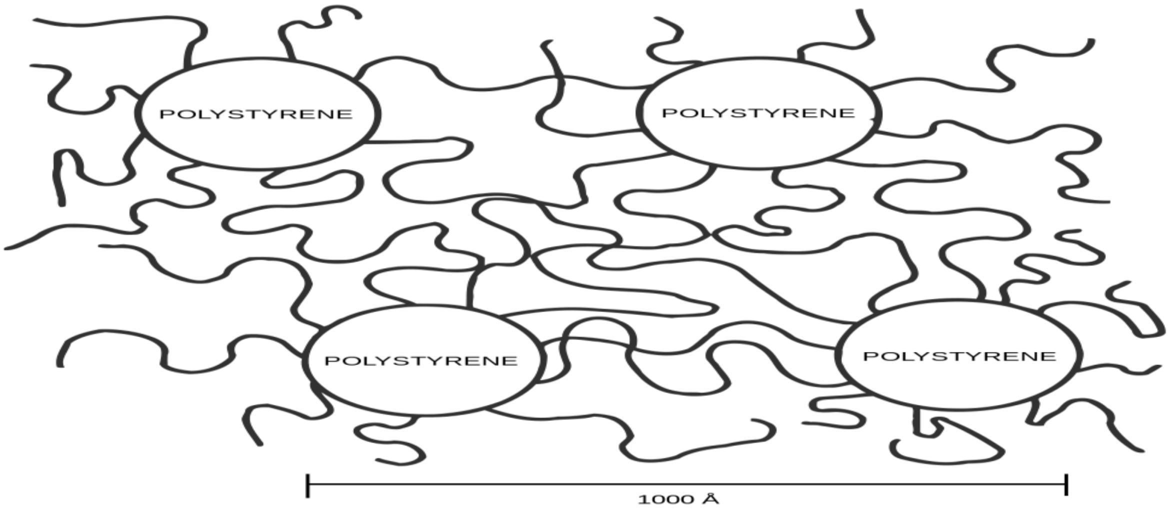


Figure 2: Schematic diagram of SBS thermoplastic rubber

Thermoplastic rubbers based on styrene-butadiene-styrene block copolymers offer rubbery appearance and simplicity of thermoplastics processing. The polybutadiene part imparts rubber properties whereas the polystyrene generates the cross-linking function. At higher temperatures, polystyrene loses its cross-linking and this is what makes it thermoplastic. A versatile hardness range can be processed by its compounding.

The following ingredients are added to TPR for use as a sole:

- Plasticizer softens the rubber and improves the melt flow properties.
- Polystyrene resins harden the rubber and raise modulus.
- Fillers are added to cheapen and harden the product.
- Stabilizers reduce breakdown due to heat and light.
- Pigments impart the required colour.

Processing

The components are first weighed out and then the following sequence of operation is followed

- Cold premixing
- Hot mixing
- Milling
- Extrusion
- Pelletizing
- Injection moulding of the compound

Advantages

- Thermoplastic Rubber is a low density compound.
- Thermoplastic Rubber generally has a good resistance to flex cracking which improves as the temperature is reduced.
- Thermoplastic Rubber has a very good slip resistance, but decreases with increasing hardness.
- It has a low processing cost and faster production.
- It has a high resilience.

Disadvantages

- The cost of the compounds is higher.

- It has poor wear resistance.
- It is poorly resistant to oils and solvents.
- Smooth moulded surfaces are difficult to obtain.
- Adhesion was a serious handicap of Thermoplastic Rubbers, which is improved by a halogenation process which needs to be carried out with utmost care in the bonding process.

1.2.4 Polyurethane (PU)[4]

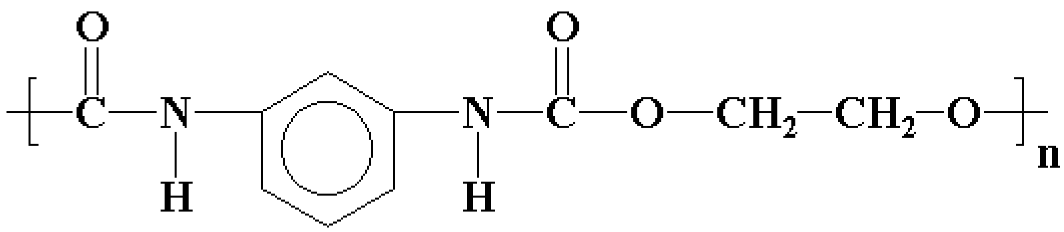


Figure 3: An example of polyurethane

Polyurethanes (PU) are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate in the presence of suitable catalysts and additives. Because a variety of diisocyanates and a wide range of polyols can be used to produce polyurethane, a broad spectrum of materials can be produced to meet specific applications. In footwear industry polyurethanes (PU) are used as cushioning foams, synthetic upper materials, adhesives and soles.

Processing

Reaction Injection Moulding systems are composed of two liquid components (isocyanate and polyol) that chemically react in a mould to form a plastic material. The polyol component contains additives, such as stabilizers, flow modifiers, catalysis, blowing agents, and pigments to modify final characteristics of the final product.

When the two liquids combine, the isocyanate reacts with the hydroxyl in the polyol to form a thermosetting polyurethane PU polymer. Cooling lines help dissipate heat from this exothermic reaction.

Advantages

- Low thermal conductivity
- Low water absorption
- Excellent adhesion to a range of materials
- Thermal stability from -160 °C to 120°C
- Flow properties suitable to fill any shape of cavity
- Good flame retardant performance
- Reinforceable with inserts
- Easily coloured integrally
- Very high mechanical strength
- Minimal demoulding time
- Surface finish can be easily improved to increase the aesthetic value

Disadvantages

- PU soling is expensive.
- There are considerable health hazards associated with RIM process.
- Polyether PU has poor oil resistance
- Heat and fire resistance is not very good
- RIM process needs very careful control for good results.

1.2.5 Choice of Polymer Matrix

A feasibility of research study was carried out for these materials. Various industrial units were visited to understand the manufacturing process of soles from these raw materials, each material having a different manufacturing process. Based on this field research, TPR (thermoplastic rubber) was the polymer material of choice as manufacturing process is easier and involves injection moulding of the molten raw material which comes in the form of granules. Also the manufacturing of the TPR (thermoplastic rubber) granules was finalised as the stage of experimentation, with the help and use of concerned industrial unit (Floyd Polyplast) as the lab for processing the experiment samples.

1.3 Sustainable and Ecological Manufacturing

The consumers and governments around the world are becoming increasingly concerned about the amount of waste that we generate, most of which eventually ends up in landfills. With the new found enthusiasm about reusing and recycling, various industries and labs around the world are exploring the options of reabsorbing the waste back into the industry. Footwear industry is no exception. Leading the charge is Nike which takes back the used shoes and shreds them to be used as turf for athletics and tennis. The other industries are doing their bit by using industrial and agricultural wastes as fillers for several of their products, as a cost reduction more than the ecological point of view, nevertheless it does take out a little bit of load from our mother nature. In shoe soles, various inexpensive, nontoxic and durable materials from renewable resources or agricultural[5] and industrial wastes are fast replacing conventional fillers such as $CaCO_3$. Use of wheat straw, wood fibre, vegetal fibres such as sisal fibre[6], rice husk, rice husk powder[7,8], groundnut husk[9] etc. as filling material is on the rise. Use of leather dust[10] and sole dust, which is abundant and is a waste product from the footwear industry itself, has also been reported, specifically as a measure to reduce the ecological burden.

In our research we started out with the most readily available footwear industry waste, i.e. leather dust of leather board and the leather sole. We proceeded to most readily available agricultural waste in India i.e. rice husk and wheat straw. Composites of various compositions were synthesized and tested on various industry parameter (tensile, tear, melt flow rate etc.) according to international standard testing methods.

The study was designed keeping in mind the currently used manufacturing processes so as to incorporate the results of this study (if any fruitful) into the process with no or minimum additional processing requirements by the shoe sole manufacturers, giving them ecological and sustainable credibility and cost benefits.

MATERIALS AND METHODS

2.1 Fillers and their Processing

Leather dust of leather board buffing and leather sole buffing were obtained from a local industrial unit and was used directly as a filler, without any further processing.

Figure 4: Photographs of leather buffing dust (a) from leather board, (b) from an intermediate step of leather sole manufacturing process, (c) from the final step of leather sole manufacturing process

Rice husk was obtained from a local mill and was sundried for a day before it was ground using a hand-held grinding machine, after two attempts to do the same with a mechanised unit failed. Rice husk is reported to contain 34-44% of cellulose, 23-30% of lignin, 13-39% of ash and 8-15% of moisture.[11,12]

Figure 5: Photographs of rice husk (a) powder, (b) bulk

Wheat straw was sourced from a local stockist of cattle feed, and was sundried for a day before it was ground using a hand held grinding machine.

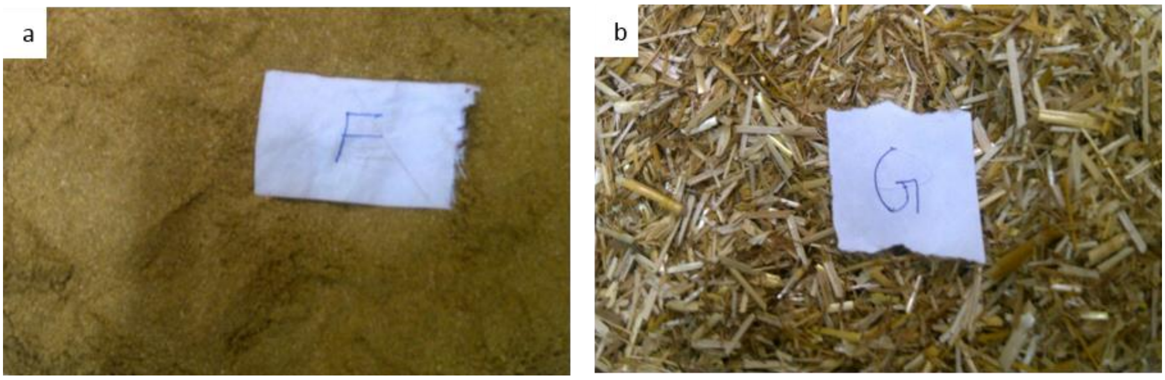


Figure6: Photographs of wheat straw/husk (a) powder, (b) bulk

The greatest task of the project was to find a grinder for our filler materials, first in the assessment being rice husk. After a month and a half of convincing from industrial level grinding units paying no heed, obviously their concerns being genuine, to local mechanised agricultural grinders agreeing to help us, with their machines getting stuck and their production being suffered, hope was not lost. Going back to old school methods was our lucky guess. But deciding to try a hand held rotating grinder, finding it was an even bigger challenge as the whole industry has been mechanised. In the end, we had our Eureka moment.

2.2 Formulation and Compounding

Table 1 shows the percentage and the source of various ingredients used in preparing the composite samples. The percentage of various fillers were varied to study the effect of filler loading on properties.

Table 1: Formulations used in the synthesis of composite samples

Ingredient	Source	W %
SBS		49
LG 411 S (NOE)	LG Chem, Korea	12.7
KTR 201 (NOE)	Korea Kumho Petrochemicals	3.2
Globalprene 1487	LCY, Taiwan	20.7
Enprene 675	En Chuan, Taiwan	12.4

SBC		20.1
Denka NSBC 210	Denka, Japan	20.1
PS		5.2
HIPS 494F	BASF, India	3.6
GPPS 145D	BASF, India	1.6
Oil N32	Apar Industries LTD.	25.7
TOTAL		100
Chemicals		
Antioxidant - Songnox 11B	Songwon, Korea	0.1– 0.12
UV Stabilizer - Songsorb 1000	Songwon, Korea	0.05 – 0.06
Fillers		
$CaCO_3$ 2TOJ	OMYA PVT. LTD.	Vary
Leather Dust	Local Industry	Vary
Rice Husk	Local Mill	Vary
Rice Husk Grounded	Local Mill + Local Grinder	Vary
Wheat Straw	Local Stockist	Vary
Wheat Straw Grounded	Local Stockist + Local Grinder	Vary

Blending of the composites was carried out in an indigenous compounding machine supplied by Extrusion Machino Craft, Delhi. The setup consists of a dispersion kneader where hot mixing and milling takes places, and via a feeder is fed into a single screw extruder which extrudes the final compound and a die face cutter or pelletizer pelletizes the compound which are then air transported for collection in the bags. The temperature in the dispersion kneader reaches around 125^oC and it takes about 25 minutes for our formulation to be hot mixed in the kneader.

2.3 Testing Methods

The property, its test standard and the standard measuring unit are given in ***Table 2.***

Table 2: Testing standards

Property	Test Standard	Equipment/Machine	Company	Unit
Specific Gravity	ASTM D-792	Specific Gravity Balance	Presto	Dimensionless
Melt Flow Index/Rate	ASTM D-1238	Melt Flow Index Tester	Presto	Grams/10mins.
Hardness (Shore A)	ASTM D-2240	Hardness (Shore A) Tester	Kori Seiki	Dimensionless
Tensile Strength	ASTM D-412	Tensile Testing Machine - Zeus Ultimo	Presto	Kg/cm^2
Elongation At Break (%)	ASTM D-412	Tensile Testing Machine - Zeus Ultimo	Presto	Dimensionless
Tear Strength	ASTM D-624	Tensile Testing Machine - Zeus Ultimo	Presto	Kg/cm
Abrasion	DIN - 53516	Rotary Drum Abrasion Tester	Prolific	mm^3

2.3.1 Specific Gravity[13]

Specific gravity (relative density) is the ratio of the density of a substance to the density of a given reference material. Specific gravity usually means relative density with respect to water.

Figure 7: Specific gravity balance

Procedure:

- The specimen is cut from the moulded sheet, weight of specimen should be 2-3 grams.
- The weight of the specimen is measured in air (W1).
- After that the weight of the specimen is measured in water (W2).
- Then the specific gravity is calculated by using the following formula:

$$Specific\ Gravity = \left(\frac{W_1}{W_1 - W_2}\right)$$

2.3.2 Melt Flow Index[14]

The Melt flow index of thermoplastic materials is defined as the rate of flow (in grams per ten minutes) of extrudates of molten resins through a jet of a specific length and diameter. The test is carried out under prescribed condition of temperature, load and piston position in a cylindrical cavity inside a heated metallic tube barrel. The test specimen may be in any form that can be introduce into the bore of the cylinder. For example powder, granules, strips of films or moulded slugs.

Figure 8: Melt Flow Index Apparatus

Procedure:

- The temperature of the melt index cylinder is controlled at 190±0.5ºC or as required.
- The apparatus is cleaned. The parts are more easily cleaned while they are hot.
- Approximately 3–4 grams of the sample is charged into the cylinder and the piston and 5 kg load is placed in the position. Some of the resin is forced out manually during the pre-heat period (3-5 minutes) before start of rate measurement, which is necessary to achieve a void free extrudate and flow equilibrium.
- Cuts of the extrudate at uniform time intervals is taken during the specified extrusion time (10 minutes).
- The average value is expressed in (grams/10 minutes).

2.3.3 Hardness[15]

The Shore Hardness is defined as the resistance to penetration by an indenter of specified shape under a defined load. There are two scales:

- Shore A is used for measuring hardness of soft elastomers (10-90 Shore A).
- Shore D is used for measuring hardness of harder elastomers (>80 Shore A).

Procedure

- This test is done on a moulded sheet.
- Moulded sheet is conditioned at room temperature for 1-2 hours.
- Then the probe of the hardness tester is penetrated on the surface of moulded sheet by soft hand.
- The reading from the hardness scale (Durometer) is noted.

2.3.4 Tensile Strength and Elongation at Break[16]

Tensile strength is the amount of force required to rupture or break a specimen. Elongation at break is the percentage increase in original length of a specimen as a result of tensile force applied to the specimen, after breakage of the test specimen. Elongation is inversely proportional to hardness and tensile strength. That is, the greater a material's hardness, and tensile strength, the less it will elongate under stress. It takes more force to stretch a hard material having high tensile strength than to stretch a soft material with low tensile strength.

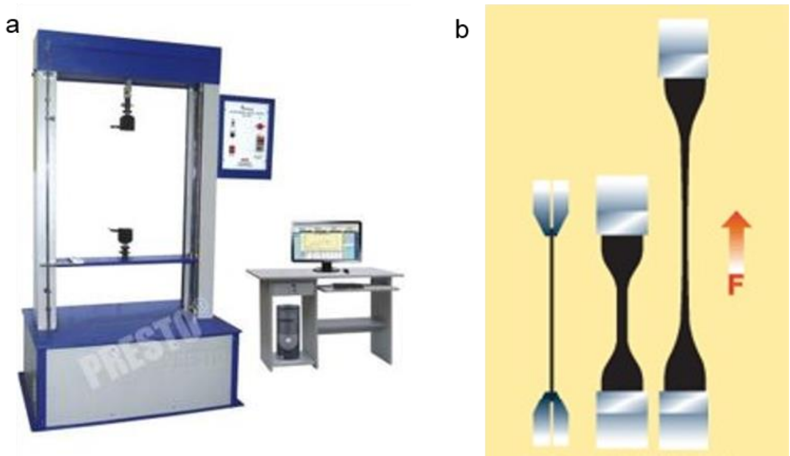


Figure 9: (a) Tensile testing machine, (b) Dumbbell shaped specimen

Procedure:

- Conditioning of the specimen is done by keeping it at room temperature for a period of 12-15 hours prior to testing.

- Dumbbell shape sample is punched from the moulded sheet with a standard punching die.
- The specimen is loaded into tensile grips.
- In the machine's software:
  - A new specimen is added by going into the specimen master window.
  - The graph scale is selected by graph setting option.
  - The required parameters are set for testing.
  - The necessary formula is selected as required in the formula selection.
  - The test starts by pressing play.
  - The test stops after the set test stop condition (breaking of the specimen) as stored is reached.
- Tensile strength is expressed in kg/cm^2.
- Elongation at break is expressed as %.

Formulae for tensile testing:

$$Tensile\ strength = \frac{FP}{T * W}$$

$$Elongation\ at\ break\ (\%) = \frac{(EB + L) - L}{L * 100}$$

FP = Maximum load supplied during test

T = Thickness of the sample

W = Width of the sample

EB = Elongation at breaking force

L = Length of the sample

2.3.5 Tear Strength[17]

Tear strength or tear resistance is resistance to the growth of a cut or nick in a specimen when tension is applied. Different specimen types are used to measure both *tear initiation* (resistance to the start of a tear, see ***Figure 10(a)***) and *tear propagation* (resistance to the spread of a tear, see ***Figure 10(b)***). The sample is placed in the tester's grips, which then exerts a uniform pulling force until the point of rupture. This force is then divided by the specimen's thickness to arrive at the tear resistance for that particular sample.

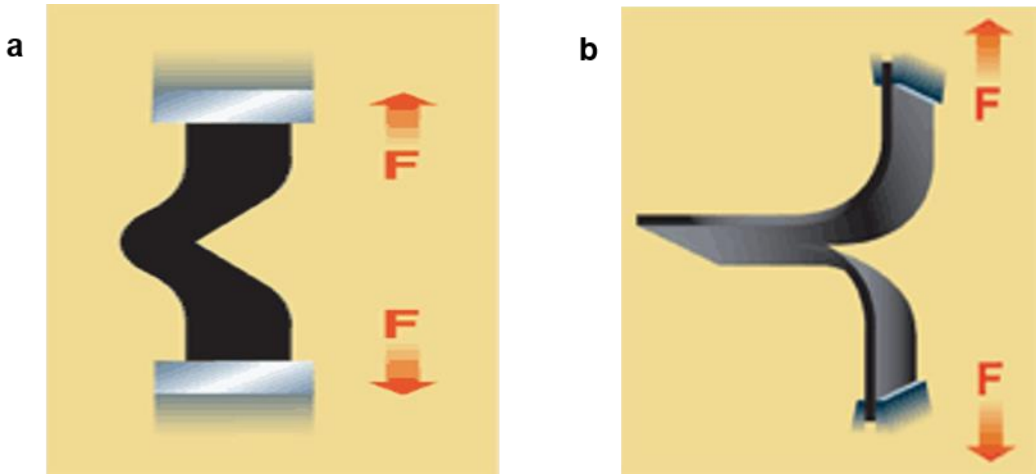


Figure 10: Tear strength testing specimens (a) Right angle for tear initiation, (b) Trouser for tear propagation

Procedure:

- Conditioning of the specimen is done by keeping it at room temperature for a period of 12-15 hours prior to testing.
- Right angle and trouser shape sample is punched from the moulded sheet with a standard punching die.
- The specimen is loaded into tensile grips.
- In the machine's software:
  - A new specimen is added by going into the specimen master window.
  - The graph scale is selected by graph setting option.
  - The required parameters are set for testing.

   - The necessary formulae are selected as required in the formula selection.
   - The test starts by pressing play.
   - The test stops after the set test stop condition (breaking of the specimen) as stored is reached.
- Tear strength is expressed in kg/cm.

Formula:

$$Tear\ strength = \frac{FP}{T}$$

FP = Maximum load supplied during test

T = Thickness of the sample

2.3.6 Abrasion[18]

Abrasion is the process of wearing down or rubbing away. Abrasion resistance is the resistance of a compound to wearing away by contact with a moving abrasive surface.

The principle of the machine relates to the measurement of the volume loss, of the sample of the product under test, following exposure to an abrasive cloth attached to a rotating drum. The sample tested is a small disc cut from the material 16 mm in diameter and under 10N of load. The drum rotates at 40 revs / min and the sample of material traverses the drum at 4.2 mm per revolution until a path length of 40 meters is achieved. This is equivalent to 84 revolutions. The results are compared to a standard rubber sample of certified performance and hence the results are corrected for any wear to the abrasive cloth. The volume loss is calculated by measuring the mass loss during exposure to the cloth and then converting to volume by measuring its specific gravity. The abrasion index is expressed in mm^3. The lower the number, the greater the resistance to abrasion by this ‘grinding’ technique.

Figure 41: Rotary drum din abrasion tester

Procedure:

- The specimen is cut from moulded sheet using a drill machine.
- The initial weight (W1) of the specimen is measured.
- The specimen is held by the holder of the testing machine.
- After that the holder is put down on the rolling wheel
- The motor is switched on and the test is allowed to run uninterrupted.
- The motor stops automatically after the completion of cycles.
- The final weight (W2) of the specimen is measured.
- The abrasion resistance is calculated by using the formula for abrasion resistance.

Formula:

$$Abarasion\ (mm^3) = \left[\frac{(W1 - W2) * 200}{219 * Specific\ Gravity}\right] * 1000$$

2.3.7 Bonding[19]

Bonding, in the footwear industry, is referred to the joining of two materials with an adhesive. In case of sole materials, this test is done to determine the strength of the bond between the sole materials to the upper materials. Test specimen are prepared by cutting a strip of the moulded sheet attached with the upper. The specimen are then peeled using a tensile testing machine and the force required to separate the upper from the sheet is measured.

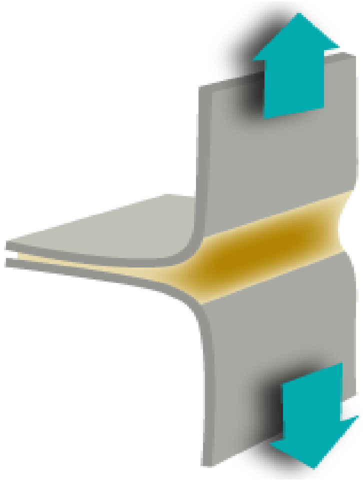


Figure 12: Test specimen for T-peel bond strength

Procedure:

- Specimen is cut from the moulded sheet in the required dimensions.
- Width of the specimen is measured.
- A knife is inserted into the adhesive layer at one end of test specimen and upper is separated from the sole material to the extent as shown in ***Figure 12***.
- The bent, unbonded ends of the test specimen are clamped in the holders of the machine.
- The test is started and a load of a constant head speed is applied.
- The machine records the various peaks, max force and average force during the test.
- The average force is then divided by the width of the specimen.
- The bonding strength is expressed in kg/cm.

Chapter 3

RESULTS AND DISCUSSION

The samples have been named as “% and Name of the filler” where the following notation hold:

NFL: No Filler Loading

A: Leather Buffing Dust from Leather Board

B: Leather Buffing Dust from an intermediate step of Leather Sole Manufacturing Process

C: Leather Buffing Dust from the final step of Leather Sole Manufacturing Process

D: Grounded Rice Husk or Rice Husk Powder

E: Rice Husk

F: Grounded Wheat Husk/Straw or Wheat Husk/Straw Powder

G: Wheat Husk/Straw

3.1 Leather Buffing Dust TPR Composite

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and leather dust as the filling material in ***Table 3*** and goes on to discuss the trends and practical challenges.

Table 3: Properties of sampled leather buffing dust TPR composites

Trial No.	1	2	3	4	5
Composition	NFL	5% $CaCO_3$	5% A	5% B	5% C
Specific Gravity	0.939	0.962	0.947	0.948	0.949
Melt Flow Index (Grams/10 min.)	51	49	35	42	41
Hardness (Shore A)	61	60	65	66	64
Tensile Strength (kg/cm^2)	69	60	63	62	63

Elongation at Break (%)	1183	1024	1013	992	1007
Tear Strength (kg/cm)	34	29	33	33	34
Abrasion (mm^3)	132	163	157	153	153

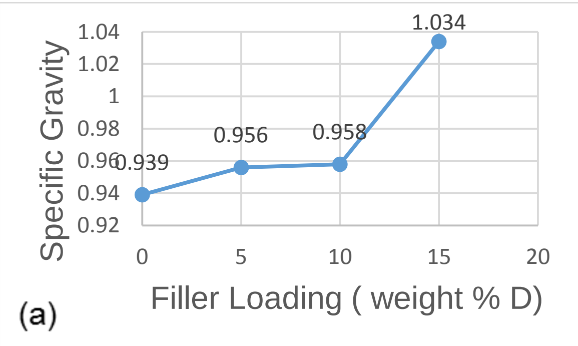
Trial No. 1 is the No Filler Loading (NFL) compound and Trial No. 2 is 5% $CaCO_3$ both of which are our reference material. Our trials with leather buffing dust as the fillers and their subsequent testing clearly show that these three composites compare well to our reference materials. All the three Trial No. 3, 4 and 5 have lower Specific Gravity than trial no. 2 which is required as lighter weight of the material is a desired property. The fillers A, B and C all harden the material. The tensile strength and abrasion resistance are reduced in comparison to NFL but they are better than in the case of trial no. 2. The elongation at break is also comparable to trial no. 2. Tear strength is very good and in case of trial no. 5, it is even the same as the NFL. The melt flow index on the other hand is reduced more noticeably probably because $CaCO_3$ is a fine powder and a non-reinforcing filler which is easy flowing when the polymer is melted. The leather buffing dust is clearly satisfying the parameters and properties required in the sole materials. But then comes the practical challenge, the leather dust becomes charred and burnt in the dispersion kneader due to the heat produced by the shear forces, giving a foul stench in the whole industrial unit, making it difficult for workers to concentrate and be productive. The charred particles also give the material a second standard look, smell and feel, rather than that of a composite. The charring may be because of the chromium present in the leather due to the tanning process, as the decomposition temperature is reported to be above 300^{o}C, well above the temperature reached in the dispersion kneader[10]. But the processing or solid waste management of the leather dust shall defeat the whole purpose of getting the waste back into the industry with minimum possible additional requirement and that of cost reduction as the processing of the leather dust will have a cost associated with it.

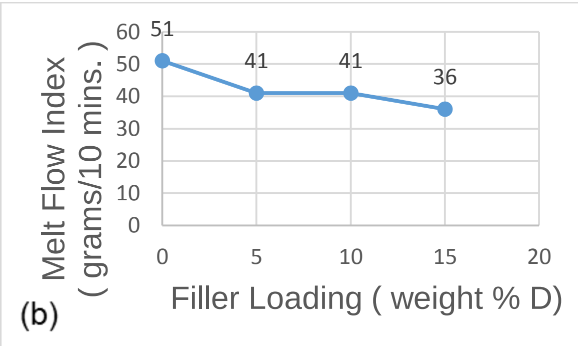
3.2 Rice Husk Powder TPR Composite

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and grounded rice husk or rice husk powder (D) as the filling material in ***Table 4*** and goes on to discuss the trends as shown in the graphs and practical suitability and challenges.

Table 4: Properties of sampled rice husk powder TPR composites

Trial No.	1	6	7	15
Composition (%D)	0	5	10	15
Specific Gravity	0.939	0.956	0.958	1.034
Melt Flow Index (Grams/10 min.)	51	41	41	36
Hardness (Shore A)	61	66	69	67
Tensile Strength (kg/cm^2)	69	60	57	40
Elongation at Break (%)	1183	1005	851	628
Tear Strength (kg/cm)	34	37	36	27
Abrasion (mm^3)	132	139	180	289





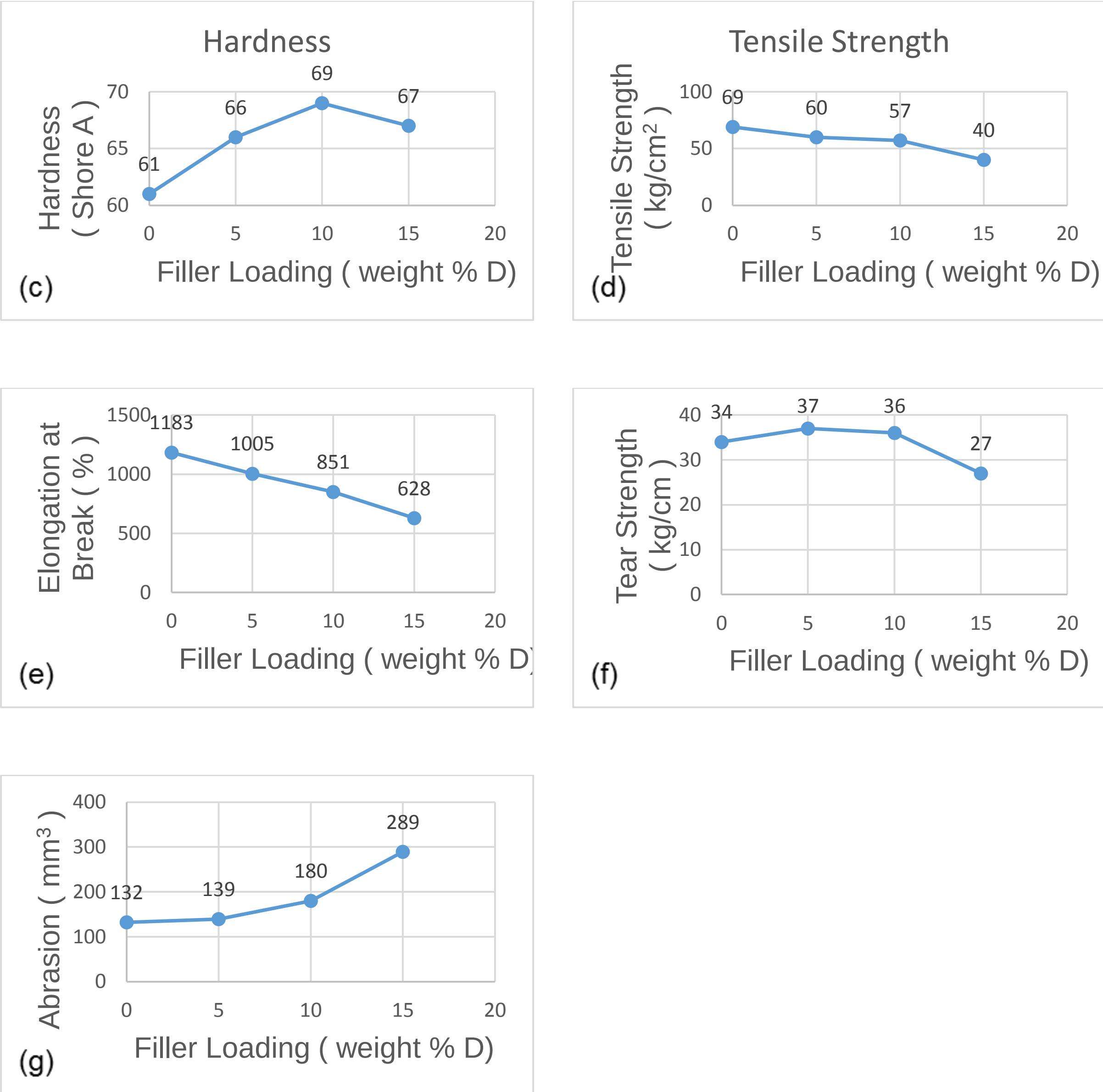


Figure 13: Parameter trends of sampled rice husk powder TPR composites with % filler loading (a) Specific gravity, (b) Melt flow index, (c) Hardness, (d) Tensile strength, (e) Elongation at break, (f) Tear strength, (g) Abrasion

The table shows the results of the various mechanical tests on composites of rice husk powder with SBS, and the graphs show us the trends. The specific gravity and abrasion increases with filler loading and takes a jump when filler loading is increased from 10 to 15 percent. The Melt Flow Index is decreasing with the increase in filler loading. The hardness and tear strength increase till 10 percent filler loading and take a dip after that as can be seen from the graph and the corresponding points for the 15 percent loading. The tensile strength and elongation decrease with increased loading of the filler with the gradient being a little higher for 15 percent. Clearly the 15 percent loading seems to be above the saturation for loading of the ground rice husk in the SBS matrix. The saturation might have led to improper dispersion of the filler at 15 percent and hence affecting the properties adversely at 15 percent loading. Practically the rice husk was pretty stable in the dispersion kneader and did not char like the leather buffing dust. Also the dispersion was good as was seen in the moulded sheets. The rice husk was procured at Rs.7/Kg. at retail rate. The wholesale cost of the same can be estimated at Rs.3.5/Kg. and with other transportation, grinding and processing should cost around Rs.5/Kg. The challenge though is to find a grinding industrial unit that would be willing to effectively and consistently give a standard product.

The idea behind using the rice husk was that it is light weight and would make the composite lighter. But that is in bulk that the rice husk is light. After grinding, the absolute density of the rice husk was way higher than the bulk, which was observed when the material was ground and the composites gave a higher specific gravity than NFL. Therefore, targeting a lower specific gravity, the rice husk in its bulk form was tried as the filler.

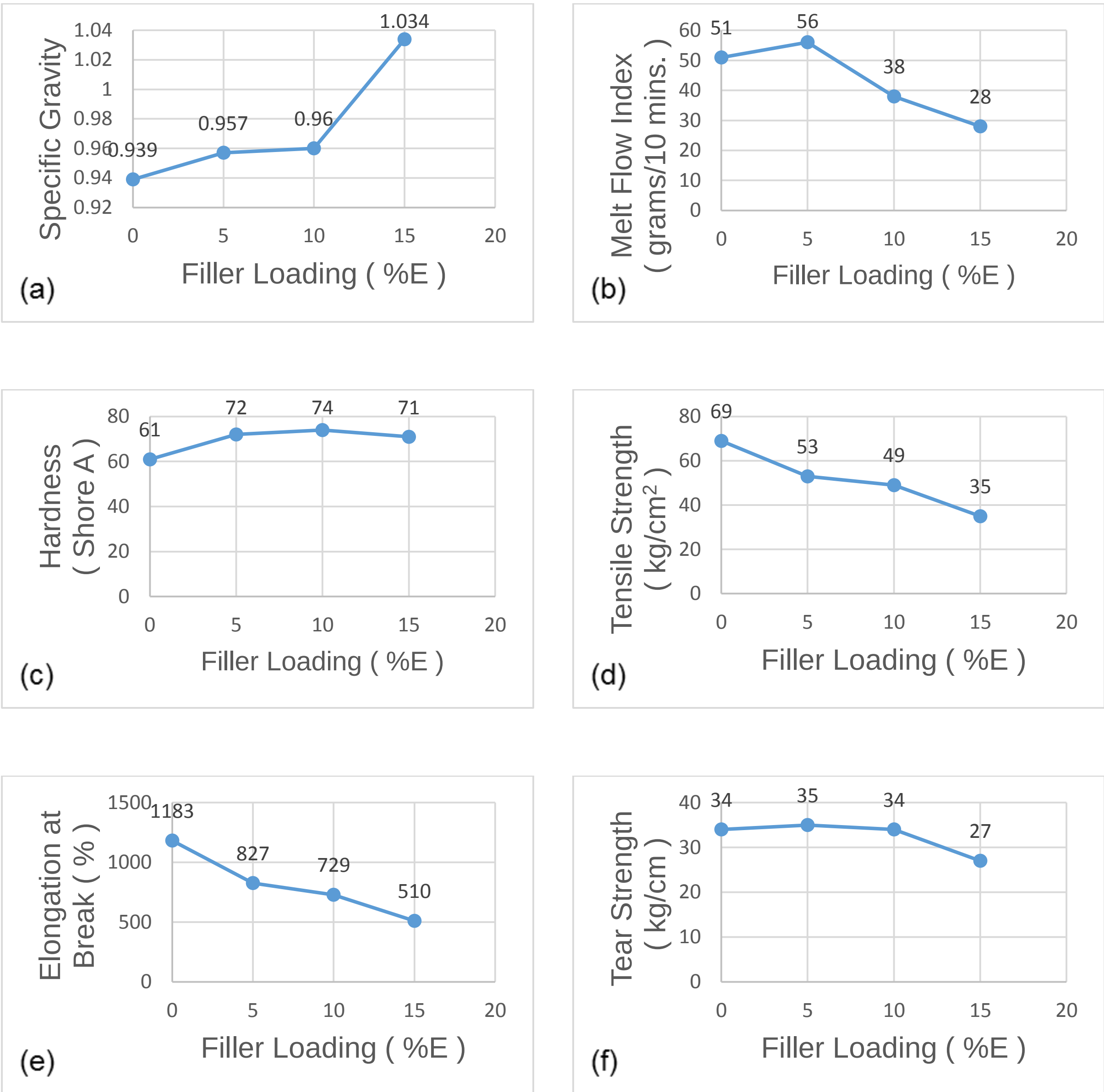
3.3 Rice Husk TPR Composite

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and rice husk (E) as the filling material in ***Table 5*** and goes on to discuss the trends as shown in the graphs and practical suitability and challenges.

Table 5: Properties of sampled rice husk TPR composites

Trial No.	1	9	10	16
Composition(%E)	0	5	10	15
Specific Gravity	0.939	0.957	0.96	1.034
Melt Flow Index (Grams/10 min.)	51	56	38	28
Hardness (Shore A)	61	72	74	71
Tensile Strength	69	53	49	35

(kg/cm^2)				
Elongation at Break (%)	1183	827	729	510
Tear Strength (kg/cm)	34	35	34	27
Abrasion (mm^3)	132	171	183	282



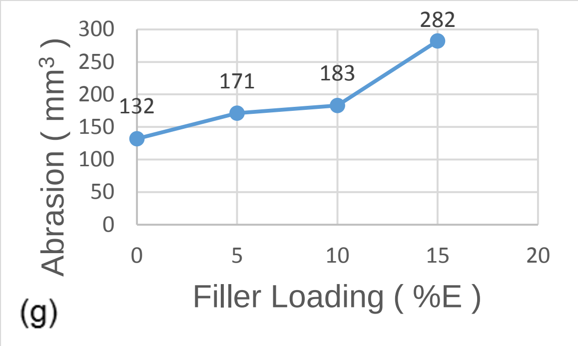


Figure 14: Parameter trends of sampled rice husk TPR composites with % filler loading (a) Specific gravity, (b) Melt flow index, (c) Hardness, (d) Tensile strength, (e) Elongation at break, (f) Tear strength, (g) Abrasion

The table and the graph shows the results of the various mechanical tests on composites of rice husk with SBS. The specific gravity and abrasion increases with filler loading and takes a jump when the loading is increased from 10 to 15 percent. The Melt Flow Index is initially increasing at 5 percent loading and then starts decreasing steeply with the further increase in filler loading. The hardness increases till 10 percent loading and slightly decreases beyond that, but it is still harder than NFL. The tear strength is pretty much the same till 10 percent loading and takes a dip at 15 percent loading as can be seen from the graph and the corresponding points for the 15 percent loading. The tensile strength and elongation decrease steeply even with 5 percent loading, and reduces further with increased loading of the filler with the gradient being even higher for 15 percent. This is probably because of the breaking of the dumbbell shaped specimen at the point of the hinge of the rice husk as it is not as strong as the polymer matrix, and because of that sudden breaking of the composite, its elongation at break is cut short. Also the dumbbell shaped specimen broke at different points of the dumbbell, hence confirming our hypothesis. Clearly the 15 percent seems to be above the saturation for loading of the rice husk in the SBS matrix. Again the saturation might have led to improper dispersion of the filler at 15 percent and hence affecting the properties adversely at 15 percent loading. Also the sharp difference in properties even at 5 percent loading with that of NFL, is due the hinge nature of the shells which also leave a cavity at some rice husks if not all. Practically the rice husk as with rice husk powder was pretty stable in the dispersion kneader and did not char like the leather buffing dust. Also the dispersion was good as was seen in the moulded sheets. The rice husk was procured at Rs.7/Kg. at retail rate. The wholesale cost of the same may be estimated at Rs.3.5/Kg. and with transportation may be Rs.4/Kg. Also there are no grinding and processing cost associated with it.

Though the motivation behind the filler was lower specific gravity, which was not observed. Clearly the filler is occupying the matrix well that the mass of the fillers is going to the polymers matrix cavities rather than the volume of the filler's contribution to the composite's volume

3.4 Wheat Straw/Husk Powder TPR Composite

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and ground wheat straw/husk or wheat straw/husk powder (F) as the filling material in ***Table 6*** and goes on to discuss the trends as shown in the graphs and practical suitability and challenges.

Table 6: Properties of sampled wheat straw/husk powder TPR composites

Trial No.	1	11	12	17
Composition(%F)	0	5	10	15
Specific Gravity	0.939	0.951	0.962	1.033
Melt Flow Index (Grams/10 min.)	51	44	46	29
Hardness (Shore A)	61	69	66	74
Tensile Strength (kg/cm^2)	69	56	47	38
Elongation at Break (%)	1183	898	773	562
Tear Strength (kg/cm)	34	36	35	26
Abrasion (mm^3)	132	172	213	336

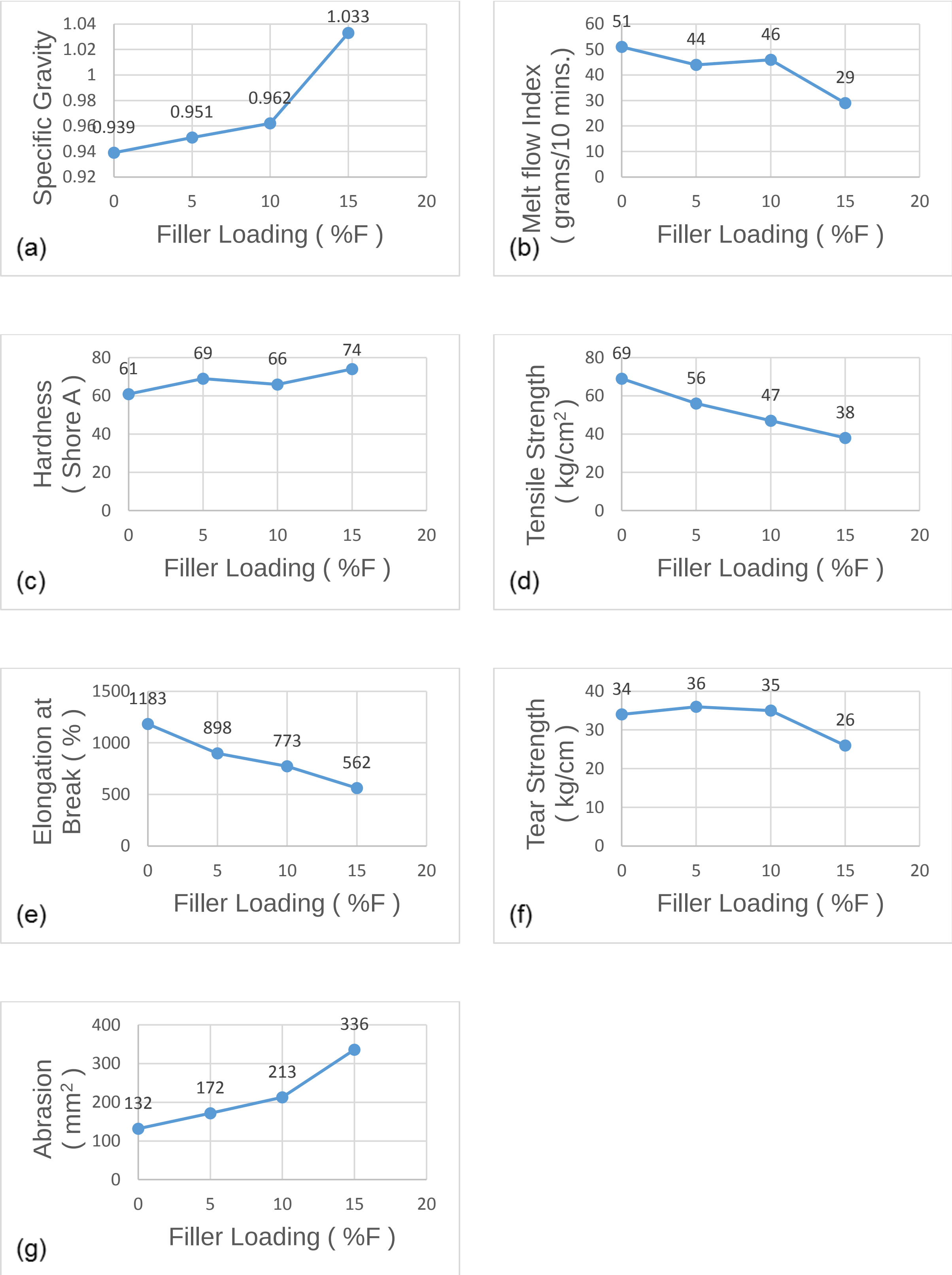


Figure 15: Parameter trends of sampled wheat straw/husk powder TPR composites with % filler loading (a) Specific gravity, (b) Melt flow index, (c) Hardness, (d) Tensile strength, (e) Elongation at break, (f) Tear strength, (g) Abrasion

The table and the graph show the results of the various mechanical tests on composites of wheat straw/husk powder or ground wheat straw/husk with SBS. The specific gravity and abrasion increases with filler loading and takes a jump when the loading is increased from 10 to 15 percent. The Melt Flow Index is decreases with the presence of the filler but has a marginal increase at 10 percent loading and reduces further at 15 percent filler loading. The hardness is increased in general with addition of the filler, but sees a marginal decrease and rises again at 15 percent loading. Tear strength is pretty much the same till 10 percent and takes a dip after that as can be seen from the graph. The tensile strength and elongation decrease with increased loading of the filler. Here also the 15 percent seems to be, if not above, then at the saturation for loading of the ground wheat straw/husk in the SBS matrix. At 15 percent filler loading, there is some saturation happening and hence affecting some of the properties adversely. Practically the wheat straw/husk was pretty stable in the dispersion kneader and did not char like the leather buffing dust. Also the dispersion was good as was seen in the moulded sheets. The rice husk was procured at Rs.7.6/Kg. at retail rate. The wholesale cost of the same may be estimated at Rs.3.5-4/Kg. and with other transportation, grinding and processing should cost around Rs.5-5.5/Kg. The challenge again, is to find a grinding industrial unit who would be willing to effectively and consistently give a standard product.

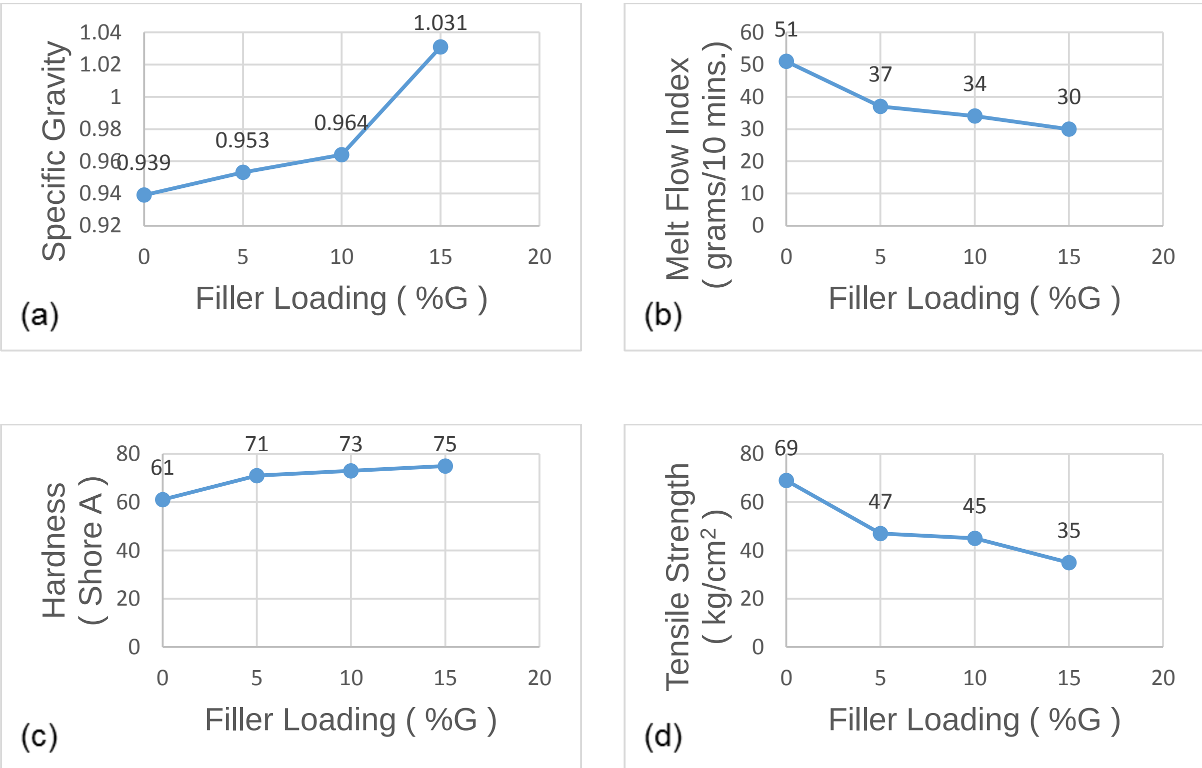
After some promising results from the rice husk experiment, the motivation behind using the wheat straw/husk was to check what other agricultural waste products can be used for similar composites that would have at least minimum standard required in the industry. Then as in the case of rice husk, the wheat straw/husk in its bulk form was tried as the filler.

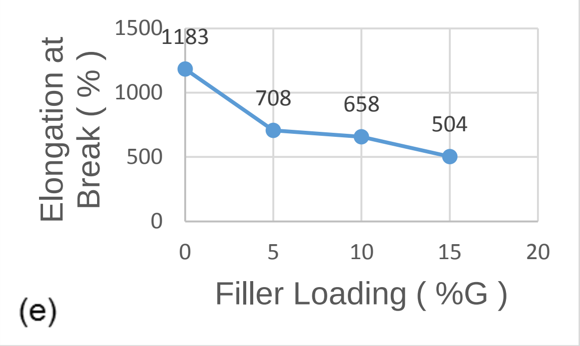
3.5 Wheat Straw/Husk TPR Composite

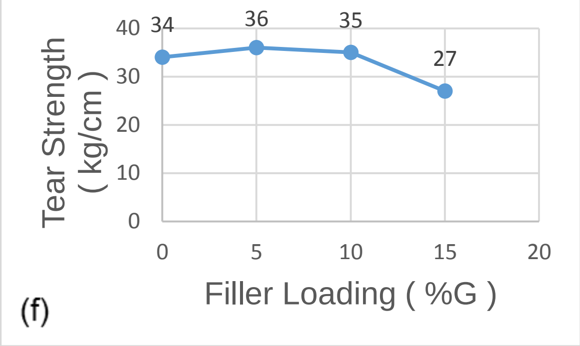
This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and wheat straw/husk (G) as the filling material in ***Table 7*** and goes on to discuss the trends as shown in the graphs and practical suitability and challenges.

Table 7: Properties of sampled wheat straw/husk TPR composites

Trial No.	1	13	14	18
Composition(%G)	0	5	10	15
Specific Gravity	0.939	0.953	0.964	1.031
Melt Flow Index (Grams/10 min.)	51	37	34	30
Hardness (Shore A)	61	71	73	75
Tensile Strength (kg/cm^2)	69	47	45	35
Elongation at Break (%)	1183	708	658	504
Tear Strength (kg/cm)	34	36	35	27
Abrasion (mm^3)	132	169	207	331







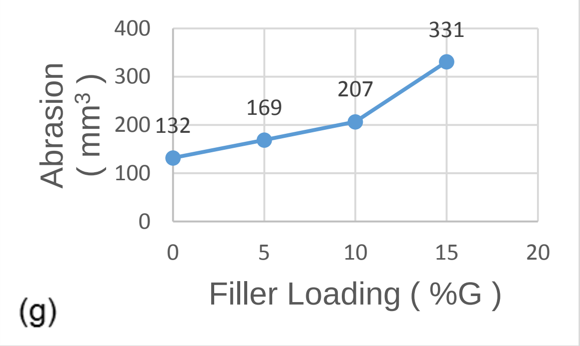


Figure 16: Parameter trends of sampled wheat straw/husk TPR composites with % filler loading (a) Specific gravity, (b) Melt flow index, (c) Hardness, (d) Tensile strength, (e) Elongation at break, (f) Tear strength, (g) Abrasion

The table and the graph show the results of the various mechanical tests on composites of wheat straw/husk with SBS. The specific gravity and abrasion increases with filler loading and takes a jump when the loading is increased from 10 to 15 percent. The Melt Flow Index takes a drop as soon as the filler is introduced and then observe a very slight decrease with the further increase in filler loading. Again the hardness increases as soon as the filler is introduced and very slightly increases beyond that, but it remains pretty much the same. The tear strength slightly increases till 10 percent loading and takes a dip at 15 percent loading as can be seen from the graph. The tensile strength and elongation decrease steeply even with 5 percent loading, and reduces further with increased loading of the filler with the gradient being even higher for 15 percent. This is probably because of the breaking of the dumbbell shaped specimen at the location of the wheat straw/husk as it is not as strong as the polymer matrix, and because of that sudden breaking of the composite, its elongation at break is also cut short. In this study also, the dumbbell shaped specimen broke at different points of the dumbbell, hence confirming our hypothesis. Clearly the 15 percent seems to be above the saturation for loading of the wheat straw/ husk in the

SBS matrix. Again the saturation might have led to improper dispersion of the filler at 15 percent and hence affecting the properties adversely at 15 percent loading. Also the sharp difference in properties even at 5 percent loading with that of NFL, is due the comparative weakness at the local points which are occupied by the wheat straw/husk and also in which orientation are they present. Practically the wheat straw/husk as with wheat straw/husk powder was pretty stable in the dispersion kneader and did not char like the leather buffing dust. Also the dispersion was good as was seen in the moulded sheets. The wheat straw/husk was procured at Rs.7.6/Kg. at retail rate. The wholesale cost of the same may be estimated at Rs.3.5-4/Kg. and with transportation may be Rs.4-4.5/Kg. Also there are no grinding and processing cost associated with it.

Experiment with this filler was basically to draw comparisons with the rice husk and wheat straw/husk powder. With an increased data set, we not only have better scope of understanding the principles behind the behaviour of the composites on various parameters tested, but also a wider scope of applications and a specific material for a particular application.

3.6 TPR Composites with 5% Filler Loading

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and various filling materials tried in the study at 5% loading in ***Table 8***.

Table 8: Properties of sampled TPR composites with 5% filler loading

Trial No.	2	6	9	11	13
Composition	5% $CaCO_3$	5% D	5% E	5% F	5% G
Specific Gravity	0.962	0.956	0.957	0.951	0.953
Melt Flow Index (Grams/10 min.)	49	41	56	44	37
Hardness	60	66	72	69	71

(Shore A)					
Tensile Strength (kg/cm^2)	60	60	53	56	47
Elongation at Break (%)	1024	1005	827	898	708
Tear Strength (kg/cm)	29	37	35	36	36
Abrasion (mm^3)	163	139	171	172	169

Trial No. 2 is 5% $CaCO_3$ which is our reference material. Our trials with agricultural waste in powder as well as bulk form as the fillers and their subsequent testing clearly show that these composites compare well to our reference material. All the four trial No. 6,9,11 and 13 have lower specific gravity than trial no. 2 which is essential as lighter weight of the material is a desired property. The fillers D, E, F and G all harden the material a lot more than $CaCO_3$. The tensile strength and elongation at break are reduced specially in the case of trial no. 9 and 13 as they are the bulk fillers and breakage was at the locally weaker points, the location points of the filling material. Abrasion resistance is pretty much the same in case of E, F and G, but is remarkably reduced in case of D. Tear strength is very good and way better than in trial no. 2. The melt flow index on the other hand is giving mixed responses, but nevertheless it is safely higher than the minimum industry requirement of 30 grams/10 minutes. All the filling materials in our study are clearly satisfying the parameters and properties required in the sole materials.

3.7 TPR Composites with 10% Filler Loading

This section summarizes the results of various mechanical tests performed on the composites made with SBS thermoplastic rubber as the polymer matrix and various filling materials tried in the study at 10% loading in ***Table 9*** and goes on to discuss the practical limitations and suitability.

Table 9: Properties of sampled TPR composites with 10% filler loading

Trial No.	8	7	10	12	14
Composition	10% CaCO3	10% D	10% E	10% F	10% G
Specific Gravity	0.986	0.958	0.96	0.962	0.964
Melt Flow Index (Grams/10 min.)	65	41	38	46	34
Hardness (Shore A)	65	69	74	66	73
Tensile Strength (kg/cm^2)	56	57	49	47	45
Elongation at Break (%)	924	851	729	773	658
Tear Strength (kg/cm)	31	36	34	35	35
Abrasion (mm^3)	196	180	183	213	207

Trial No. 8 is 10% $CaCO_3$ which is our reference material. Our trials with agricultural waste in powder as well as bulk form as the fillers and their subsequent testing clearly show that these composites compare well to our reference material. All the four trial No. 7, 10, 12 and 14 have lower specific gravity than trial no. 8. The fillers D, E, F and G all harden the material a lot more than $CaCO_3$. The tensile strength and elongation at break are very good for trial no. 7 and reduced comparatively in the case of trial no. 10 and 14 as they are the bulk fillers and breakage was at the locally weaker points, the location of the filling material. This can be further probed by the SEM analysis of the cracked samples, a slot for which is awaited. Anyway it can be improved by adding maleic anhydride to our formulation as a compatibilizer[8,6,20] between the hydrophilic fillers and hydrophobic polymer matrix. Abrasion resistance is almost the same but is slightly better in case of rice husk and rice husk powder. Tear strength is very good and way better than in trial no. 8. The melt flow index is being reduced here, with rice husk powder and wheat straw/husk powder being better than the bulk fillers. All the filling materials in our study are clearly satisfying the parameters and properties required in the sole materials. But then comes the practical challenges, first and foremost is the requirement of the grinder in the case of D and F, and that too which can consistently give a fine product, as in our case a hand held grinder was used and the particle size can vary and hence affect the composite properties. Also the filling materials leach their colour out to the composite, as we did not use any colouring dyes. This poses as a limitation that the composites can only be used in darker colours. But the abundant availability or dumping of these agricultural wastes best suits our motivation, reducing wastage, making ecological materials for not just shoe soles, but for any application that requires similar properties.

3.8 Further Testing – Bond Strength

After shortlisting the better lot of our samples, they were put on to check for bond strength. The results for trial 7, 8, 10, 12 and 14 are summarized in the ***Table 10***.

Table 10: Bond strength of selected composite samples

Trial No.	Composition	$F_{average}$ (kg/cm)
7	10% D	4.04
8	10% $CaCO_3$	6.5
10	10% E	7.08
12	10% F	5.79
14	10% G	5.24

The table shows the values for all the samples are well above the minimum required standards (3kg/cm), and trial no. 10 showed the best bond strength.

Conclusion

All the composites synthesized in the study gave satisfactory results on the various parameters tested. In general addition of any filler, studied here, results in an increase in specific gravity, hardness and abrasion. Also it leads to decrease in tensile strength and elongation at break. Tear strength is the same with a slight improvement upto 10% filler loading. Melt flow index is well above the minimum required. As far as the extent of filler loading is concerned, 15% is above the saturation limit of the polymer matrix, as all the properties change drastically from 10% loading to 15% loading. 5% and 10% loading both give results which are very much acceptable and hence 10% is a more optimum filler loading contributing more towards the waste utilization and sustainable development. All the composites at 10% loading passed the bonding strength requirement. Comparing the composites with fillers in bulk forms and the powder forms, the latter gives better results compared to former, as finer particles can be disperse uniformly, whereas the bulk forms leave a lot of local weak points, which results into comparatively poor properties in our testing. All the fillers studied leach out the colour to the composite and hence pose a little limitation to the colours that can be obtained. Due to the charring, leather dust is not practical to use, and hence overall the rice husk is better than wheat straw/husk in both the bulk forms as well as the powder forms. Hence ground rice husk or rice husk powder at 10% loading is the best of the composites studied. The compatibility and interfacial interaction between the hydrophilic fillers and hydrophobic polymer matrix need to be further probed with an SEM analysis and can be further improved by adding maleic anhydride in our compounding, percentage of which will also need to be optimised and may also lead to properties better than the original formulation without the fillers.

The composites filled with rice husk and wheat straw/husk give better resulting properties than $CaCO_3$ filled composite, and offer a cost advantage to the NFL or original compound with no filler loading. Hence this may contribute to an easier shift towards sustainability in the near future.

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