

UTILIZATION OF LOW COST ADIPOSE TISSUE WASTE AS A SOURCE OF STEARIC ACID FOR USE IN RUBBER ACTIVATION

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Abstract— Stearic acid was extracted from adipose tissue which was obtained from a waste heap from a local tannery. The waste adipose tissue was prepared for use by cutting, mixing, cleaning and refrigeration. By solvent extraction using methyl ether, a solid fat was obtained which was then hydrolyzed using water at 60°C and heterogeneous catalyst stones of calcium and magnesium oxide. Chemical characterization of stearic acid white flakes for parameters such as the melting point, specific gravity, iodine value, acid value and copper and manganese content was performed. A fatty acid yield of 68% was obtained. The iodine value of 10.02 and the melting point of 50.3 °C show a reasonable degree of saturation and stability. A high level of 198.89 acid value was obtained. The absence of copper and manganese, content which were determined qualitatively, indicates the suitability of the extracted stearic acid for rubber compounding without being a catalyst of ageing. Its specific gravity of 0.8533 indicates its lightness in respect to rubber compounding. Physical tests on the rubber compounded with the stearic acid were performed according to SATRA standards for general product safety. Simulated vulcanization tests on the rheometer were within 2 minutes, which is suggestive of activation. The rubber had a tensile strength of 6.527×10^3 , abrasion resistance of 0.96 and hardness of 75, which are all indicative of a good service life of rubber compounded with the stearic acid.

Keywords: stearic acid; style; waste adipose tissue; rubber; vulcanization)

1. INTRODUCTION

Waste adipose tissue is obtained from a tanning process known as fleshing which is done to remove the flesh side of the hide using a fleshing machine at a local leather industry. The tannery processes an average of 6000 kg of hides a day, yielding approximately 200 kg of fleshing daily destined for the landfill. The manufacture of stearic acid using fat extracted from the waste adipose tissue serves as a major waste management program. While there is significant motivation for such a project from a job creation point of view, especially in a developing region such as Zimbabwe, there is also significant scientific motivation for undertaking a project of this nature.

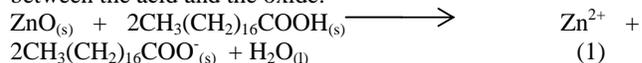
The flesh side (adipose tissue) contains excess fat, flesh and connective tissues, which must be removed before the addition of tanning chemicals to reduce wastage of the

chemicals.^[1] The fat is removed from the adipose tissue by solvent extraction using a soxhlet extractor and serves as the raw material in the manufacture of stearic acid.

Stearic acid is the most common occurring fatty acid in animal and vegetable fat.^[3] Pure stearic acid is a white, waxy solid material, which is odourless and tasteless.^[3] However, because of its natural origin pure stearic acid is hard to obtain. Instead stearic acid usually includes minor amounts of other fatty acids of different carbon length. These trace impurities can cause the acid to vary in molecular weight, solubility, melting point, colour, odour and other physical and chemical properties.^[2]

The stearyl residues or fatty acids can be removed from the glycerol backbone in the fat through a variety of techniques, which include hydrolysis when refluxed with acids or bases or when acted upon enzymatically by the enzyme lipase. They can also be hydrogenated from other unsaturated fatty acids.^[4]

The extracted stearic acid is widely used in rubber compounding as an activator for organic accelerators.^[5] The activator system comprises of the stearic acid and zinc oxide, where the Zn^{2+} ions are made soluble by salt formation between the acid and the oxide.



This reaction accounts for the high concentration of Zn^{2+} ions formed thus increasing the overall rate of cross-link formation and the extent of cure. Stearic acid has other wide spread uses, for example, in lubricants, soaps, pharmaceuticals, cosmetics, shoe and metal polishes and food additives.^[6] The physical and chemical properties of stearic acid greatly affect the overall properties of rubber compounds, hence characterisation is done to verify if it meets the minimum requirements done on a compounded rubber to attest the quality of the stearic acid produced.^[7]

In this work, utilization of stearic acid from adipose tissue waste and its suitability in rubber compounding is reported. The effectiveness of the extracted stearic acid is then compared against the commercial stearic acid being used for rubber compounding. The study is aimed at utilising the fleshing destined for the landfill in rubber compounding and hence is a major waste reduction program. formatter will need to create these components, incorporating the applicable criteria that follow.

2. MATERIALS AND METHODS

2.1 Sampling and sample preparation

The waste adipose tissue samples were taken from a local tannery situated in Gweru, Zimbabwe. The tannery has a beam house in which the fleshing process is done. Each heap was divided into quadrants and a sample was taken from each of the quadrants. The samples were then mixed to form one composite sample. The samples were collected using sampling shovels and put in sampling containers. The fleshing was first cut into small pieces and then ground using a cutter mill to get uniform samples. The prepared samples were mixed thoroughly and kept in a clean, dry airtight container.

2.2 Reagents used^[2,8,9]

Adipose tissue (Bata Shoe company), methylene chloride (reagent grade), distilled water, extracted fat, calcium oxide and magnesium oxide catalyst stones, natural rubber, stearic acid, zinc oxide, sulphur, mercaptobenzthiazole, carbon black.

2.3 Instrumentation used

Oven, mixing roll mill, steam-heated press, teledyne taber abraser, (model 503 standard abrasion tester, patent number 2287148), tensile testing machine, (Lhormagy), rheometer, (100S Monsanto), durometer shore instrument, (Instron Wilson)

2.4 Methods

2.4.1 Fat extraction^[10]

Fleshing (10 g) was placed in an extraction thimble, and covered with a grease free cotton swab to prevent it from floating out of the thimble during extraction. Methylene chloride (50 mL) was added into a 125 mL extraction flask and extracted for 8 hours. The solvent was distilled off from the fatty residue. The residue was then dried at 100 °C for 3 hours and cooled in a dessicator.

2.4.2 Hydrolysis of fats^[8]

The extracted fat was emulsified in a conical flask using water at 60 °C and poured at the top of the column packed with the stones of heterogeneous catalyst of calcium oxide and magnesium oxide stones and the fat flowed through the catalyst stones down into the column, splitting by hydrolysis the molecules of glyceryl esters and separating the fatty acids from the trialcohol. The stearic acid and the glycerol were collected at the bottom of the column and separated by density difference. To separate by density difference, a decanter was used.

2.4.3 Chemical characterisation of the stearic acid^[10]

2.4.3.1 Melting point

Stearic acid (1 g) was placed in a capillary tube and placed inside the melting apparatus. A thermometer was placed inside the apparatus. The sample was heated at 50°C carefully by controlling the temperature with the rheostat and the temperature at which the stearic acid melted completely recorded.

2.4.3.2 Iodine value

Stearic acid (0.2400 g) was weighed into three 250 mL conical flasks and 20 mL of carbon tetrachloride added. Carbon tetrachloride (20 mL) was also added to each of two additional flasks to serve as blanks. Wijs reagent (25.0 mL) was pipetted into each flask. The flasks were stoppered, the contents mixed by swirling and stored in a dark cupboard. After 30 minutes, 10 mL of 30% potassium iodide solution and 100 mL of distilled water were added to the sample solution. The solution was then titrated immediately with a standard 0.1N thiosulphate solution until the yellow colour almost disappeared. Starch indicator solution (1 mL) was added and titrated drop wise with vigorous swirling to disappearance of the blue starch – iodine colour. The blanks were titrated in the same manner.

2.4.3.3 Acid value

Stearic acid (1.0012 g) was weighed into a conical flask and dissolved in 25 cm³ ethanol by gentle heating. Two drops of phenolphthalein indicator solution were added. The sample solution was titrated against 0.1 M potassium hydroxide solution.

2.4.3.4 Copper content

Stearic acid (0.5001 g) was placed in a dry test tube. Ammonium hydroxide solution (4 mL) was added to it. The sample solution was gently shaken. Then 1 mL of sodium diethyldithiocarbamate solution was added.

2.4.3.5 Manganese content

Stearic acid (1.0013 g) was weighed into a test tube and 3 mL of HNO₃ were added to it and gently shaken for a few minutes. In another test tube the same amount of red lead and 3 mL of concentrated nitric acid and were added and shaken gently for a few seconds. Both tests tubes were heated continuously for 5 minutes until both solutions were boiling. The two solutions were then mixed in hot conditions and the undissolved matter settled down.

2.4.3.6 Specific gravity

A clean dry 50 mL bottle was completely filled with ethanol. The weight of the filled bottle was taken as W₁ and 10 mL of ethanol was poured off, and the weight of the bottle taken again as W₂. Stearic acid (1.0003 g) was added to the bottle containing ethanol and the weight was recorded as W₃. The specific gravity bottle was then topped up to the 50 mL mark and the fourth weight taken as W₄.

2.4.4 Incorporation of stearic acid into the rubber mix

Natural rubber (100.0021 g), stearic acid (0.5001 g), zinc oxide (6.0003 g), sulphur (3.5100 g), mercaptobenzthiazole (0.50012 g) and carbon black (1.0004 g) was mixed thoroughly on a mixing roll mill to produce a thin sheet of compounded rubber ready for vulcanization in the steam – heated presses.

2.4.5 Vulcanization

The compounded rubber was cut into dimensions slightly smaller than those of the cavities. Pressure was applied for 12 minutes to the moulds. The moulds were quickly removed and plunged into cold water for 10 minutes. The sheet was wiped dry and retained for 24 hours before testing.

2.4.5.1 Test for vulcanizability

A 2.0015 g sample of compounded rubber was cut and placed in the die cavity of a rheometer. The rheometer was closed and set at a temperature of 165 °C and a pressure of 3.5 bars was applied for 3 minutes and a graph of the curing characteristics recorded.

2.4.6 Characterisation of the physical and mechanical properties of the vulcanized rubber

2.4.6.1 Abrasion resistance

The vulcanized rubber was cut into three 5 cm x 5 cm squares specimens with a center hole. Each specimen was weighed accurately on a balance and clamped into a sample holder on the Taber abraser and abraded for 1000 revolutions using freshly resurfaced calibre wheels, 1000 g load and 70% suction. The specimen was then removed from the sample holder, the abraded particles lightly brushed away and the specimen reweighed.

2.4.6.2 Tensile strength

Three test pieces were cut from the molded dump-bell rubber sheets along the grain direction. The thickness of each test piece at the middle was maintained at 2.5 mm and the width at 0.6 cm. Each test piece was clamped into the grips of tensometer. Elongation at break recorded after application of stress.

2.4.6.3 Hardness

Three test pieces from the moulded spherical rubber pieces were clamped onto a durometer and the penetration of the indenter measured.

2.5 Statistics

Each experimental parameter for the mechanical properties was performed at least in triplicate, and data values were reported as mean values and their standard deviations. For the graphic depiction of the data, each point represents a mean value. Microsoft Excel was used to calculate mean and standard deviations.

3. RESULTS AND DISCUSSION

In this work, stearic acid used in production at the local manufacturing concern was used as the standard and the extracted stearic acid as the sample. A percentage yield of 68% was obtained relative to the reported Twitchell process which gave a 90% percentage yield.^[11] The difference could have been due to the use of different sources of the fat. The fat used in the Twitchell process was from soya beans. Soya

beans contain no significant amount of conjugated unsaturation.^[12] Although the tallow used for the sample production contained higher amounts of saturated fatty acids, other fewer constituents are conjugated and thus render the hydrolysis of the fat difficult. The Twitchell process has a higher percentage yield due to a prolonged reaction time (30 days) as compared to the continuous fat splitting process using the CaO. MgO catalyst,^[11] which took only 5 hours to produce the 68% yield. The fat splitting process has a good industrial projection since a reasonable yield is obtained in a relatively short time.

3.1 Chemical characterisation of stearic acid

3.1.1 Melting point

The melting point of the standard stearic acid was 52.3 ± 0.1 °C^[10] and 50.3 ± 0.6 °C for the sample. The melting point of the sample which is 50.3 °C is lower than that shown in the specifications of Bata standards organization, with the minimum being 52 °C.^[13,14] Fig. 2 shows the relative melting points of stearic acid standard and of sample.

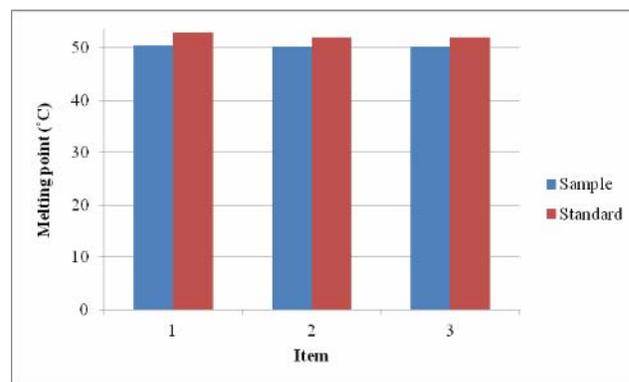


Fig. 1. Melting point of stearic acid

The value of the melting point is a measure of purity of the compound. The melting points of the samples were generally lower than those of the standards attributed to the presence of unsaturated acids, like linoleic and linolenic acids, which due to their double bonds lower the melting point. The double bonds break up the regular alternating structure of the hydrocarbon chain in the stearic acid allowing the unsaturated acids to readily fit into the regular crystal lattice.^[2]

3.1.2 Iodine value

Iodine value for the sample was 10.02 and for the standard, 10.93 and the two values were very much comparable. The stearic acid was reacted with an excess of iodine monochloride solution. The halogens were added quantitatively to the double bonds in the unsaturated fatty acids. The unreacted halogens were determined by titrating with thiosulphate. The iodine number is defined as the grams of iodine reacting with 100 g of acid.

The iodine values for both the sample and the standard are in the range of specifications for compounding, which is between 10 and 12.^[12]

3.1.3 Acid value

The acid value for the standard was 209.75 and that for the sample was 198.89. This shows that 1g of the stearic acid produced can neutralize 100 milligrams of potassium hydroxide. Relating to rubber activation, the stearic acid should react with zinc oxide. Hence the acid value shows whether the stearic acid produced can activate zinc oxide. Both values of the standard and that of the sample conform to the international standards specifications. The values show that the stearic acid produced has a high acidity. Fig.2. shows acid values and iodine values in stearic acid as compared to those of the standard (Sample 4).

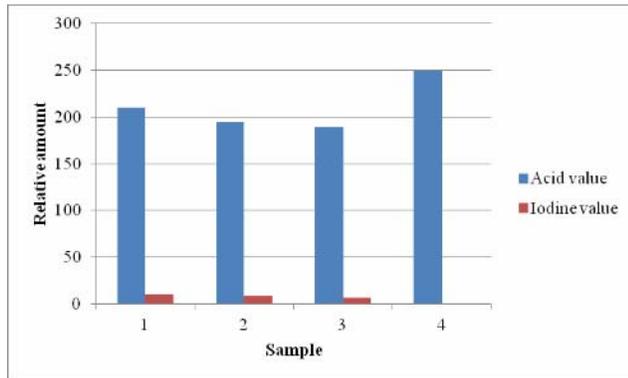


Fig 2. Column graph to show the variation of acid value and iodine value.

From Fig.2., the acid value of the standard stearic acid is higher than that of the extracted stearic acid samples. The standard stearic acid had an iodine value of zero. This is because the more the amount of unsaturated acids in the stearic acid produced, the less the acid available to neutralize the basic groups present in the rubber mix, especially zinc oxide for the rubber activation.

3.2 Qualitative analysis of metal ions

3.2.1 Copper

Table 1 shows that there are no copper ions present in the standard and sample stearic acid. The absence of copper in the stearic acid makes it suitable for compounding of rubber.

Table 1. Qualitative determination of copper

Test	Observation	Inference
To 0.5 g of stearic acid, 4ml of NH_4OH were added and the mixture shaken gently. 1 ml of sodium diethyldithiocarbamate was then	No apparent change was observed. The solution remained colourless for the sample and the standard.	No copper is present in stearic acid for both the sample and the standard.

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Copper cations contaminate the rubber mix and result in the generation of free radicals. This would result in the fast deterioration of the rubber matrix, which results in the premature ageing of the rubber articles or products produced.

3.2.2 Manganese

Table 2 shows the test for the presence of manganese in the stearic acid samples and standards. The tests show that manganese was absent in both the stearic acid samples and the standard.

Table 2. Qualitative determination of manganese

Test	Observation	Inference
To 1 g of stearic acid, 3 ml of HNO_3 were added. To 1 g Pb_3O_4 , 3 ml HNO_3 were added. The test tube with stearic acid was boiled. The test tube with Pb_3O_4 was also and the two mixed.	Sample : No apparent colour was observed. The solution remained colourless. Standard: The solution remained colourless.	Sample: No pick colouration to show the presence of manganese. Standard: No pick colouration to show the presence of manganese.

The absence of manganese in the stearic acid extracted shows that it can be safely used in compounding without the risk of degrading the compounded rubber and manganese has a deleterious effect to vulcanized rubber by being a catalyst of ageing. The vulcanized rubber tends to craze and crake in the presence of the Manganese II when exposed to UV light.

3.2.3 Specific gravity

The rubber compounded with the sample stearic acid has an average specific gravity of 0.8533 and that compounded with the standard is 0.8401. Both values fall within the range of the accepted value of the specific gravity which is 0.80-0.86.^[10]

Fig. 3 shows the relative specific gravities of the samples and the standards.

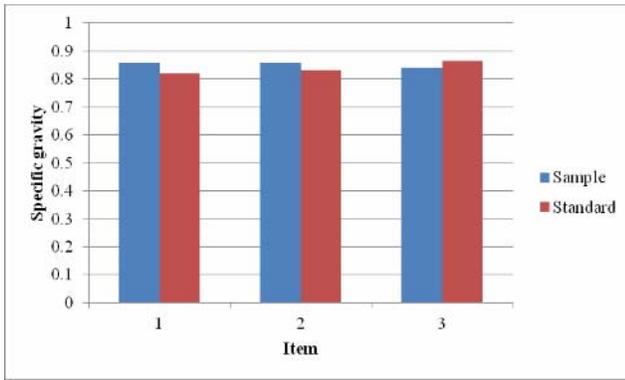


Fig. 3. Relative specific gravities of samples and standards

During rubber compounding the weight of the reagents is not as important as their volume component, hence the need to determine the specific gravity. Thus during designing of compounds, the reagents are added in 100 parts per rubber. This then projects if the compounded rubber will be of the required weight and thus adding to the comfort of the resultant rubber product.^[9]

3.3 Characterization of the physical and mechanical properties of the vulcanized rubber

3.3.1 Vulcanizability

Table 3. Cure to equilibrium or maximum torque

	S1	S2	S3	X1	X2	X3
Minimum Torque	20	22	24	21	22	22
Maximum Torque	35	40	37	33	40	36
Ts at 2 min	30	32	30	35	34	43
Tc 90	63	60	65	56	63	61
Straight line at 100% cure	71	70	73	62	69	70

Figs. 4 and 5 show typical rheometer graphs for the sample and standards respectively. The shapes of the curves are similar indicating the suitability for use of the extracted stearic acid.

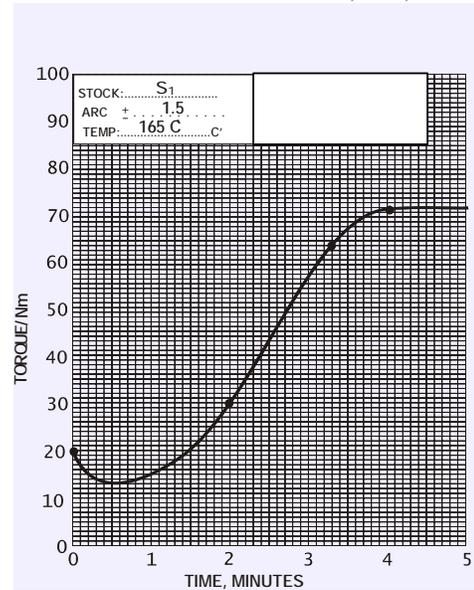


Fig. 4. Typical rheometer vulcanization graph for the samples

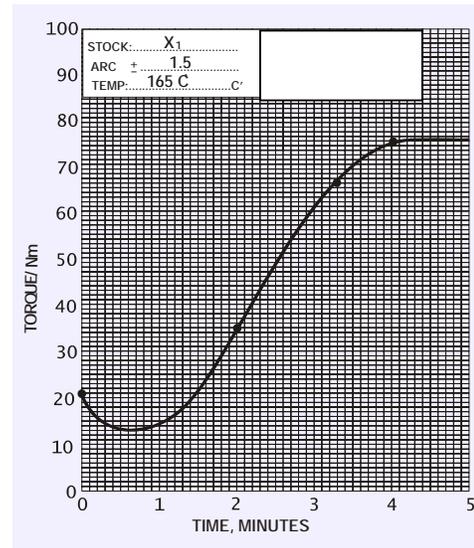


Fig. 5. Typical rheometer vulcanization graph for the standards

The minimum torque is proportional to the viscosity of the uncured compound and for both the standard and sample, the values vary. This is so because of the limitations of mill mixing, which does not produce 100% uniformity.

T_s at 2 minutes is the time to incipient cure or scorch time, which is a measure of process safety. The rheometer simulates the curing or vulcanization of the rubber mix in a press or boiler. At 2 minutes the torque of both the standard and the sample rubber was higher than the minimum torque. This shows that the shear stress exerted on the rubber had increased by the rotating disk of the rheometer. This was due to the formation of cross-links in the rubber matrix as vulcanization occurred.

T_s at 2 minutes shows the success of the extracted stearic acid as an activator of the accelerators of the vulcanization process. In the absence of stearic acid the torque would not increase but would at a time later.

T_c at 90, is a measure of full torque development at 90% of cure. This reports on the progress of the vulcanization process. For both the standard and sample rubbers, the vulcanization process was progressing well.

The straight line at 100% cure is the fully cured torque and is a measure of shear modulus or stiffness of the compound.^[9] All the compounds were relatively stiff and this shows that they can be used in the production of shoe top-pieces.^[15]

3.3.2 Abrasion resistance

Fig. 6. shows the relative mass losses in rubber activated with extracted stearic acid and the one activated with standard stearic acid. Rubber activated with standard stearic acid was associated with higher mass losses relative to rubber activated with stearic acid extracted from waste adipose tissues.

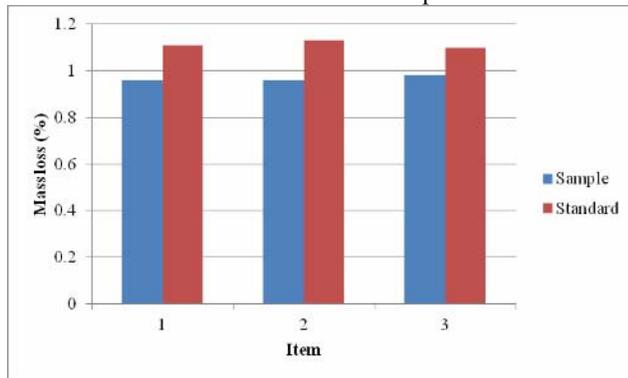


Fig. 6. Graph of relative mass losses of samples and standards

The lesser the loss of rubber particles, the better the wear performance of the top-pieces. According to SATRA standards the percentage loss should be less than 1.0.^[15] The average resistance value shown by the sample of 0.97 predicts a better wear performance than that of the standard which gave an average of 1.11.

3.3.3 Tensile strength

Tensile strength can be used as a measure of deformation of the back part or heel counter under specific load conditions to give an indication of the back part rigidity and therefore, the risk of distortion of wear. Fig. 7 shows the relative tensile strengths of rubber samples and standard rubber

samples.

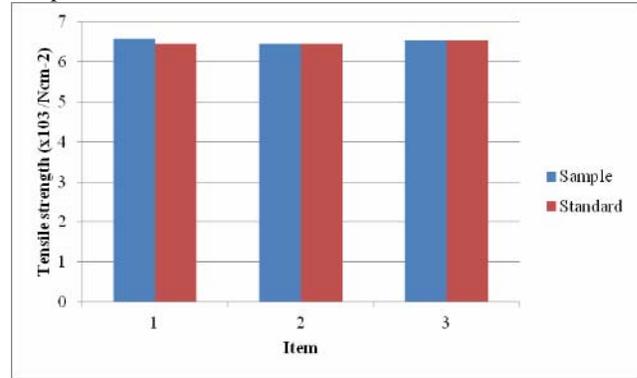


Fig. 7. Relative tensile strengths of samples and standards

SATRA looks for a minimum force to cause detachment of 500N and provided the value is consistently obtained, few wear problems are encountered. Most manufacturers, however, prefer to work to higher figures and thus provide a larger safety margin. Hence the average tensile strength for the sample is $6.5270 \times 10^3 \text{ Ncm}^{-2}$ and the standard, $6.4829 \times 10^3 \text{ Ncm}^{-2}$. This projects a good service life of the heel counter.^[15]

3.3.4 Hardness

Fig. 8 shows the relative hardnesses of the rubber samples and standard rubber. The graph shows that the rubber samples have significant greater hardness relative to the standard rubber samples.

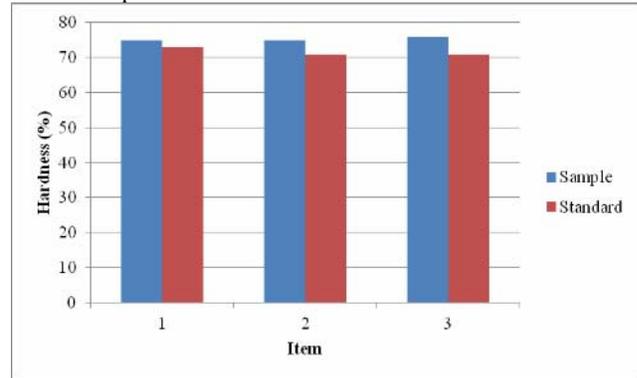


Fig. 8. Graph of sample and standard relative hardness

Generally both slip resistance and attachment security are governed by hardness within a given material type, but in different directions so there is a trade off of one against the other. With increasing hardness of material, the security of attachment tends to increase but the slip resistance tends to decrease.^[15]

4. CONCLUSION

The stearic acid was extracted successfully from the waste adipose tissue obtaining a percentage yield of 68% hence the project is viable and can be implemented. The stearic acid extracted from waste adipose tissue gave comparable and even better effects on compounded rubber

based on physical properties such as tensile strength, hardness, abrasion resistance and vulcanizability.

5. ACKNOWLEDGEMENTS

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