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Utility Value of Solubilized Animal Hair in Commutative Recycling of Damaged Hides and Skins

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Abstract
Hides with defects lose value and are often discarded thereby constituting economic waste. Seemingly damaged skins were obtained from the abattoir. Using mechanical, enzymatic and chemical hair removal processes, three hide samples were prepared and subsequently powdered to fine particle size. Keratin obtained from the unhairing process through alkali hydrolysis of the hair was used in varied quantities in combination with synthetic (Methylourea formaldehyde resin) and natural tanning materials as binders, were used to form sheaths of 5mm thickness; shrinkage, tensile, percentage elongation tests and degree of water absorption were carried out on the sheaths. Statistical analysis of the results substantiated the results obtained and places this product in good stead as a substitute for top surface covering in rigid structural applications, where low degree of water imbibition, good tensile strength, abrasion resistance and good flame retardancy maybe desired. Correlation analysis of results clearly shows the impact and extent of the addition of solubilised keratin on the properties of recycled skins.
Keywords: Animal hair, beam house waste, unhairing, solubilises, syntan, commutative recycling.

1. Introduction

Tannery damages occur as, grain damage due to over liming, over breathing, sand spots, bate specks, blood spots, decay specks, mould, marbled grain and salt stains on the leather. The beam house's waste generates a great amount of untanned hides and skins, which eventually, are converted to non-nutritionally-good meat "Kpomo" (local name). Because these raw hides and skins are subjected to inspection before tannage is carried out on them, a lot of them are rejected while some get damaged during tannage and are turned to cast-offs (Flarnerty, 1965).
Some other wastes sources are trimmings from untanned hides with hair, untanned hides without hair (fleshing, glue stock), chrome-tanned and vegetable tanned shavings, splits and trimmings and often, hair and bristles (Bocciardo & Ewolo, 1953).
Mechanical damages occur through acerbic wire contact, grain damage, branding and processing mistakes which reduce the value of leather. Defects also occur during the curing process.
'Stains' are caused by the presence of metallic contaminants which may have entered during one of several handling processes e.g. transportation, salts of liquors used in the tannery or the drum employed for tanning, vein damage by bacteria within the leather, which initiates autolysis by enzymes that diffuse through the walls of vertical blood vessels of the reticular layer. Unfortunately, these are all active before the salting process is carried out on the skins.
The use of protein polymer Keratin in the recycling of damaged skins is to impact structural strength and possibly, improve the chemical attributes of the already damaged hides and skins. The tendency for keratin to impact such properties to the skins can be appreciated by the fact that keratin has a cross-bonded polypeptide chain with very stable links of primarily disulphide bridge of the amino acid cystine, great insolubility, and resistance to mild acid or alkali. The ever-depleting vegetable and mineral tannin material agents as a result of overdependence, encourages the search and use of synthetic tanning materials (syntans) despite their increasing cost.
Work had been done elsewhere in the utilization of waste keratinous materials in preparing modifier for phenolic plastics (Knitzinger, 1953), adhesives (US Pat. App. 20090069541, 2009), livestock feed (Furiong, 1953). as well as flavoring agent in consumable products like human hair and food ingredients (VeggieBoards - Vegetarian Forum, 2005). This guides the use of the protein material as reinforcing filler in the attempt to eradicate the waste generated by damaged skins so as to give an additional value added beam house processing product output.

2. Experiment

2.1 Materials
Skins were obtained from a local abattoir in Zaria, Kaduna State, Nigeria. They skins were unhaired, sundried and treated differently by having (1) untanned, (2) Vegetable tanned (3) chrome tanned (4) veg-chrome tanned. The skins were cut into small pieces of about 10mm then ground into powder using a Thomas mill model 4. 10%

Methanol stabilized Formalin, Ammonia Solution, Urea and Ammonium Chloride were all bought from BDH Ltd, Pool, England. A Carver hydraulic press (compression molding machine) was obtained from G. D. Carver Ltd, USA. A Thomas Wiley Laboratory Mill, Model 4. Tensometer type 'N' series number 9875, by Monsanto Tensometer Co., Ltd UK was also obtained and used. The shrinkage test was done at Physical Testing Laboratory College of Leather Technology, Zaria, using a locally adapted experimental set up.

2.2 Method

The urea – formaldehyde (UF) resin, was prepared by reacting the methanol stabilized formalin and urea in a mole ratio of 1:2 at a controlled pH of 8 using ammonia solution. An initial temperature of 30^{o}C was maintained for 40 minutes initiating conditioning and dissolution of the urea. The temperature was then increased to 70^{o}C and maintained for 60 minutes under reflux. The resin was then concentrated to approximately 40% of its original volume at the end of a cook time of 90 minutes. The reaction was carried out in a 0.5 litre heat-controlled vessel fitted with a reflux condenser and a mechanical stirrer. The pH value of the solution was continuously monitored by an attached pH meter. A predetermined pH value of the initial Formaldehyde was adjusted by the addition of a 0.5M solution of sodium hydroxide. The reaction was considered complete when the water tolerance reached 250% at a cook time of 173 minutes and pH of 9.5. At the end of the reaction, 59 grams of ethanol were added to the reaction solution to help stabilize the reaction. Once the solution cooled to room temperature, the viscosity was measured.

Constant weights of the powdered skin and leather samples were blended with varied quantities of resin and catalyst (based on the weight of pelt). The blends were evenly spread on one half of a pair of flat mould then covered with the other half. The mould was introduced into the press and subjected to a pressure of 25 tons at a temperature of 50^{o}C for 10 minutes to ensure complete cross-linking reaction for the blend. The product was ejected from the mould, cooled and cut into strips for analysis. Keratins was obtained from the unhairing process through controlled alkali hydrolysis, which only disoriented the three dimensional structure and fragmented the peptide linkage and disulphide bonds into relatively unstable thiol (SH) bonds. An uncontrolled and exhaustive hydrolysis produces amino acids like threonine, arginine, serine, cystine and cysteine, destroying the inherent mechanical attributes of the structural protein.

3. Analysis

3.1 Tensile Strength Test

The tensometer was used in the analysis of the tensile strength test as well as the degree of extensibility. The value of the weight of the load at break of sample was noted.

3.2 Shrinkage/Boil Test

The test is done according to standard method (US Pat. App. 20090069541,2000). All corresponding temperatures at start of shrinkage were recorded.

3.3 Moisture Absorption (Relative)

Equal dimension of samples were cut from each of the four product classes and the values recorded before immersion in water for 24hrs. The strips were re-measured and re-weighed after 24hrs and the difference gave the degree of water absorbed by the individual strips of leather samples.

3.4 Percentage Elongation at Break

Record was made during the tensile analysis, of the initial lengths before and final lengths at break and the difference was expressed as a percentage of the initial length.

3.5 Statistical Analysis

Results obtained were expressed as mean values of six tests and statistically analyzed for significance in variations between sampling stations. The t-test was used for variations between various keratin treatment and the sheaths using openstat written by William G. Miller 18th September, 2008.

4. Results

See tables and figures below

5. Discussion

The high values observed by the chrome and veg-chrome tanned samples over the vegetable tanned and the sample with any form of tanning could be attributed to possible binding of the keratin materials to the ionic chromium and the collagen molecule due to the acidic and basic polar amino acids (Ofoegbu *et al.,* 2000) constitution and this initiates the observed good thermal stability of these leather samples. Analysis of variance results revealed no significant difference in elongation and breaking loads among materials studied with different keratin concentrations. An indication that changes in keratin concentrations could have influence on the strength of material (elongation and breaking load) in the same manner. Similarly, significant variations were found between different treated materials as regards to their strength with some few exceptions showing no significant

difference. Apart from the binding with the collagen material, the controlled alkali hydrolysis of keratinous materials yields a good number of polar carboxylic amino and other functional groups with the sulphur atom/molecule which are made accessible by the peptides of the keratin. The plausible disulphide linkages make possible products with good thermal and high shrinkage temperature values. Figures 1 and 2 showed remarkable differences in the values of relative moisture absorption, this is as a result of the initial processing of the skin with different tanning agents and as is expected, the chrome tannage gives a better bond interlocking than the veg-chrome followed by vegetable and least of all the untanned. But this result is a better end product from earlier works where the keratinous material was not used (Ofoegbu *et al.,* 2000), showing the remarkable improvement in this property (moisture absorption resistance) with the incorporation of the soluble keratin material. It is evidenced that reasonable results (moisture absorption resistance) can be obtained with incorporation of only 16% keratinous substance with little or no difference when values above 16% and below 21% are used. This tells us that with a little amount of this material, a very high degree of moisture/water absorption result can be obtained from this recycled materials making them a worthwhile value-added products.

It was observed that the keratinous materials, even with exposure to the atmosphere, stayed stable for as long as 4-5 months, this is explained by the fact that during the formation of cross-links, the reactive groups of the collagen polypeptide chain (-OH, -COOH, $-NH_2$) were rendered uncreative by the bonds between –OH groups of the syntan, prompting the formation of various cross-links that aided in the polypeptide chain stabilization. This crosslinks formed prevented attack from bacteria or other micro organisms. From the two figures, it is seen that the Keratin filler sample yielded better results than the Syntan samples. This could be as a result of the Keratin filling the intermolecular spaces more efficiently, giving it higher resistance to water. Also the quantity of Keratin needed to have the same result is lower compared to that of the syntan sample.

Figures 3 and 4 showed that the average shrinkage temperature differed remarkably from one sample to the other with the untanned skin having the least values. This is a direct effect of the extent and degree of tannage evidently supported by the chrome tanned, having the highest 70^{o}C and keratin concentration 16% and the untanned skin with only keratin added giving a good value of 67.5^{o}C, which is a higher value when compared with earlier stated result of untanned skin having 64.3^{o}C (Sehgal *et al*., 1984). This shows the extent of the binding and filling of the skin by the keratinous protein that was added depicting an increase in level of tannage of about 1.5% over the untanned material without the keratin incorporation.

Figure 5 shows that the Chrome tanned has a highest breaking load followed by the Chrome-Vegetable and then the Vegetable tanned. This could be as of the cross linking between the material and the tanning material.

Figure 6 shows that the untanned skin has a higher elongation than the tanned one. This means that the tanned ones are brittle. The values obtained from the moisture absorption tests gives a general understanding that the incorporation of the syntan and keratinous compound improves the ability of these sheaths to resist the penetration of water molecules into the inter layers of the recycled products. The plausible explanation is obtained from the understanding that the syntan enhances the degree of tannage and presents a closely knitted web of interlocked functional groups while the keratinous mass ultimately fills up any residual space and being oleophillic in nature, resists the penetration and retention of moisture/water molecules from entering the sheath matrix. The high values observed by the chrome and veg-chrome tanned samples over the vegetable tanned and the sample without any form of tanning could be attributed to possible binding of the keratin materials to the ionic chromium and that a collagen molecule has both acidic and basic polar amino acids and this will lead to the binding of the polar groups of the keratin to these polar amino acids, initiating the observed good thermal stability of these leather samples. Apart from the binding with the collagen material, there is the evidence that controlled alkaline hydrolysis of keratinous materials, a good number of polar carboxylic amino and other groups with the sulphur atom/molecule, are made accessible by the peptides of the keratin.

As shown on Table 1, significant positive correlation ($p < 0.01$) was found between keratin concentration and untanned skin elongation, mild positive correlation between keratin concentration and vegetable tanned elongation. Negative correlation were observed between keratin concentration and other parameters studied, except that breaking load of chromed tanned and vegetable-chromed tanned are significant ($p < 0.01$). Positive correlations between keratin concentrations and parameters could indicate its influence on material strength (elongation) of untanned skin and vegetable tanned skin, though more in untanned skin. While negative correlation between keratin concentrations and parameters could explain the non-effect of change in keratin concentrations on strength of materials (elongation and breaking load) studied. Also, as shown on Table 2 significant positive correlations ($p < 0.01$) were found between keratin concentration and shrinkage temperature of materials studied. Significant negative correlations ($p < 0.05$) were observed between keratin concentration and water absorption of materials studied. Positive correlations between keratin concentrations and materials could indicate its influence on material strength (shrinkage temperature) of the studied materials. Negative correlation between keratin concentrations and parameters could explain the non-effect of change in keratin concentrations on water absorption capacity of studied materials

6. Conclusion

From the results obtained, it is feasible to cumulatively recycle cast-offs from the leather industries into useful materials for the construction industry. These products have properties that are of encouraging dispositions and diverse utilities. This technology will enhance the profit margin of the leather industry, creating jobs for smaller industrial sectors in areas like particle boards, acoustic panels and top coatings while eliminating the unwanted wastes that are generated by the processing of hides and skins giving a cyclebility status to this industry. More research is continuing in the area of recycling these leather cast-offs for other different end uses and we hope in the nearest future, the technology will be perfected and made simpler for the small and medium enterprises.

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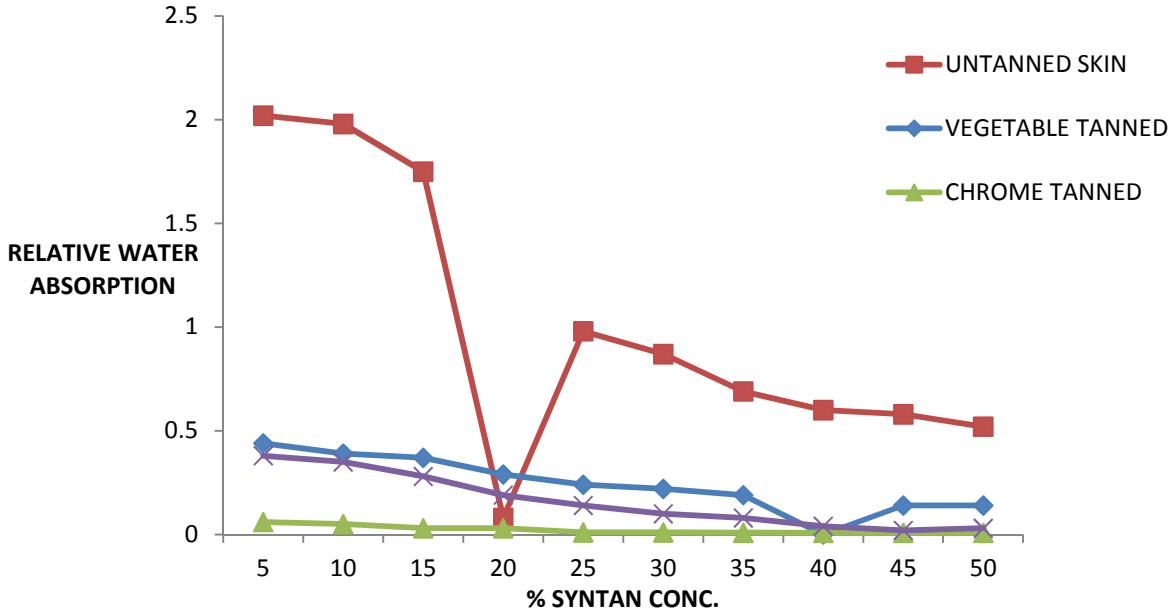

Figure 1. Graph of Relative Water Absorbed by Sample as against the Concentration of Keratin used

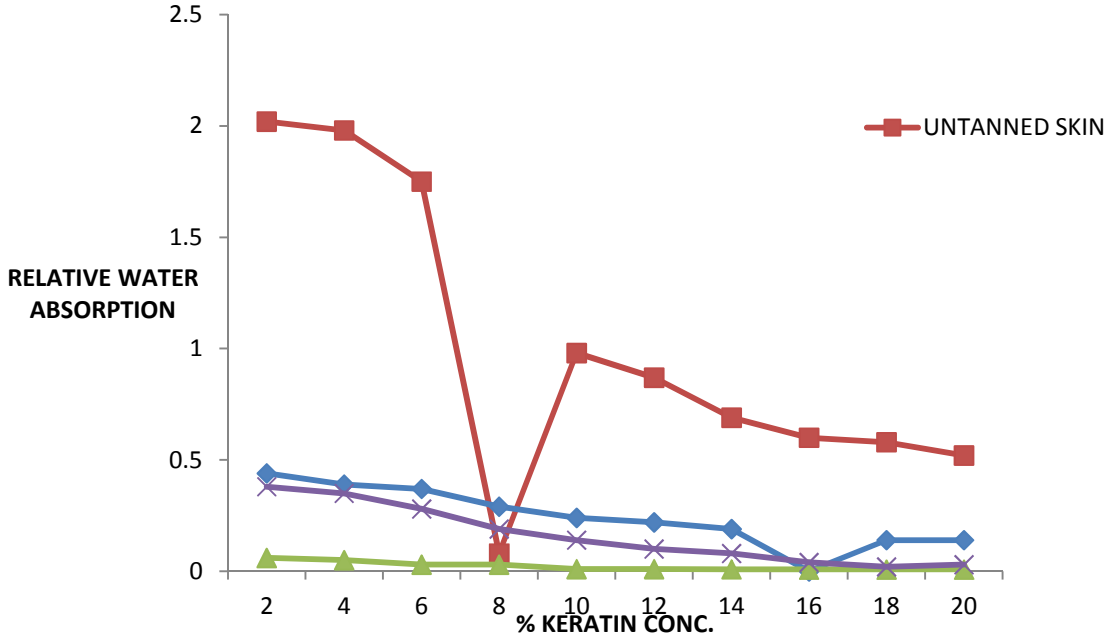

Figure 2. Graph of Relative Water Absorbed against the Concentration of Keratin Filler

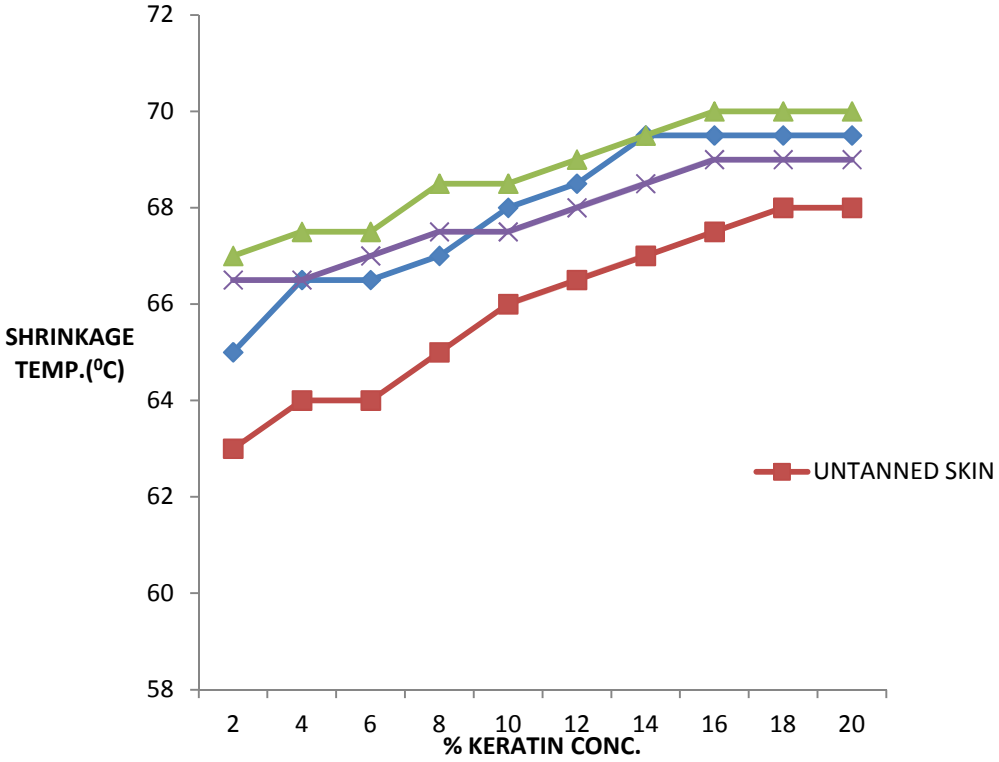

Figure 3. Shrinkage Temperature Relative to % Syntan Concentration

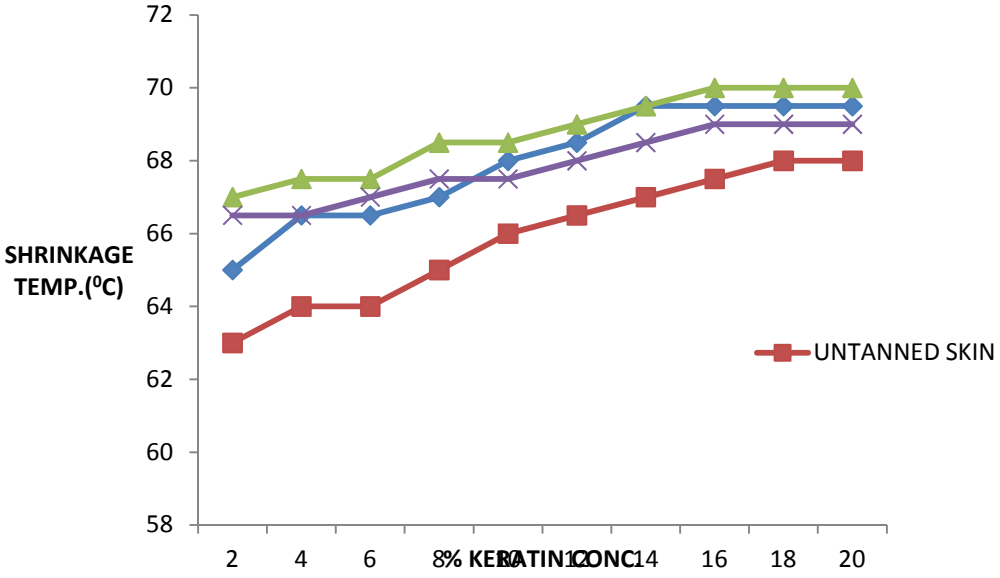

Figure 4. Shrinkage Temperature Relative to % Keratin Concentration

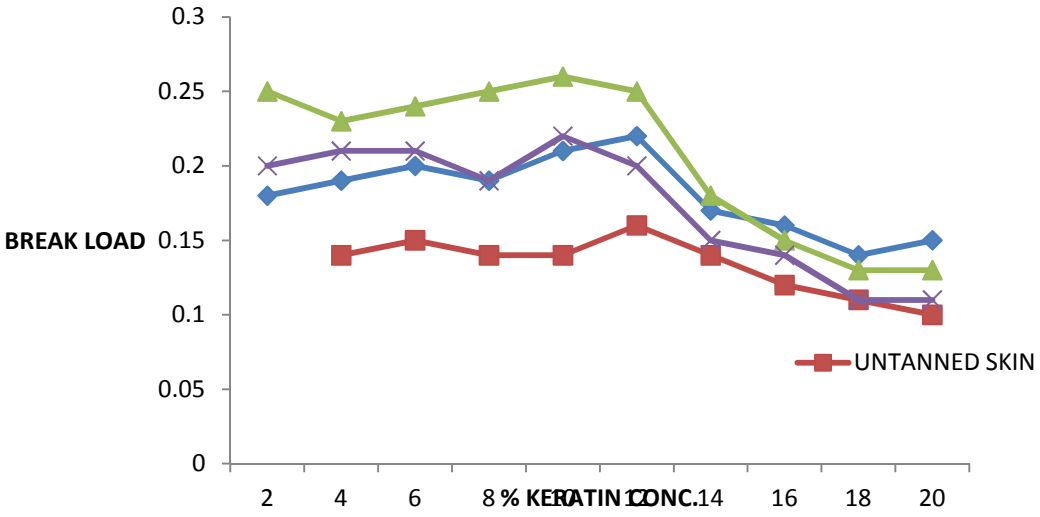

Figure 5. Effective Amount of Load at Break against % Keratin Concentration

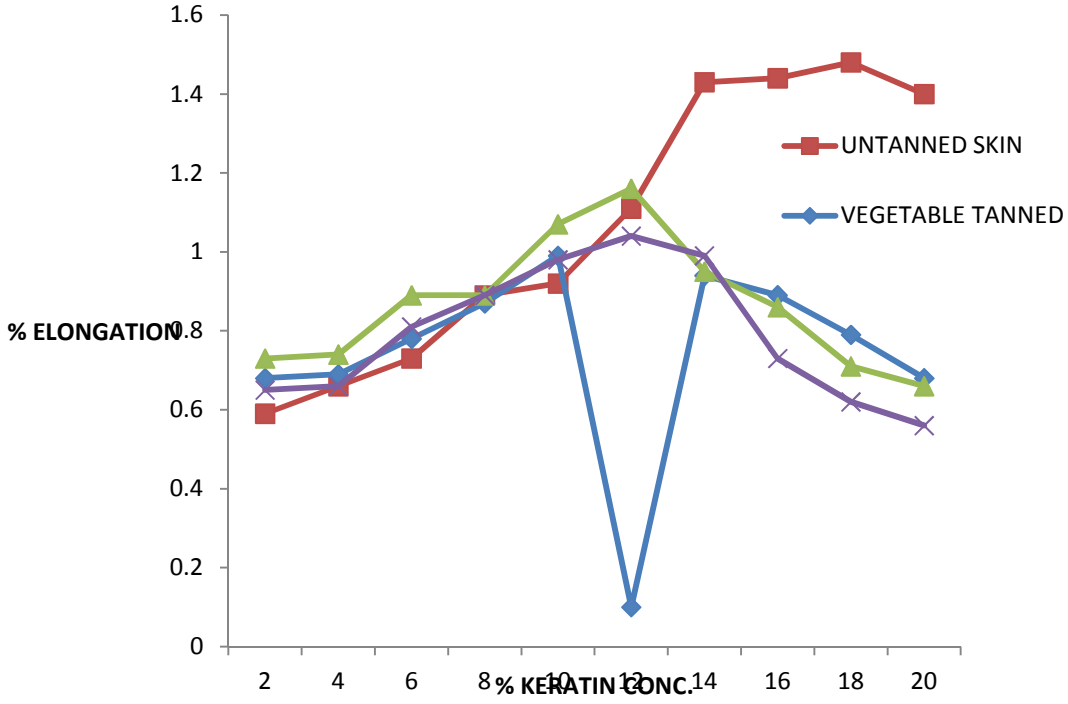

Figure 6. % Elongation against % Keratin Concentration

Table 1. Statistical correlation between % keratin used, material elongation and breaking load is as shown below

Parameters	VAR1	VAR2	VAR3	VAR4	VAR5	VAR6	VAR7	VAR8	VAR9
VAR1	1.000								
VAR2	0.959**	1.000							
VAR3	0.042	0.098	1.000						
VAR4	-0.081	-0.036	-0.268	1.000					
VAR5	-0.120	-0.034	-0.121	0.953	1.000				
VAR6	-0.522	-0.474	-0.086	-0.294	-0.290	1.000			
VAR7	-0.614	-0.642*	-0.370	0.764**	0.706*	-0.014	1.000		
VAR8	-0.839**	-0.844**	-0.201	0.543	0.545	0.282	0.912**	1.000	
VAR9	-0.864**	-0.868**	-0.149	0.508	0.484	0.215	0.911**	0.968**	1.000

**Significant at $p < 0.01$
* Significant at $p < 0.05$

KEY FOR TABLE 1:
VAR 1: KERATIN CONCENTRATION (%)
VAR 2: % ELONGATION UNTANNED SKIN
VAR 3: % ELONGATION VEGETABLE TANNED
VAR 4: % ELONGATION CHROME TANNED
VAR 5: % ELONGATION VEGETABLE-CHROME TANNED
VAR 6: BREAKING LOAD UNTANNED SKIN
VAR 7: BREAKING LOAD VEGETABLE TANNED
VAR 8: BREAKING LOAD CHROME TANNED
VAR 9: BREAKING LOAD VEGETABLE-CHROME TANNED

Table 2. Statistical correlation between %keratin used, shrinkage temperature and relative water absorbed by samples.

Parameters	VAR1	VAR2	VAR3	VAR4	VAR5	VAR6	VAR7	VAR8	VAR9
VAR1	1.000								
VAR2	0.985**	1.000							
VAR3	0.955**	0.983**	1.000						
VAR4	0.977**	0.987**	0.971**	1.000					
VAR5	0.980**	0.973**	0.952**	0.988**	1.000				
VAR6	-0.744*	-0.763*	-0.732*	-0.813**	-0.778**	1.000			
VAR7	-0.975**	-0.995**	-0.978**	-0.986**	-0.971**	0.815**	1.000		
VAR8	-0.865**	-0.902**	-0.919**	-0.867**	-0.855**	0.750**	0.927**	1.000	
VAR9	-0.964**	-0.983**	-0.967**	-0.977**	-0.969**	0.832**	0.995**	0.944**	1.000

**Significant at $p < 0.01$
* Significant at $p < 0.05$

KEY FOR TABLE 2:
VAR 1: KERATIN CONCENTRATION (%)
VAR 2: SHRIKAGE TEMPERATURE UNTANNED SKIN
VAR 3: SHRIKAGE TEMPERATURE VEGETABLE TANNED
VAR 4: SHRIKAGE TEMPERATURE CHROME TANNED
VAR 5: SHRIKAGE TEMPERATURE VEGETABLE-CHROME TANNED
VAR 6: REL. WATER ABSORPTION UNTANNED SKIN
VAR 7: REL. WATER ABSORPTION VEGETABLE TANNED
VAR 8: REL. WATER ABSORPTION CHROME TANNED
VAR 9: REL. WATER ABSORPTION VEGETABLE-CHROME TANNE