

# Natural Rubber - Leather Composites

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**Abstract:** Leather is a fibrous protein consisting of collagen in a three dimensionally crosslinked network. Chrome tanning of leather improves the appearance of leather but at the same time emits both solid and liquid chrome leather wastes. Scrap rubber recycling using untreated and neutralized leather fibrous particles in natural rubber has been studied. Vulcanization, mechanical, morphological and swelling properties of the natural rubber – scrap rubber composites containing neutralized leather have been discussed. Use of chrome leather particles has been found to improve the consumption of scrap rubber powder in natural rubber formulations. Polymer composites based on leather wastes as fillers are reported to be useful for many applications such as in construction materials, automobile interior moldings, heat and sound insulating boards, shoe soles, flooring materials and moldings with good anti-static properties, air permeability and good appearances.

**Keywords:** *Leather waste, neutralization of leather, scrap tyre, rubber recycling, natural rubber, polymer composites.*

## Introduction

Scrap tyres and other waste rubber products poses two major problems such as wastage of valuable rubber materials and disposal of worn-out tyres mainly leading to environmental pollution. Various approaches of scrap rubber recycling including retreading, reclaiming, landfilling, incineration, pyrolysis, ultrasonic devulcanization, application in road pavement by asphalt modifications and reuse as a filler in plastics and rubber compounds has been studied. Scrap rubber is used for extending the virgin rubber compounds, reducing the cost of the rubber compounds and minimizing the raw fresh elastomer requirements. In rubber formulations the amount of consumption of scrap rubber is very low and the use of ground scrap rubber, as fillers in rubbers have been widely studied<sup>[1-2]</sup>. Addition of scrap rubber even at low concentration to a virgin rubber compound adversely affects physical properties. If a rubber compound incorporating more than 50% of scrap rubber with good physical properties and were of low cost, there would be many rubber product development can be achieved and an effective utilization of scrap rubber. Mixing of scrap rubber above 50% with virgin natural rubber has been found to be very difficult and physical properties also drops significantly. To overcome this problem, waste leather has been used to improve the physical properties and to solve the problem of incorporation of scrap rubber with virgin natural rubber.

Leather is a natural polymer consisting of collagen fibers crosslinked in a three dimensional structure. Chrome leather tanning results in improved appearance, physical properties and chemical and biological resistance to leather but the process leads to emission of solid and liquid wastes into the environment. The entire leather operations such as

trimming, shaving and cutting result with more than 50 % of the raw hide being rejected as waste. Processing of one ton wet salted hide yields only 200 kgs of leather but over 600 kgs is rejected as solid waste<sup>[3]</sup>. Of the total waste, more than 50 % is considered as potentially hazardous because of the presence of the chromium. An important consideration is the possibility of the oxidation of trivalent chromium to hexavalent chromium, which is considered to be even more hazardous<sup>[4]</sup>.

When waste leather fibers are added to elastomers, the former could function as short fiber reinforcement for the matrix provided the inherent fibrous nature of the former is retained during processing. Since processing of elastomers is carried out relatively at high temperatures, retention of the fibrous nature in leather under such conditions however is very difficult. It is therefore prudent to use and consider the leather waste in the particulate form and study its effectiveness either as filler or as a processing aid in elastomer formulations. Use of leather in rubber formulations is then bound to affect the vulcanization characteristics and vulcanizate properties of the rubber significantly as it is a biomaterial with many reactive functional groups present in it, apart from large quantities of trivalent chromium. Natural rubber - scrap rubber vulcanizates containing untreated leather particles reduces the vulcanization characteristics and mechanical properties of the compound, but improves the incorporation and higher amount of loading of scrap rubber. In order to improve the vulcanization characteristics and mechanical properties, leather particles are neutralized to remove its acidic nature. In this present investigations the effect of neutralized leather particles on the vulcanization, mechanical, morphology and swelling properties of natural rubber - scrap rubber composites has been investigated.

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## Experimental

### Preparation of neutralized leather particles and compounding with rubber

Waste chrome leather shavings, obtained from a local tannery, contains Chromium 2.5 % and Nitrogen 11.21 %. The untreated leather fibers were dried at 100 °C for 15 minutes in an air oven and after cooling to ambient temperature, they were shredded into fine particles. The untreated leather particles were used in natural rubber – scrap rubber composites in our earlier work<sup>[5]</sup>. The untreated leather particles were acidic in nature which would interfere with the vulcanization of rubber compound. To overcome the acidic nature, 1% solution of urea, aqueous ammonia and sodium bicarbonate were used separately as neutralizing agents. After neutralization, the leather particles were separated by filtration and the excess water was removed. The resultant cake was dried in sunlight for 2 days followed by drying in a hot air oven at 100 °C for 15 minutes.

Compounding was done on a laboratory scale two roll rubber mixing mill (Santosh Model, Mumbai) as per the base formulation given as follows: Natural rubber (RSS Grade) - 100 phr, neutralized chrome leather particles 100 - phr, scrap rubber of 40 mesh particle size -100 to 600 phr, Zinc oxide – 10 phr, Stearic acid - 4 phr, dibenzothiazyl disulphide (MBTS) - 3 phr, Tetra methyl thiuram disulphide (TMTD)- 2 phr and N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) – 2 phr, aromatic process oil- 20 phr and Sulphur- 5 phr were used for compounding. Scrap rubber and neutralized leather powders were mixed uniformly and homogeneously by a tumbling process and kept ready for further use. Natural rubber was masticated and after a smooth band was formed on the mill, the scrap rubber-leather particles mixture with process oil was added followed by the addition of antioxidant, zinc oxide and stearic acid. After complete mixing and band formation were ensured, accelerators and sulphur were added finally. Appropriate nip gaps were maintained and 3/4<sup>th</sup> cuts were made during the mixing process in order to get uniform compound quality.

### Testing

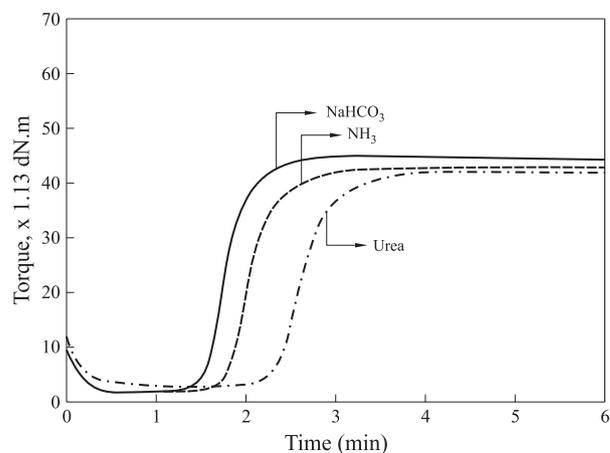
Vulcanization characteristics of the compounds thus developed were measured at temperatures of 140 °C and 150 °C, using an Oscillating Disc Rheometer (Monsanto ODR-2000 Model). Tensile sheets for the evaluation of mechanical properties were compression molded using a 40 ton hydraulic press at 140 °C for their optimum cure time, as obtained from the Rheometer. Mechanical properties of the moulded specimens were measured according to ASTM D 412 and ASTM D 624 standards, using a Computer controlled Shimadzu precision Universal Testing Machine at a cross-head speed of 500 mm/min. Shore A hardness of the vulcanizates was measured in a Durometer according to ASTM D 2240. Morphological studies were carried out for the cryo-fractured vulcanizates, after gold coating the specimens, using a scanning electron microscope (JSM 840A,

JEOL, Japan). Swelling ratio, expressed as % weight, was determined in toluene, water and 0.5% NaOH after immersing the vulcanizates in the medium for equilibrium swelling. The crosslink density was measured using Flory-Rhener equation<sup>[6]</sup>.

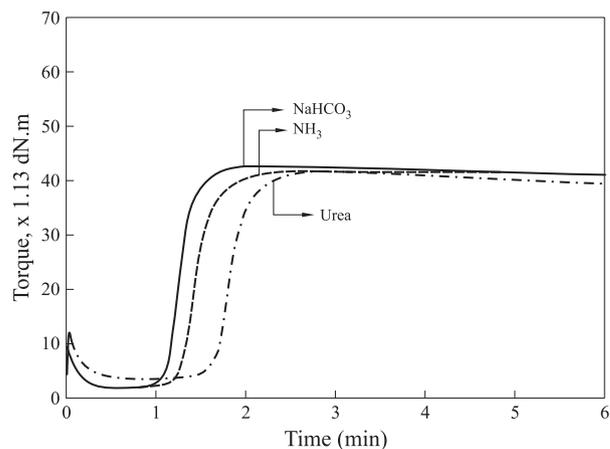
## Results and Discussion

### Vulcanization studies

Vulcanization characteristics for natural rubber-scrap rubber compounds containing neutralized leather wastes at 140 and 150 °C are shown in Figures 1 and 2 respectively. The measurements have been carried out for a period of 6 minutes based on previous experiments. From Figure 1 it can easily be seen that significant improvement in the vulcanization characteristics as evident from the increase in the maximum torque obtained for compounds containing neutralized leather wastes. As expected, neutralization of leather has made more curatives available for the curing process of the rubber phase thereby resulting in maximum torque values and higher cure rate with a corresponding reduction in the scorch time. Sodium bicarbonate treated leather has shown maximum torque value than ammonia and



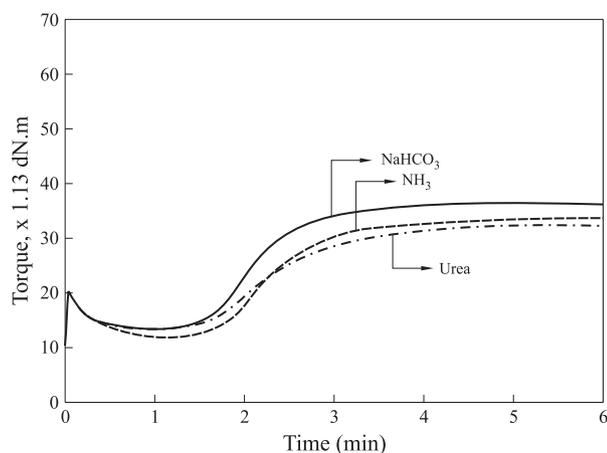
**Figure 1.** Effect of neutralized leather on vulcanization characteristics of scrap rubber (100 phr) compounds at 140 °C



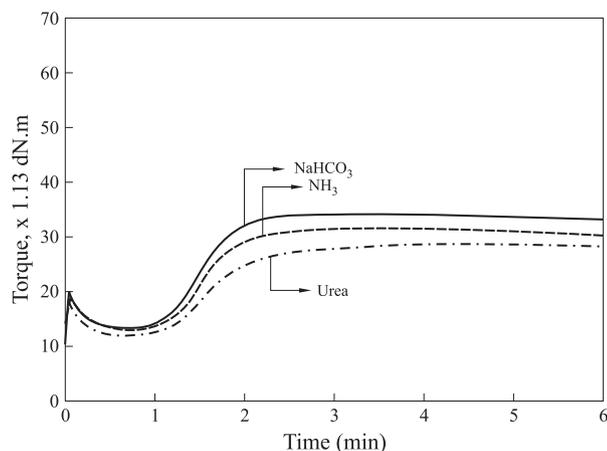
**Figure 2.** Effect of neutralized leather on vulcanization characteristics of scrap rubber (100 phr) compounds at 150 °C

urea treated leather compositions when compared with the untreated leather compounds.

When the vulcanization temperature of the compounds is increased to 150 °C, considerable amount of reversion can be observed as shown in Figure 2. Reversion occurs approximately after 4 minutes for all the treated leather compounds. Though neutralization has improved the vulcanization rate and imparted better modulus characteristics, reversion is more or less unaffected when compared with the compounds containing untreated leather wastes. When the quantity of scrap rubber is substantially increased to 500 phr, the maximum torque values are found to be considerably reduced even in the presence of treated leather wastes although the minimum torque values are found to increase as can be seen from Figures 3 and 4. While the reduction in the maximum torque can be attributed to the dilution effect of large quantity of scrap rubber with respect to the curatives the increase in the minimum torque in these compositions is simply due the physical stiffening effect of the scrap rubber of large quantity on the matrix before the onset of vulcanization. This is reflected in the poor mechanical properties of the composites as the scrap rubber loading is increased. Large quantities of scrap rubber results in poor flow characteristics of the rubber



**Figure 3.** Effect of neutralized leather on vulcanization characteristics of scrap rubber (500 phr) compounds at 140 °C



**Figure 4.** Effect of neutralized leather on vulcanization characteristics of scrap rubber (500 phr) compounds at 150 °C

compound as indicated by the higher initial viscosity of the compound. The basis for increasing the loading of scrap rubber to as high as 600 phr for 100 parts of virgin natural rubber is due to the fact that, in the absence of leather, incorporation of scrap rubber beyond 400 phr has been found to be very difficult while preparing the compounds. Though it has been possible to increase the scrap rubber loading up to 600 phr, the compounds containing more than 600 phr are not included in the present work because of very poor vulcanization characteristics and mechanical properties. However, in presence of leather, large quantities of scrap rubber, even up to 800 phr, could be incorporated into just 100 parts of virgin natural rubber. Leather therefore facilitates the incorporation of scrap rubber into the virgin matrix without any difficulty.

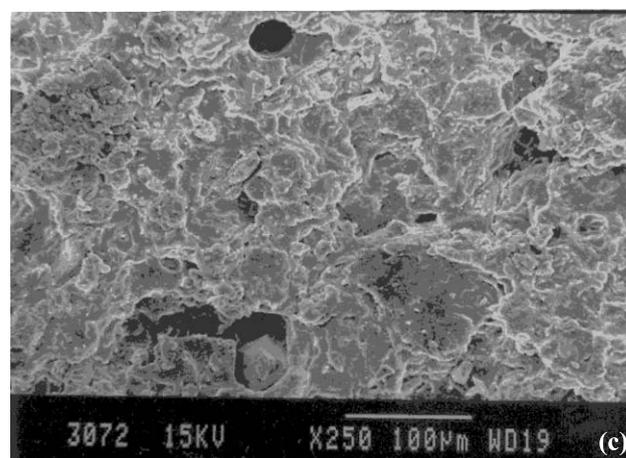
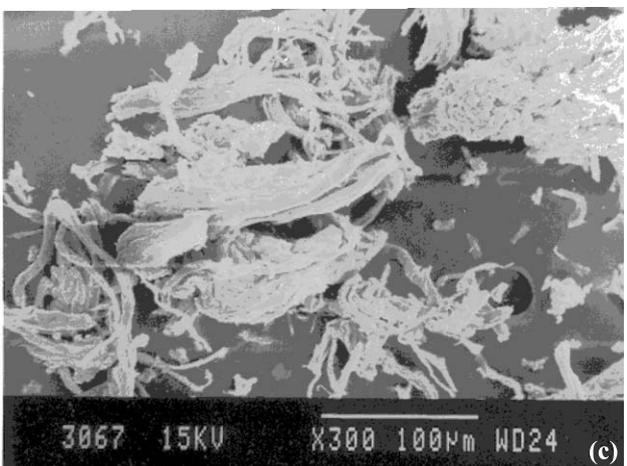
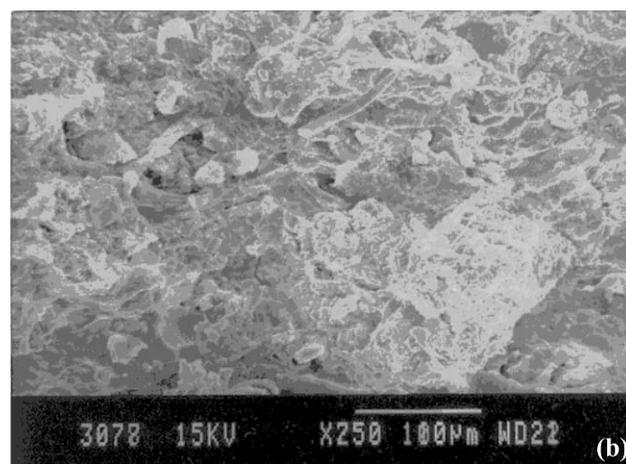
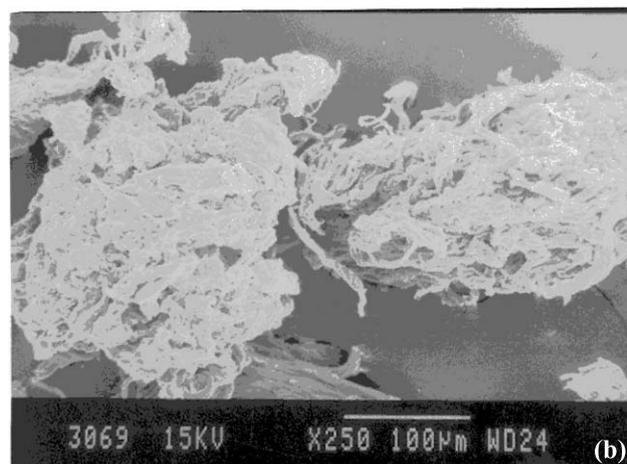
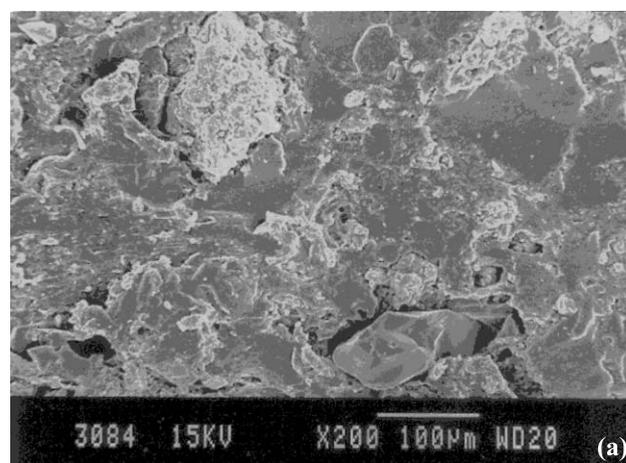
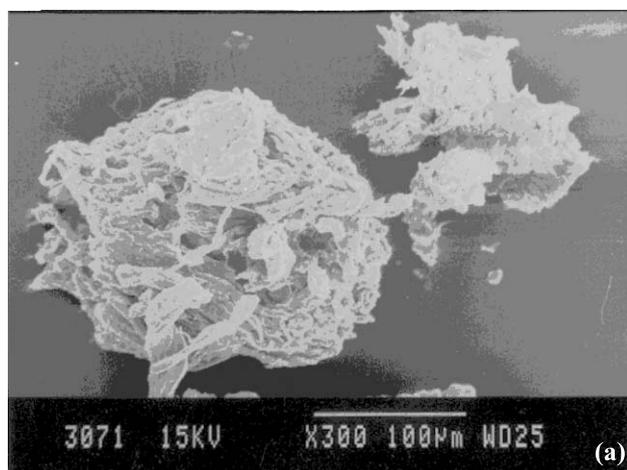
### SEM studies

The SEM micrographs of the neutralized leather particles with sodium bicarbonate, ammonia and urea are shown in Figures 5a, 5b and 5c respectively. The opening-up of the knitted structure is more evident when the shredded particles are treated with various neutralizing agents. The opened-up leather morphology is desirable as it could help in improving its mechanical interlocking with rubber matrix apart from improving the dispersion. The shredded form of leather, even after neutralization, appears to retain much of its fibrous structure to a major extent.

The SEM micrographs of natural rubber – scrap rubber vulcanizates containing sodium bicarbonate, ammonia and urea treated leather particles are presented in Figures 6a, 6b and 6c respectively. In case of the vulcanizate containing sodium bicarbonate treated leather, an improvement in adhesion between the matrix and the particles could be seen from Figure 6a though there appears to be some amount of de-bonding and fractured surface of the leather particles. Dispersion of leather particles in the rubber phase has been found to be good in both the cases as can be seen from the diffused boundaries between the leather particles and the matrix. The relatively opened-up leather particles are also found to exist as a continuous phase along with the matrix. In these cases the leather particles could have dispersed well while mixing and fused well during vulcanization at high temperature and pressure. The better dispersion and fusion characteristics could be attributed to the relatively spongy nature of the neutralized leather particles.

### Mechanical properties

The effects of neutralization of leather particles with sodium bicarbonate, ammonia and urea and scrap rubber loading on the mechanical properties of the natural rubber vulcanizates are shown in Table 1. Vulcanizates containing neutralized leather have exhibited significant improvements in mechanical properties when compared with those containing untreated leather. Improved mechanical properties can be directly attributed to better cure characteristics of the compounds and the increased crosslink density in the final



**Figure 5.** Morphology of: a) Sodium bicarbonate treated leather; b) Ammonia treated leather and c) Urea treated leather

vulcanizates. The increase in crosslink density could explain the relatively lower elongation at break values of the vulcanizates containing neutralized leather than those containing the untreated ones. Better dispersion of the neutralized leather particles in the rubber matrix and higher interaction of the opened-up leather structure with the matrix could be other important factors for the improved mechanical properties.

**Figure 6.** Morphology of natural rubber-scrap rubber vulcanizates containing: a) Sodium bicarbonate treated leather; b) Ammonia treated leather and c) Urea treated leather

When compared with bicarbonate treated leather particles, ammonia treated leather particles have been found to be ineffective in improving the mechanical properties of the final vulcanizates. On the other hand urea treated leather is found to impart best mechanical properties than sodium bicarbonate and ammonia treated leather containing compositions. Among the three neutralizing media, ammonia being the strong base might have washed away a large quantity of the low molecular

**Table 1.** Mechanical properties of natural rubber-scrap rubber vulcanizates containing neutralized leather particles

Neutralized leather	Scrap rubber (phr)	Tensile Strength (MPa)	Elongation at Break (%)	100% Modulus (MPa)	Tear Strength (N/mm)	Hardness (Shore A)
Sodium bicarbonate	100	5.16	100	4.99	25.5	78
	200	5.22	152	4.36	28.4	74
	300	5.32	174	3.93	28.6	72
	400	5.50	193	3.81	28.9	70
	500	5.73	210	3.36	29.8	68
	600	4.50	182	3.24	26.7	65
Ammonia	100	4.85	135	4.35	24.1	76
	200	5.08	180	4.14	24.3	73
	300	5.17	194	3.99	25.0	69
	400	5.21	196	3.57	25.5	67
	500	5.26	200	3.21	26.5	66
	600	4.53	185	3.19	25.8	65
Urea	100	5.40	184	4.49	26.08	64
	200	6.71	269	3.64	26.48	58
	300	6.66	254	3.27	27.45	55
	400	6.01	224	3.00	28.59	54
	500	5.84	226	2.97	27.88	53
	600	5.72	230	3.20	26.58	52

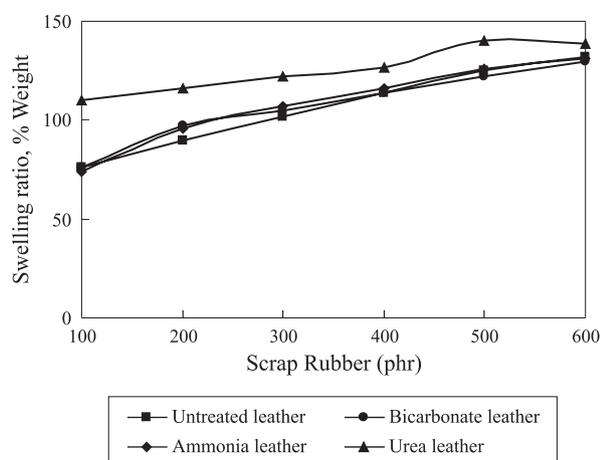
weight leather fractions, which are essential for strong adhesion between the matrix and the reinforcement. Absence of this fraction could be one of the reasons for the inferior mechanical properties of ammonia treated leather composition when compared with sodium bicarbonate or urea treated leather. Urea could interact with leather by making strong bonds with the many functional groups available in leather. Urea at the other end can also interact with large number of residual rubber chemicals present in scrap rubber thereby forming a strong interface between the matrix and the leather.

### Swelling analysis

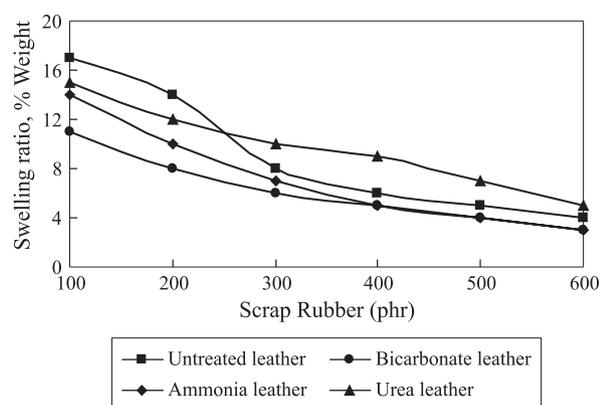
Water plays an important role on the properties of leather as with other proteins. Earlier studies on water vapor absorption<sup>[7]</sup> indicate that within the range of water uptake which is possible from the vapor phase, the affinity of water uptake for collagen is not diminished by chrome tanning. Both hide and leather become brittle and unpleasant to touch if the water present in the system is completely removed. During vulcanization at high temperatures, some of the water molecules present in the leather fibers would be completely removed. Since leather is known for its excessive swelling in aqueous media, it would be of great interest to study the

swelling behaviour of vulcanizates containing leather. In organic solvents, however, the swelling would be controlled by such factors as the number of cross-links in the vulcanized elastomer, nature of the solvent and polymer and polymer-filler interaction. Swelling behaviour of rubber vulcanizates containing large quantities of scrap rubber in presence of leather assumes significance because, swelling studies could reveal the type of transformation that might have taken place during consolidation at high temperature and pressure.

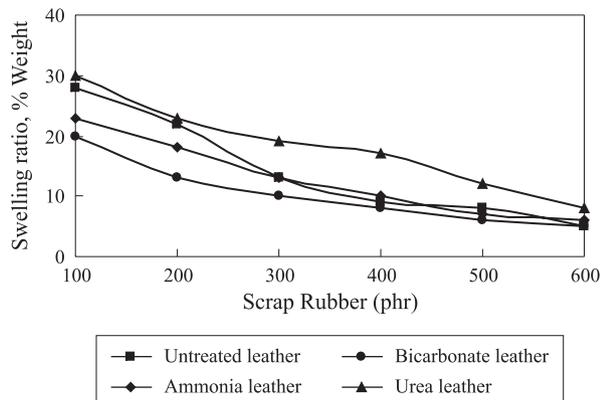
The swelling behaviour of natural rubber – scrap rubber vulcanizates containing both untreated and neutralized leather particles in toluene, water and NaOH are shown in Figures 7, 8 and 9 respectively. When sodium bicarbonate and ammonia treated leather particles are incorporated, the swelling ratio values in toluene are found to be relatively lower than the corresponding compositions containing untreated leather. This can be attributed to the better cross-linking that could have taken place in the rubber phase due the loss of acidic nature of leather. This is further evident from the fact that the crosslink density values of vulcanizates containing sodium bicarbonate treated leather are marginally higher when compared with the vulcanizates containing untreated leather. Interestingly, ammonia, being a relatively strong base, has resulted in lower



**Figure 7.** Swelling behaviour in toluene for natural rubber-scrap rubber vulcanizates containing leather



**Figure 8.** Swelling behaviour in water for natural rubber-scrap rubber vulcanizates containing leather



**Figure 9.** Swelling behaviour in NaOH for natural rubber-scrap rubber vulcanizates containing leather

crosslink density values when compared with the bicarbonate treated or even untreated leather. As majority of the low molecular weight fraction of the leather could have been dissolved in ammonia and washed away, contribution to the physical cross-linking among the leather particles is minimized. Also, these low molecular weight fractions could very well act as bridges connecting the leather particles and the matrix. Since they have been washed away with ammonia, poor adhesion results between the matrix and the leather particles. This leads

**Table 2.** Effect of scrap rubber loading on crosslink density of natural rubber-scrap rubber vulcanizates in the presence of leather

Scrap rubber (phr)	Crosslink density ( $10^{-4}$ gm mol/cc)			
	Untreated leather	NaHCO <sub>3</sub> leather	Ammonia leather	Urea leather
100	3.0	3.0	3.2	1.6
200	2.2	2.0	2.1	1.4
300	1.9	1.8	1.7	1.3
400	1.5	1.4	1.4	1.2
500	1.3	1.3	1.3	1.1
600	1.2	1.2	1.2	1.1

to an increased swelling in toluene associated with an overall reduction in the crosslink density values for vulcanizates containing ammonia treated leather (Table 2). As a neutralizing agent for leather, urea has been found to be inferior when compared with sodium bicarbonate and ammonia. This is evident from the relatively higher swelling ratio of vulcanizates containing urea treated leather when compared with those of bicarbonate and ammonia treated leather particles. This can be best understood from the fact that urea treated leather has resulted in lower maximum torque values in the Rheometer analysis which is also supported by the lower crosslink density values (Table 2).

Swelling ratio values for vulcanizates in water and sodium hydroxide are presented in Figures 8 and 9 respectively. Though water is an integral part of leather, when the latter is combined with large quantities of scrap rubber and consolidated through the vulcanization process, the interaction and subsequent swelling of leather in water is considerably reduced because of the essentially hydrophobic nature of the rubber matrix. Even in the presence of very high rubber content, high swelling ratio of the vulcanizates in sodium hydroxide is an indication that leather can still interact strongly with aqueous media, especially under alkaline conditions, though is an integral part of the composite. Thus in the vulcanizates, presence of rubber restricts the swelling of leather in aqueous media whereas the swelling of rubber in an organic medium has been considerably reduced by the presence of leather thereby offering a synergistic resistance to swelling to the vulcanizates.

## Conclusion

Suitably neutralized leather wastes can assist the addition of large quantities of scrap rubber into a virgin rubber matrix without affecting the vulcanization characteristics seriously. The natural rubber-scrap rubber compositions containing treated leather could be processed safely in the temperature range of 140 - 150 °C without much reversion in the matrix. Morphological studies of treated leather particles have revealed a loosely bound structure when compared with the closely knitted fibrous structure of the untreated leather. The

treated leather particles when combined with large quantity of scrap rubber in the presence of small quantity of virgin natural rubber is found exist as a continuous phase in the rubber matrix with a diffused boundary with the matrix. Mechanical properties of natural rubber-scrap rubber vulcanizates containing neutralized leather particles is found to impart better vulcanizate properties when compared with the vulcanizates containing only scrap rubber and untreated leather particles. These vulcanizates have exhibited considerably reduced swelling in toluene and a marginal increase in swelling in aqueous environments. Neutralization of leather particles, in general, has further reduced the swelling of the vulcanizates both in organic and aqueous media. The mutual restriction of swelling of the elastomer matrix by the presence of leather and vice-versa are an indication of the existence of co-continuous morphology in these vulcanizates.

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