

Recycling of Chrome-Tanned Leather Waste in Acrylonitrile Butadiene Rubber

Salwa H. El-Sabbagh,¹ Ola A. Mohamed²

¹*Polymer and Pigments Department, National Research Center, Cairo, Egypt*

²*Chemistry of Tanning Materials and Leather Technology Department, National Research Center, Cairo, Egypt*

Received 27 February 2010; accepted 31 October 2010

DOI 10.1002/app.33692

Published online 25 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Chrome-tanned leather waste generated in huge amount from leather industry causing environmental problem; this leather waste was used as filler in acrylonitrile butadiene rubber before treatment and after treatment with ammonia solution and sodium formate. Different formulations of acrylonitrile butadiene rubber/leather waste (untreated–treated with ammonia solution—treated with sodium formate) composites are prepared. The formed composites exhibit a considerable improvement in some of their properties such as rheometric characteristics especially with composites loaded with treated leather waste. Tensile strength, modulus at

100% elongation, hardness, and Young's modulus were improved for composite loaded with treated leather. Crosslinking density in toluene was increased by the incorporation of leather wastes treated or untreated resulting in decreases in swelling equilibrium. Distinct increase in the ageing coefficient and the thermal stability for composites loaded with both treated and untreated leather. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 979–988, 2011

Key words: leather waste; rubber (NBR); recycling; thermal stability; mechanical properties

INTRODUCTION

Leather is a natural polymer consisting of collagen fibers crosslinked in a three-dimensional structure; the conventional leather tanning results in improved appearance, physical, chemical, and biological properties of leather. At the same time, this industry is highly polluting as it produces large amounts of organic and chemical pollutants. Wastes generated by the leather processing industries pose a major challenge to the environment, according to conservative estimates, about 600,000 tons per year of solid waste are generated worldwide by leather industry, and ~40–50% of the hides are lost to shavings and trimmings.

Everyday, a huge quantity of solid waste, including trimmings of finished leather, shaving dusts, hair, fleshing, trimming of raw hides, and skins are being produced from the industries. Chromium, sulfur, oils, and noxious gas (methane, ammonia, and hydrogen sulfide) are the elements of liquid, gas, and solid waste of tannery industries.¹ Leather waste management is a global environmental problem, and so

the disposal of municipal solid waste has become an environmental issue of growing concern.²

The management of such waste may be handled through the famous 4Rs, that is, reduction of source, reuse (reutilization), recycling, and recovery. These wastes are partly used, but mainly they are deposited in storage yards or burned in air causing hazards to the environment.³

Many authors and Taylor et al.^{4–6} try to get gelatin from these leather wastes through alkaline and enzymatic hydrolysis. Berry et al.^{7,8} have proposed and interesting to use them as source of chromium III. In previous studies, these wastes were used as filler for nylon 6 and paper making.

It is also possible to use leather waste particles as a filler of polymer. Andreopoulos et al.⁹ have incorporated leather wastes into PVC with dioctyl phthalate as plasticizer. The addition of the leather wastes caused that density and hardness of the composites increased, whereas their tensile properties were considerably deteriorated with the incorporation of leather. Leather dust with silica was used as a filler of PVC.¹⁰

Rubber is one of the most versatile materials of construction being used throughout the world. The rubber industry relies heavily on the use of fillers to improve performance durability and service life of its products. Reinforcement of elastomers enhances properties such as tear strength, abrasion resistance, and adhesion.¹¹

Correspondence to: O. A. Mohamed (olaashraf2000@yahoo.com).

Acrylonitrile butadiene rubber (NBR) is widely used in industry, its main uses in oil seals, tire, and tubes, because it has resistance attack by oils and solvents. NBR has irregular chain structure, that is, amorphous; they do not crystallize when stretched to its ultimate strain and, consequently, NBR is not self-reinforced, and so this type of rubber requires a reinforcing filler to improve its mechanical properties and competitive properties of the vulcanization, and cement dust was used as filler for this purpose.¹²

Chronska et al.¹³ have investigated the addition of the buffing dust to rubber mixes. They concluded that the mechanical properties are improved, and resistance to thermal aging as well as electric conductivity and crosslink density of vulcanizates are increased.

At the institute of polymers and dye technology, studies on utilization of solid chrome-tanned leather wastes were carried out,^{14,15} shavings of chrome-tanned leather have been used to fill rubber such as 1,4-isoprene rubber and carboxylate butadiene acrylonitrile rubber (XNBR), and the obtained biodegradable vulcanization show good usable properties.

The aim of the present work is to evaluate the effect of leather dust waste on the properties of NBR, before and after surface modification of this waste by ammonia, and sodium formate to enhance the surface interaction between the leather dust waste and rubber matrix.

MATERIALS AND METHODS

Materials

Rubber

NBR, acrylonitrile content 33%, Mooney viscosity ML (1 + 4) at 100°C = 45, specific gravity 1.17, and ash content 0.5% (Bayer Chemicals).

Accelerators

N-cyclohexyl L, benzothiazole sulfonamide (CBS); pale gray; nonhygroscopic powder; melting point 95–100°C; and specific gravity 1.27–1.31.

Antioxidant

N-isopropyl *N'*-cyclohexyl paraphenylene diamine; purple gray flakes have density 1.17 g/cm³.

Curing agent

Sulfur pale yellow powder of sulfur element; purity 99.9%; melting point 112°C; specific gravity 2.04–2.06.

Activator

Zinc oxide; fine powder, purity 99%; specific gravity 5.6; stearic acid: melting point 67–69°C; specific gravity 0.838.

Filler

Chrome-tanned leather wastes supplied by local tannery located in Misr-Elkadima region, Cairo, Egypt.

All rubber ingredients were fine chemicals imported from Aldrich Company.

METHODS

Treatment of leather dust

Chrome-tanned leather wastes were subjected to multistage of disintegration to prepare leather dust and then sieved through 0.2 mesh to have the same size. Leather dust produced divided into three equal parts: first part was untreated, second part treated with 1% ammonia solution, and third part treated with 1% sodium formate to overcome the acidic nature of dust. After neutralization, the dust particles were separated by filtration, the resultant dust dried at room temperature for 2 days, then in oven for 15 min, and then added with different ratios to rubber matrix.

Techniques

Rubber ingredients were accurately weighted and mixed on a laboratory size two roll mill (diameter 470 mm and width 300 mm) at friction ratio 1 : 1.4, speed 16 rpm. The rubber was mixed with ingredients including leather wastes with different ratios (2, 4, 6, 8, and 10%) according to ASTM (D 15-72; 2007) under careful control of temperature, nip gap, and sequence of addition of ingredients. The rubber formulations of composites were presented in Table I.

Vulcanization was carried out in a single-daylight electrically heated autocontrolled hydraulic press at 162°C ± 1°C and pressure 4 MPa. The compound rubber vulcanization was tested according to standard methods:

- ASTM D 2084-07; 2007 for determination of rheometric characteristic using a Monsanto Rheometer model 100.
- ASTM D 412-06, ASTM D 624-07; 2007 for the determination of physicomechanical properties using Zwick Tensile Testing Machine (model-1425).
- Thermal oxidative ageing was carried out according to ASTM D 573 (2007).
- Thermogravimetric analysis: thermal analysis of treated and untreated samples was carried out from 50 to 450°C under nitrogen atmosphere at heating rate 10°C/min with TGA Perkin–Elmer.
- Swelling was determined according to ASTM method D 471-06 (2006). It was possible to make use of the swelling data to calculate the

TABLE I
Formulations of the Composites

Ingredients	Ratio (%)	Phr
NBR	89.681	100
Stearic acid	1.79	2
Zinc oxide	4.48	5
CBS	1.35	1.5
<i>N</i> -isopropyl <i>N'</i> -cyclohexyl paraphenylene diamine	0.9	1
Sulfur	1.79	2
Leather	0, 1.76, 3.46, 5.1, 6.69, 8.23	0, 2, 4, 6, 8, 10

average molecular weight between two successive crosslinks (M_c) by the application of the well-known Flory–Rehner equation.^{16,17}

The crosslinking density can be calculated as

$$\text{Crosslinking density} = 1/2M_c$$

$$1/2M_c = -\frac{1}{2\rho V_0} \frac{[\ln(1 - V_R) + V_R + \mu V_R^2]}{(V_R^{1/3} - 1/2V_R)}$$

where ρ is the density of rubber, V_0 is the molar volume of swelling solvent absorbed (toluene $V_0 = 106.3$ cc/mol), and V_R is the volume fraction of the swollen rubber that can be obtained from the mass and densities of rubber samples and the solvent. μ is the interaction parameter between the rubber and toluene, which is 0.39 for NBR.

- f. Hardness (shore A), this was determined according to ASTM D 2240 (2007).
- g. Scanning electron microscopy, using SEM (JXA-840 A) Electron Probe Micro Analyzer Japan Jeol.
- h. Transmission electron microscope (TEM), using (Jeol JX 1230) technique with microanalyzer electron probe (Germany).

RESULTS AND DISCUSSION

Measurement of particle size of chrome-tanned leather waste

TEM technique was used to determine size of filler particles, and it is known that the particle sizes have got important influence on their dispersion in rubber matrix and consequently on its mechanical properties. Figure 1(a–c) showed particle size of untreated leather waste and that treated with ammonia and sodium formate, it can be observed that size of untreated particles is in the range 68–85 nm; but after treatment, the particle size decreases with obvious ratio and reaches to 39–58 nm for particles treated with ammonia and 5–11 nm for particles

treated with sodium formate. These so-fine particles provide a reinforcing effect seemed as fibers linking the matrix tightly forming more homogenous matrix.

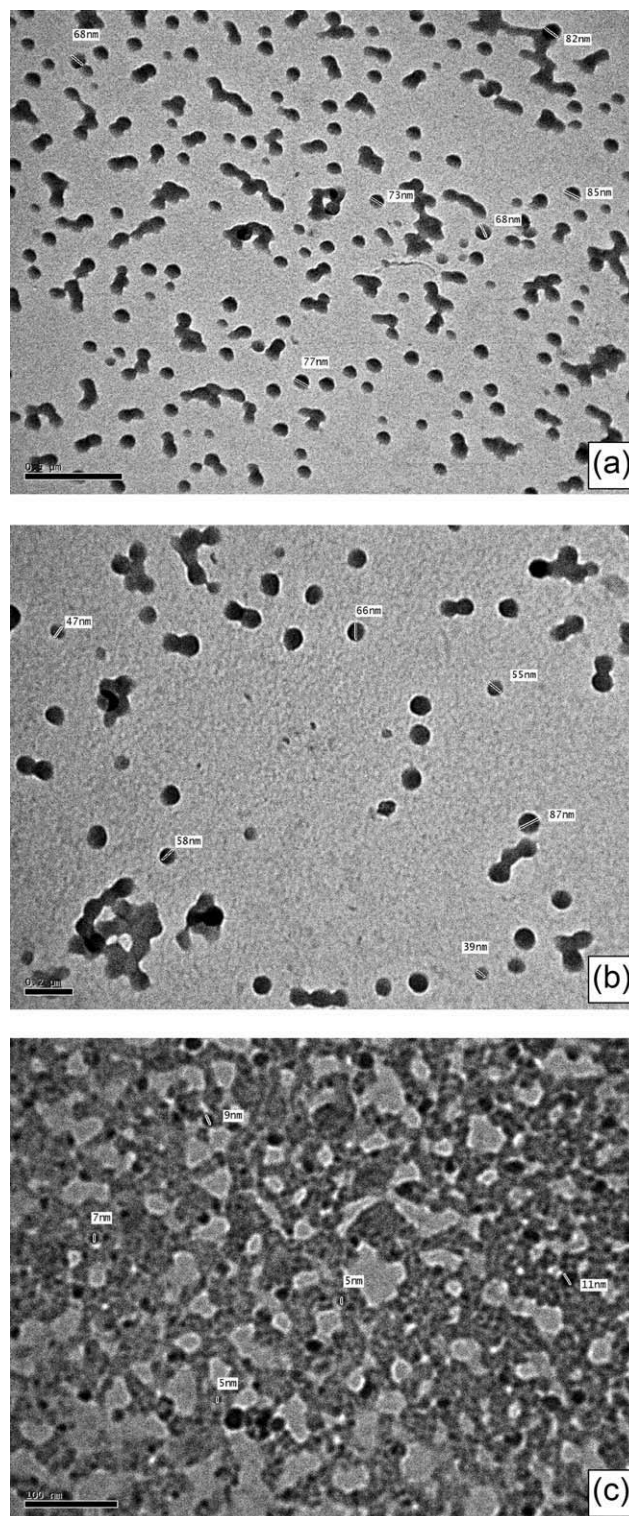


Figure 1 (a) Transmission electron microscope (TEM) for untreated leather waste. (b) TEM for leather waste treated with ammonia. (c) TEM for leather waste treated with sodium formate.

TABLE II
Rheometric Characteristics of NBR/Leather Composites at 425 K (152°C ± 273°C)

Filler content %	M_L (dN m)	M_H (dN m)	T_{c90} (min)	T_{s2} (min)	Curve index (min^{-1})	ΔL (dN m)	α_f
<i>Untreated</i>							
0	5	36	7.75	4.375	29.63	31	–
1.76	3.5	39.5	10.5	4.25	16	36	8.07
3.46	4	46	12.75	3.75	11.11	42	8.87
5.1	4.5	53	12.5	3.75	11.43	48.5	9.4
6.69	4.75	52	10	3.625	15.69	47.25	6.55
8.23	5	49	11	3.375	13.11	44	4.19
<i>Ammonia</i>							
1.76	4	69	7.5	3.5	25	65	54.83
3.46	5	72	10	4.25	17.39	67	29.03
5.1	5.5	77	14.5	3.875	9.412	71.5	21.8
6.69	6	77.5	16	3.813	8.51	71	16.13
8.23	7	78	16	2.25	7.27	71	12.9
<i>Sodium formate (HCOONa)</i>							
1.76	4.5	70	16.5	4.31	8.2	65.5	55.65
3.46	4.75	75	15.25	4.25	9.09	70.25	31.65
5.1	5	76	14.75	4.25	9.52	71	21.5
6.69	7	79	13.5	4	10.53	72	16.5
8.23	7	81	11.75	2.25	10.53	74	13.87

The influence of addition untreated and treated leather on the rheological properties of NBR mixes

Fillers play an important role in the rheological properties of NBR, enhancing favorable physical properties of rubber; it can also modify processing characteristics and reduce cost of the produced compounds. To determine the effect of untreated and treated leather dust wastes on the properties of rubber goods, it is necessary to study the rheological properties of the uncured NBR-containing untreated leather and treated leather wastes and then evaluate the physicomechanical properties of their produced vulcanization. Table II shows the rheometric characteristics of NBR formulations containing different concentrations of leather waste before and after treatments. It is clear that the maximum torque increases with loading for all compositions, and maximum torque (M_H) gives an idea about the shear modulus of a fully vulcanized compound at the vulcanization temperature.¹⁸ This increase in the maximum torque with increasing filler loading is attributed to the presence of filler in the matrix that reduced the macromolecular mobility and consequently increased the torque of the vulcanization.

Comparing the value of M_H for the different treatments, it can be seen that it increases in the order:

Untreated leather < treated with ammonia < treated with sodium formate

This indicates that leather samples treated with sodium formate and ammonia in the NBR/leather composites improved the interaction between the filler and the matrix than the untreated leather, which may cause more effective transfer of the stresses from matrix to filler.

Minimum torque (M_L) is an indirect measure of the viscosity of the compound,¹⁹ the increase in

minimum torque found in these compositions is simply due the physical stiffness of the vulcanized test specimen taken at the lowest point of the curve. Also, the optimum cure time (t_{c90}) increases with filler content up to (5.1%) and decreases; the same trend was observed with curve index.

On the other hand, the rheometric characteristics show that the maximum change in curometer torque during vulcanization increased. The ratio between the increase in torque of loaded (NBR) composite and that of gum (control) was depending on the type of filler. The reinforcing parameter [α_f , the activity of chrome-tanned leather waste (protein filler)] deduced from rheological properties was used to characterize the reinforcement of filler, according the following equation²⁰:

$$\frac{\Delta L}{\Delta L_0} - 1 = \alpha_f \frac{m_f}{m_p}$$

where ΔL is the maximum change in torque during vulcanization for filled rubber (mix with chrome tanned leather waste), ΔL_0 is the maximum change in torque during vulcanization for rubber gum (mix without chrome tanned leather waste), m_f the parts by weights of filler in the compound, and m_p the parts by weight of polymer (NBR). The addition of untreated or treated leather to NBR clearly increases the increment of torque (ΔL); this increase in maximum torque ascribed to the degree of the crosslinking of rubber phase. In other words, the protein of leather cause increases in the crosslinking degree of vulcanization.¹⁵

The calculated values of the activity of chrome leather waste filler (α_f) for all compositions are listed in Table II. It is observed that the values of α_f

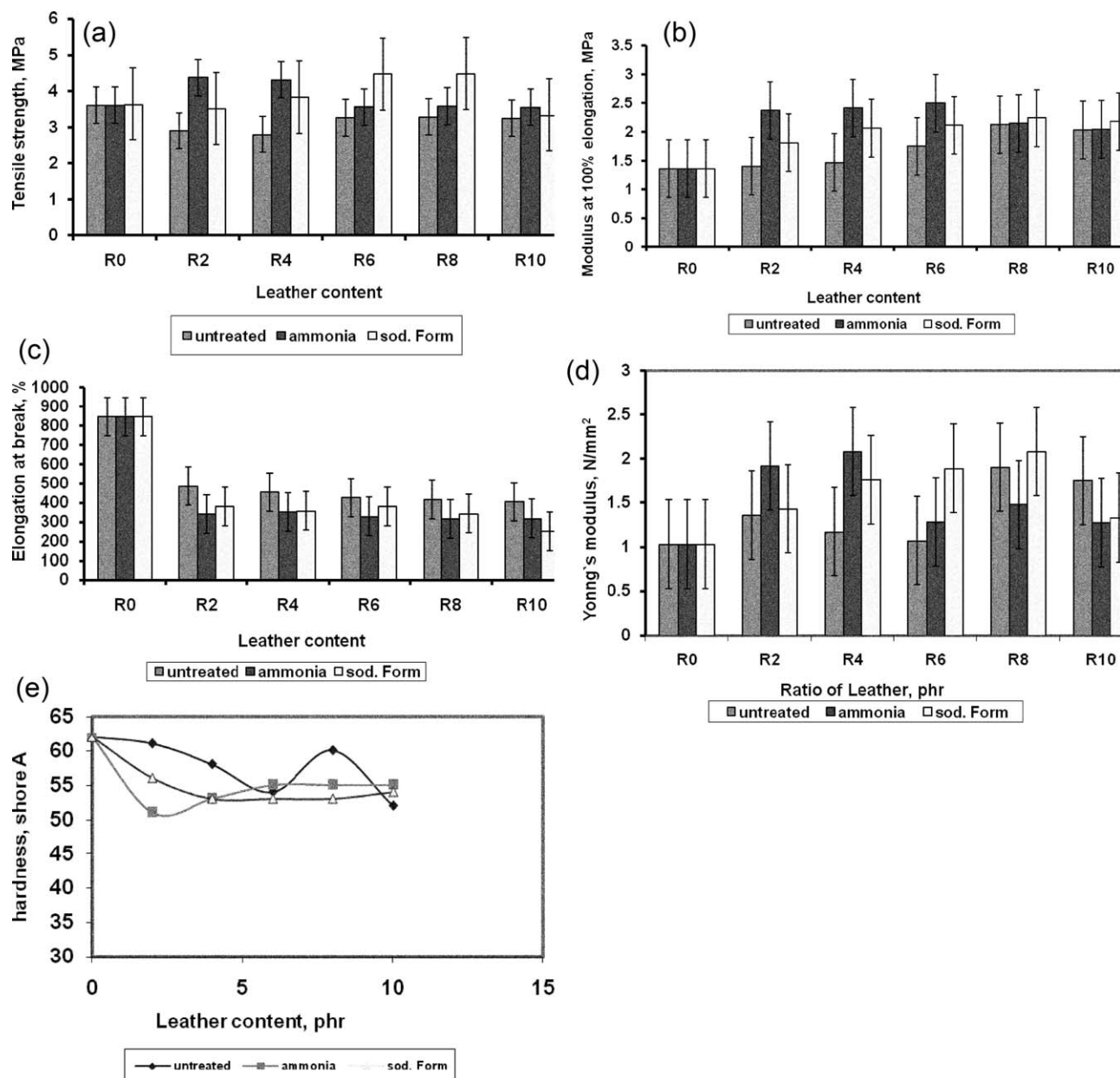


Figure 2 (a) The tensile strength of NBR loaded with untreated and treated leather. (b) The modulus at 100% elongation of NBR loaded with untreated and treated leather. (c) The elongation at break of NBR loaded with untreated and treated leather. (d) The relation between Young's modulus and ratio untreated and treated leather. (e) The value of hardness of NBR loaded with untreated and treated leather.

increase as the concentration of untreated leather increases up to 5.1% and then decrease. The highest value of α_f was found at 1.76% for both treated leather with ammonia and sodium format then decreased. This means that the best ratio was found to be 5.1% for untreated and 1.76% of treated leather.

The influence of addition of untreated and treated leather on the mechanical properties of NBR mixes

Figure 2(a–d) shows the mechanical properties of the composites as a function of leather wastes loading

(0, 1.76, 3.46, 5.1, 6.69, and 8.23%) before and after treatments. The addition of untreated leather wastes with different ratios to NBR decreases the tensile strength until reaching the loading 5.1%, and further loading leads to an approximately constant value. The elongation at break values shows a decrease as untreated leather waste concentration increases; this may be due to the decrease in flexibility resulting from the increase in crosslink density and stiffness. The decrease in tensile strength and elongation at break for untreated leather can be attributed to the interference of leather wastes as filler in NBR chains,

TABLE III
Swelling Characteristics for NBR Vulcanization in Toluene with Untreated and Treated Leather

Leather ratio (%)	Equilibrium swelling (Q_m , %)	Soluble of reaction (%)	Q_f/Q_g	Molecular weight between cross linking M_c (g/mol)	$\nu \times 10^4$ (mol/cc; cross linking density)
<i>Untreated leather</i>					
0	189	1.24	–	2063	2.42
1.76	183	0.92	0.97	1946	2.57
3.46	176	0.78	0.93	1817	2.75
5.1	165	0.54	0.87	1624	3.08
6.69	156	0.48	0.83	1474	3.39
8.23	147	0.66	0.79	1332	3.75
<i>Treated leather with ammonia</i>					
1.76	133	3.07	0.70	1125	4.44
3.46	127	2.41	0.67	1042	4.799
5.1	120.3	2.18	0.64	949	5.27
6.69	120	1.66	0.63	892	5.60
8.23	115	1.41	0.634	948	5.27
<i>Treated leather with sodium formate</i>					
1.76	154	2.67	0.81	1439	3.47
3.46	128	2.2	0.67	1061	4.71
5.1	126.5	1.91	0.66	1041	4.83
6.69	118	1.77	0.62	922	5.42
8.23	116	2.04	0.61	959	5.21

which cause reduction in the mobility of rubber chain. The interference is created through the physical interaction between NBR and leather chain. Also, it may be due to the presence of defect and flaws in composite material compared to control one; also, the tensile strength enhancement for treated leather due to smaller particle size that helps in improvement dispersion of the leather particle of the rubber matrix.

Although the addition of leather wastes treated with ammonia to NBR improves the tensile strength initially (1.76 and 3.46%), then with further loading decreases, and approximately has the same level. In case of leather wastes treated with sodium formate, the tensile properties increase with increasing the leather content up to 6.69% and then decrease. The gradual increase of the tensile strength initially could be attributed to the improvement in the interfacial bonding between leather wastes treated with ammonia or with sodium formate and the rubber matrix.²¹ This is due to the fineness of treated particles allowed them to give more homogenous texture to rubber composites, rendering it with better mechanical properties.

These properties were confirmed by the modulus at 100% elongation, hardness, and Young's modulus (%).

The influence of addition leather waste on equilibrium swelling and crosslinking density of the NBR vulcanization

The equilibrium swelling of the NBR vulcanization containing treated or untreated leather wastes was evaluated to the extent of crosslinking densities. The calculated values of the crosslink density according to Flory–Rehner, equation, are given in Table III. It was

observed that as the ratio of leather waste increase, the equilibrium swelling Q_m decreased while crosslink density increased. On the other hand, the value of equilibrium swelling of composite containing untreated leather is found to be relatively higher than the corresponding compositions containing treated leather, this is attributed to better crosslinking that could have taken place in rubber phase due to the decrease in acid nature of leather. This is further evident from the fact that the crosslink density values vulcanization containing sodium formate-treated leather are marginally higher when compared with the vulcanization containing untreated leather. Although leather wastes treated with ammonia being relatively strong base have resulted in improving crosslink density values when compared with the untreated leather or even sodium formate treated. As the crosslink density increase, the molecular weight of the composite decreases especially for treated leather, this leads to forming bridges connecting the leather particles with the matrix.

Also, it can be seen that Q_f/Q_g decreases with increasing leather content; this may be attributed to some sufficient adhesion between the treated leather and NBR rubber. The lower the Q_f/Q_g values, the higher will be the extent of interaction between leather and rubber matrix (where Q_f is defined as grams of solvent/g of filler and Q_g is defined as grams of solvent/gram of gum rubber).

Scanning electron microscopic studies

Scanning electron microscope offers the simplest investigation procedure, because it reveals surface

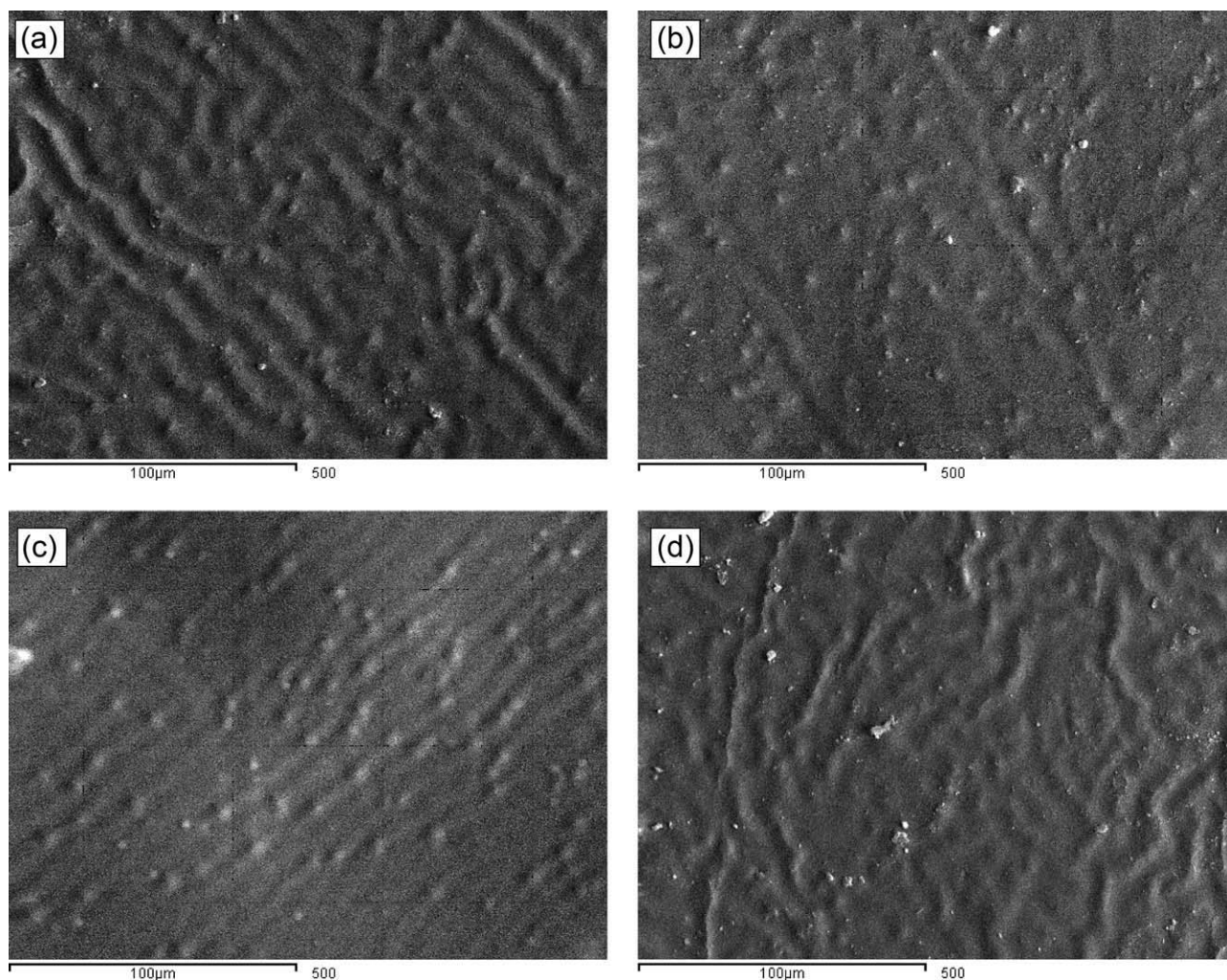


Figure 3 (a) SEM of control by magnification 500 \times . (b) SEM of NBR with untreated leather waste by magnification 500 \times . (c) SEM of NBR with treated leather waste with ammonia by magnification 500 \times . (d) SEM of NBR with treated leather waste with sodium formate by magnification 500 \times .

features.²² Figure 3(a) shows the morphology of NBR vulcanization without addition of leather, and lamellae were obtained resembling cavities irregularly distributed all over the surface. Although in NBR vulcanization loaded with untreated leather, it can be seen that dispersion of the untreated leather particles in the rubber phase resulted in reduction of the number of cavities and cracks. However, the untreated leather dust particles are distributed in scattered planes and seem to have smoother surface with a reduction in the matrix deformation as illustrated in Figure 3(b). On the other hand, the SEM micrographs of NBR vulcanization containing with leather particles treated with sodium formate and ammonia are presented in Figure 3(c,d), respectively. The treated leather particles could have better dispersion, and fusion characteristics attribute to the relatively spongy nature of the neutralized leather particles.

Thermal properties

Effect of thermal oxidative ageing on NBR loaded with leather dust wastes

The properties of rubber mixtures are affected by many factors, and ageing is one of them. The ageing of rubber deteriorates is a physical property, in both operating and storage conditions resulting in cracking, increased tackiness, and hardness. Rubber vulcanization containing different concentrations of untreated and treated leather waste were subjected to thermal ageing at 90°C for various periods up to 7 days. The ageing coefficients (S) are calculated from the tensile strength (σ_R) and elongation (ϵ_R) after and before thermal ageing from the following equation¹⁵:

$$S = \frac{(\sigma_R \times \epsilon_R)_{\text{after ageing}}}{(\sigma_R \times \epsilon_R)_{\text{before ageing}}}$$

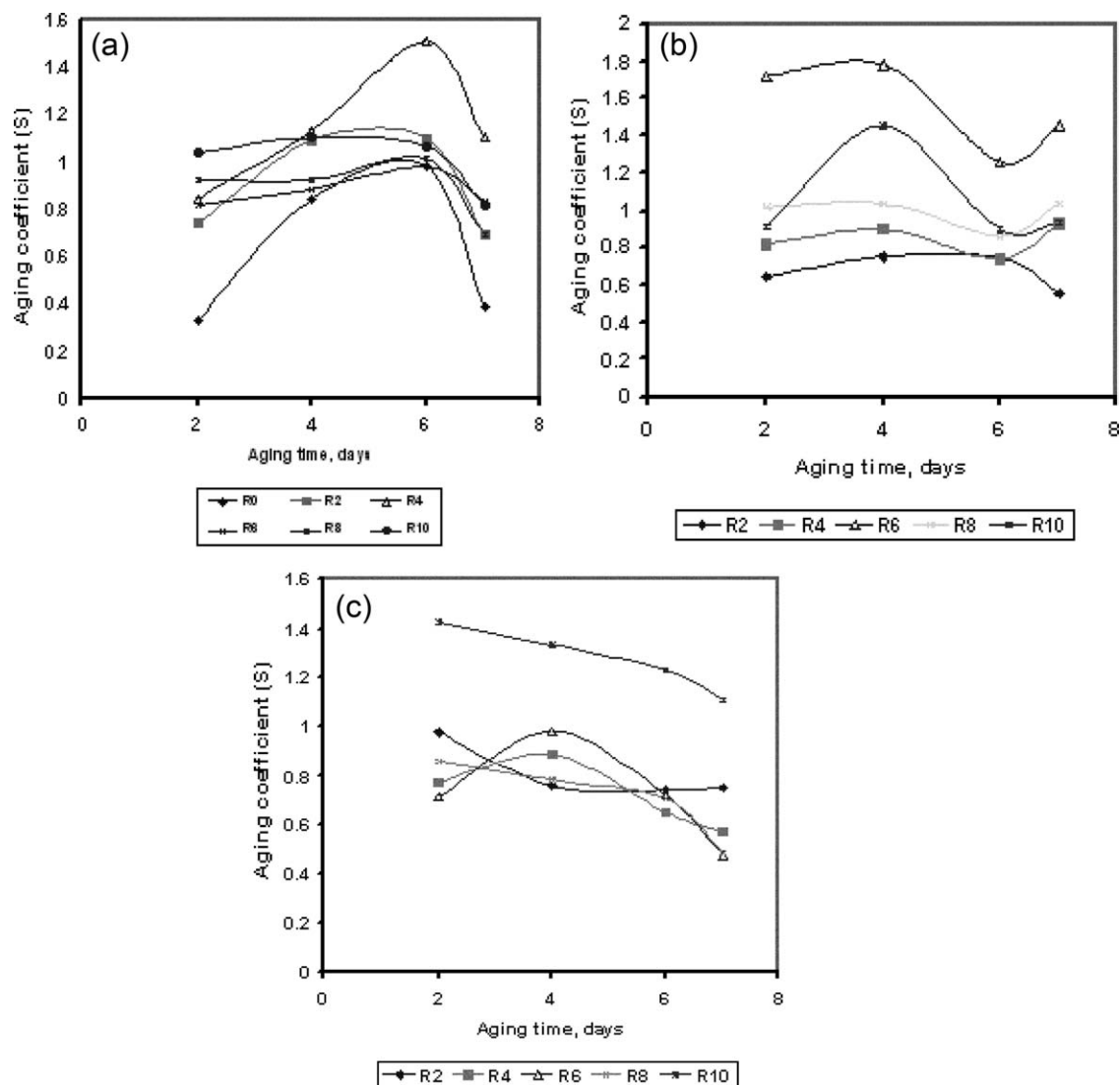


Figure 4 (a) Dependence of the ageing coefficient on the ageing time for NBR/untreated leather composite. (b) Dependence of the ageing coefficient on the ageing time of NBR/treated leather with ammonia. (c) Dependence of the ageing coefficient on the ageing time of NBR/treated leather with sodium formate.

The data are presented in Figure 4(a–c); it can be observed a distinct increase in the ageing coefficient of both rubber samples loaded with treated and untreated leather waste and dropped in NBR vulcanization without leather; control one. The ageing coefficient indicates that there is an increase in thermal resistance of both composite loaded with untreated and treated leather waste, this enhancement in thermal ageing is due to the presence of the leather dust protein crosslinked with chrome.

Thermal gravimetric analysis

TGA has been carried out to evaluate thermal behavior of control one (NBR) and rubber matrix loaded with untreated or treated leather. From Figure 5(a–d), it is clear that the four curves show a measure of one degradation step of the polymer, which normally takes place

via bond scission along the main chain of the polymer (NBR); as seen from the figures, the initial temperature of decomposition has a higher value by adding the untreated or treated leather as a result of crosslinking with chrome, which increases the stability of matrix.

Moreover, as it can be observed from Figure 5(a–d), which by adding leather waste particles treated with sodium formate to rubber matrix, the curve shows a lower slope, suggesting that the degradation process occurs at a broader temperature range, and the rate of this phenomenon is slowed down. The above-described results are summarized in Table IV, in which the matrix degradation temperature and the corresponding on set increase with the addition of leather waste to NBR. On the other hand, some exothermic peaks observed in DTA curve indicate that the vulcanization of rubber or NBR/leather untreated or treated was incompletely cured.²³ There is shift in exothermic

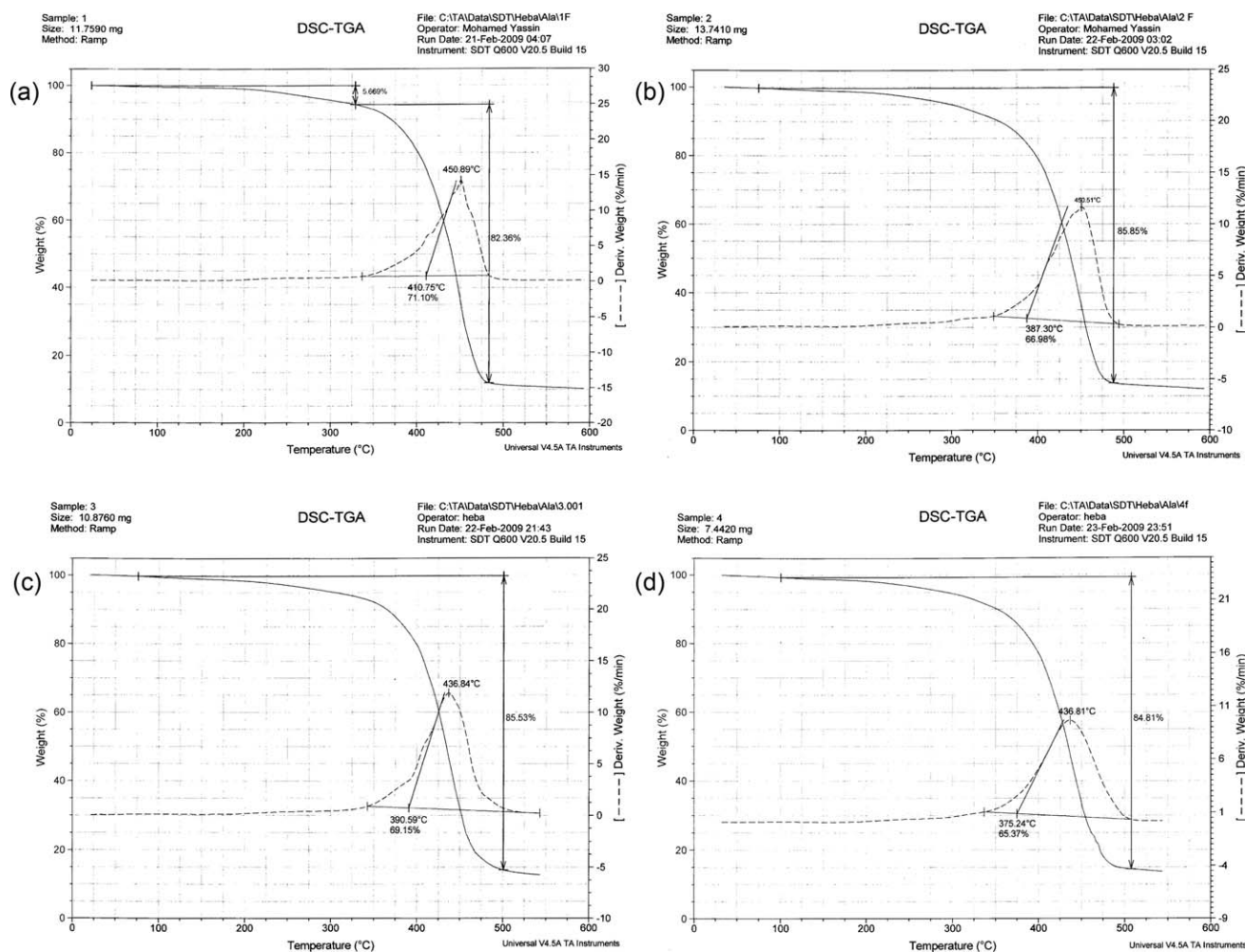


Figure 5 (a) TGA of control. (b) TGA of NBR with untreated leather waste. (c) TGA of NBR with treated leather waste ammonia. (d) TGA of NBR with treated leather waste with sodium formate.

peak after adding (untreated or treated) leather waste to rubber. From the above results, it can be deduced that by adding treated or untreated leather dust to NBR exhibits better thermal stability than NBR alone.

CONCLUSIONS

The above research can be summarized as follows: chrome-tanned leather was disintegrated into dust and

incorporated into NBR before and after neutralization with ammonia and sodium formate solution with different concentrations. The resultant NBR/leather composites showed the following characteristics:

1. Improvement in rheological properties.
2. The physicomaterial studies indicate that the tensile strength and Young’s modulus were affected by the addition of untreated leather dust and that treated with ammonia or sodium

TABLE IV
Main TGA Results

	Transition 1		Transition 2		Loss of weight % at 300°C
	Onset 1	Degradation temp. maximum 1 of DTA	Onset 2	Degradation temp. maximum 2 of DTA	
NBR	330 (5.669%)	350 (7%)	375 (12%)	450 (60%)	11
NBR/untreated leather	275 (3.75%)	300 (5%)	325 (7.5%)	460 (70%)	13
NBR/treated leather/ammonia	287.5 (3.5%)	310 (5.7%)	375 (13%)	455 (65%)	14
NBR/treated leather/sodium formate	125 (6.465%)	175 (8%)	325 (27%)	451 (55%)	37

formate. The initial increase in these properties is due to the enhancement in crosslink density and forming homogeneous composite. The value of tensile strength or rupture strain was decreased with further loading of leather particles.

3. Increase the crosslink density of vulcanization for both treated and untreated leather waste leading to reduction in equilibrium swelling.
4. The composites system shows enhancement in the ageing coefficients, which indicate the resistance of both untreated and treated leather to thermal ageing.
5. Addition of untreated and treated leather dust to NBR exhibited better thermal stability than NBR blank.
6. Leather waste as filler will reduce the cost of final rubber matrix.

References

1. Ravichandran, K.; Natchmuthn, N. *Polimeros* 2005, 15, 12.
2. Wark, D. T. *Blends and Alloys to 200—Structural Performance and Feed stock Implications*, ECM International Conference, Advances in High Performance Polymer Blend and Alloys, May, 1991.
3. Przepiorkowski, A.; Stanczak, M. *Przemyst Chem* 2003, 82, 2.
4. Taylor, M. M.; Diefendorf, E. J.; Thompson, C. J.; Brown, E. M.; Marmer, W. N.; Cabeza, L. F. *J Soc Leather Technol Chem* 1996, 81, 5.
5. Taylor, M. M.; Diefendorf, E. J.; Brown, E. M.; Marmer, W. N. U.S. Pat. no. 5,271,912 (1993).
6. Taylor, M. M.; Kolomaznik, M.; Mladek, M. *J Am Leather Chem Assoc* 2000, 2, 43.
7. Mohamed, O. A.; El Sayed, N. H.; Abdelhakim, A. A. *J Appl Polym Sci* 2010, 118, 446.
8. Ola, A. M.; Nesrine, F. K. *J Appl Polym Sci* 2010, 118, 1713.
9. Andreopoulos, A. G.; Tarantili, P.A. *J Macromol Sci A* 2000, 37, 1353.
10. Panov, A. K.; Minskar, K. S.; IL'ina, T. F.; Panov, A. A. *Int Polym Sci Technol* 2001, 28, 84.
11. Ansarifar, A.; Lim, H. P.; Nijhawan, R. *Int Adhes Adhes* 2004, 24, 9.
12. Hussain, A. I.; El-Sabbagh, S. H.; Abadir, I. F. *J Elastom Plast* 2003, 35, 161.
13. Chronska, K.; Przepiorkowzka, A. *J Hazard Mater* 2008, 151, 348.
14. Chronska, K.; Przepiorkowska, A. *Ann Polish Chem Soc* 2005, 1, 371.
15. Przepiorkowska, A.; Prochon, M.; Zaborski, M. *J Soc Leather Technol Chem* 2004, 88, 223.
16. Parks, C. R. *Rubber Chem Technol* 1982, 55, 1170.
17. Zhang, G. A.; Zhou, M. H.; Ma, J. H.; Liang, B. R. *J Appl Polym Sci* 2003, 90, 2241.
18. Shah, V. *Handbook of Plastic Testing Technology*; Wiley: USA, 1998.
19. Malini, K. A.; Kurian, P.; Ananthraman, M. R. *Mater Lett* 2003, 57, 3381.
20. While, J. R.; Thomas, E. L. *Rubber Chem Technol Rev* 1984, 57, 457.
21. Przepiorkowska, A.; Chronska, K.; Zaborski, M. *J Hazard Mater* 2007, 141, 252.
22. Wolff, S. *Rubber Chem Technol* 1996, 69, 325.
23. Behera, D.; Kar, S.; Banthia, A. K. *Pigment Resin Technol* 2005, 34, 184.