

# Nano-Sized Chalk-Protein Deposits as Filler of Elastomers

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**ABSTRACT:** One of the generally applied filler in rubber industry is commercial chalk—divided calcium carbonate. In aim to prevent from the agglomeration of calcium carbonate particles during mixing with rubber, calcium carbonate is modified. It rely on changing hydrophilic properties on hydrophobic properties acting surfactants as higher fatty acids, their salts, esters, higher aliphatic liquor, vegetable oils, or amine. The aim of present studies was to separate chalk and precipitating degraded proteins and fats about nano-sized from two kind of environmen-

tally noxious tannery effluents which came from processes of liming with degradation of hair structure. Obtained deposits were examined by FTIR spectroscopic, particles size measurements, zeta potential, microanalysis and then these deposits were used as fillers of rubber mixes such as NBR and XNBR. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 800–805, 2009

**Key words:** nano-sized deposits; calcium carbonate; liming processes; nitrile rubber; tannery effluents

## INTRODUCTION

Many tanneries are faced with a serious problem of the utilization of effluents resulting from leather dressing, where the largest part of liquid waste originates from so-called beamhouse, i.e. soaking, unhairing, and liming operations. Despite the implementation of technology with reduced water consumption, the effluents still amount to about 80% of wastewater from all the manufacturing processes.<sup>1</sup>

Most tanneries use the liming process to unhair hides by destroying the hair structure due to a low price of chemicals, good repeatability of results, and easy control of the process.<sup>2</sup> The effluents from the liming process contain two groups of contaminations:

- Organic foulings, mainly products of degradation of non-collagen proteins, proteins of hair, bristle, and epidermis as well as fatty substances.
- Inorganic foulings, mainly lime and calcium compounds, residual chlorides after preservation, sodium sulfide, and sulfates.

A high value of chemical oxygen demand COD (18 330–30 250 mg O<sub>2</sub>/L) and overall nitrogen (1410–5900 mg N/L) content of these effluents give rise of considerable concern.

The aim of the present study was to separate the nano-sized chalk and co-precipitating degraded proteins and fats from these environmentally noxious

effluents and to use the obtained deposit as a filler for rubber mixes that are filled usually with commercial chalk—divided calcium carbonate.

To prevent from the agglomeration of calcium carbonate particles during mixing with rubber, calcium carbonate is modified by changing its hydrophilic properties to hydrophobic by coating its particle surface with surfactants such as higher fatty acids, their salts and esters, higher aliphatic alcohols, waxes, mineral oil, or aliphatic amines. There are also known processes of the reduction of calcium carbonate surface energy in order to facilitate its dispersion in polymers on a polar matrix.

Lipińska et al.<sup>3</sup> have increased the activity of a precipitated calcium carbonate as filler for elastomers by its modification with divalent compounds such as amino acids or unsaturated acids, especially sorbic acid.

Yang et al.<sup>4</sup> have developed a process of “wet layer” to improve the morphology of calcium carbonate particles. The preparation of calcium carbonate nanoparticles in the presence of terpinol has been reported.<sup>5</sup> Wang et al.<sup>6</sup> have obtained nanoparticles of calcium carbonate in the form of argonite and calcite in the presence of polyacrylamide.

Calcium carbonate in the form of hollowed particles were obtained by the interfacial reaction in the presence of polyoxyethylene monooleate surfactant in benzene.<sup>7</sup>

A process for the preparation of calcium carbonate with a unique morphology that allows its use as filler for paints and rubber mixes has been presented by Wei et al.<sup>8</sup> Wu et al.<sup>9</sup> reports on a process for the preparation of calcium carbonate nanoparticle in situ

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in a medium of polymethacrylate, incorporated into epoxyde rubbers.

A process for the preparation of nanofiller to be used in elastomers, especially butadiene-acrylonitrile rubbers or carboxylated butadiene-acrylonitrile rubber, in the form of modified calcium carbonate consists in that the effluents from hide liming or additional liming are utilized to precipitate calcium carbonate being modified by the coprecipitating degradation products of proteins and fats. This process is a subject of patent application<sup>10</sup> and the present study.

### EXPERIMENTAL METHODS

Two types of tanning effluents: gray liming liquors (pH 11.8) from cow hide liming processes combined with unhairing resulting in hair structure destruction and effluents from additional hide liming were used to precipitate deposits 1 and 2 which were then dried at a temperature of 90°C, disintegrated and sieved through a 0.2 mm mesh. The resultant deposits were characterized using the following methods:

- IR analysis, FTIR spectrophotometer, transmission method;
- Elementary analysis of sulfur and nitrogen contents;
- Zeta potential measurement (Zetasizer 2000); pH control with 0.1M NaOH and 0.1M HCl solutions;
- Particles size measurement (Zetasizer Nano S90); prior to measurement samples were treated with ultrasound for 1 h;

The composition of the effluents was determined before and after deposits separation. Table I shows the results for:

- Effluent from cow hide liming processes combined with unhairing resulting in hair structure destruction (Effluent 1).
- Effluent from additional hide liming (Effluent 2).

The analysis of effluents was based on the determination of chemical oxygen demand (COD). COD was determined by the dichromate method (COD<sub>Cr</sub>) according to the standard PN-74/C -04578.03.

The separated deposit from effluents was used as a filler for butadiene-acrylonitrile (NBR, Nipol N41) and carboxylated butadiene-acrylonitrile rubber mixes (XNBR, Krynac X7.50).

On the basis of rheometric tests, was determined the kinetic of rubber mixes vulcanization at a temperature of 423 K according to the standard PN-ISO 3417 : 1994 (vulcameter with an oscillating rotor WG-02). The method rely on measuring the torque

**TABLE I**  
**Analytical Effluents Indicator for Unhairing with Destruction of the Hair Structure before and after Deposits Separation**

	Effluent 1 [mgO <sub>2</sub> /L]	Effluent 2 [mgO <sub>2</sub> /L]
COD before deposit separation	7139.2	28 712
(pH)	(12.00)	(11.77)
COD after deposit separation	6751.2	28 556.8
(pH)	(7.0)	(6.9)

moment as a function of vulcanization time with the shearing strain of a sample caused by the rotor oscillation at a constant frequency and amplitude. The obtained rheometric curves were used to calculate:

- The increase in the torque of mix:  $\Delta L = L_{HR} - L_L$  where,  
 $L_{HR}$  – maximum torque of the rotor [dNm];  
 $L_L$  – minimum torque of the rotor [dNm];
- Optimal vulcanisation time  $\tau_{0.9}$ —time, after which the torque reaches the value:

$$L_{0.9} = 0.9 \Delta L + L_L$$

Vulcanization of the mixes was carried out in a vulcanization mold at a temperature of 423 K for their optimal times ( $\tau_{90}$ ).

The tensile strength of vulcanizates was tested according to the standard PN-ISO 37 : 1998 with a Zwick apparatus, model 1435, before and after aging (72 h at 343 K, PN-88/C-04207).

The equilibrium swelling measurements in water were carried out at a temperature of 298K  $\pm$  1 K for 48 h.

The equilibrium swelling measurements in toluene, toluene, and ammonia vapor were carried out according to the standard PN-ISO 1817 : 2001/ Ap1:2002.

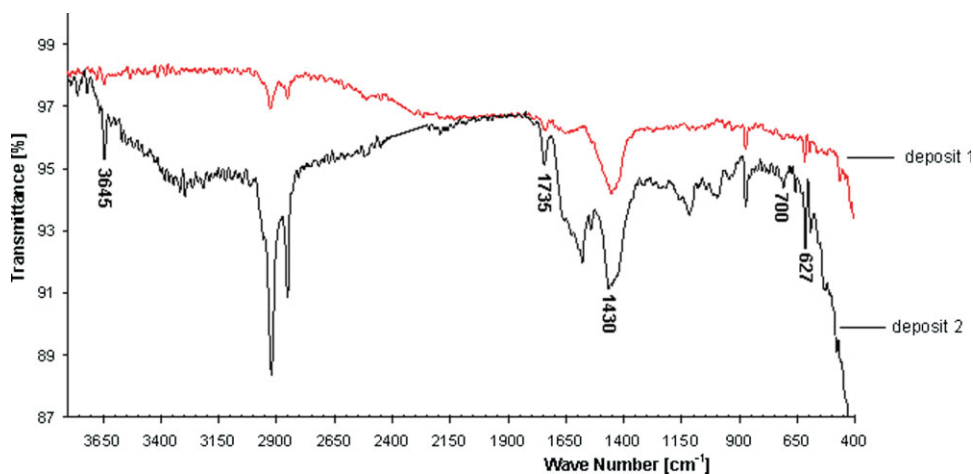
Scanning Electron Microscopy—SEM, Baltek SCDO95 (Sputter Coated) LEO 1530.

### DISCUSSION OF TEST RESULTS

#### IR spectroscopy of the deposits 1 and 2

Knowing the composition of tannery effluents from unhairing with the destruction of hair structure combined with liming, it was expected to find in the deposit calcium carbonate, sulfates, fatty acids, oligopeptides, amino acids and amines. Therefore, there are given wave numbers with characteristic maximum of these compounds<sup>11</sup>:

- An increase in silicone concentration caused an increase in heat stability.



**Figure 1** FTIR spectrums: deposit 1 separated from the gray liming; deposit 2 separated from the white liming. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

- Valence pulsation of C—S, 570–705  $\text{cm}^{-1}$
- Sulfates ( $\text{SO}_4^{2-}$ ), 610–680  $\text{cm}^{-1}$
- Calcium hydrogen carbonate ( $\text{HCO}_3^-$ ), 695–980  $\text{cm}^{-1}$
- Calcium carbonate ( $\text{CO}_3^{2-}$ ), 1423  $\text{cm}^{-1}$
- Fatty acids, 1210–1320  $\text{cm}^{-1}$
- Oligopeptides, peptides, 1485–1560  $\text{cm}^{-1}$
- Salts of amines, 2250–2700  $\text{cm}^{-1}$
- Amino acids, 2360–2640  $\text{cm}^{-1}$

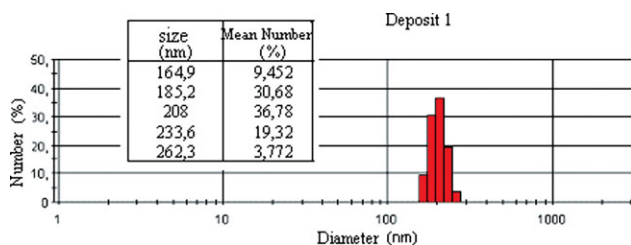
The obtained FTIR spectrums of the separated deposits from the effluents are shown in Figure 1. From the FTIR spectrums of these deposits it follows that they contain calcium carbonate, as shown by the band at wave number 1430  $\text{cm}^{-1}$ . The maximum at wave number 1147 and 1250  $\text{cm}^{-1}$ , derived from stretching vibration of C—O and at wave number 1735  $\text{cm}^{-1}$  being characteristic of stretching vibration of ester groups C=O indicate the presence of fatty products in the obtained deposits. One can also find in these spectrums the vibration of C—S of cystine at wave number 702  $\text{cm}^{-1}$  and of sulfates – a maximum at wave number 627  $\text{cm}^{-1}$ . The presence of these compounds is also confirmed by the sulfur

content: deposit 1 – 1.32% and deposit 2 – 0.33%; found by the elemental analysis.

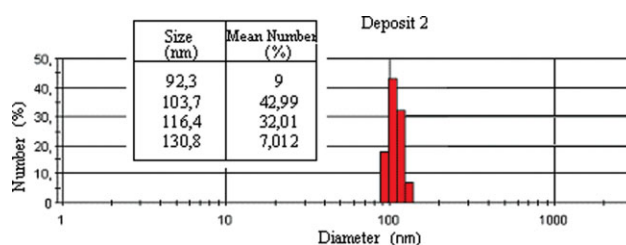
The separated deposits show a characteristic absorption of stretching vibration N—H within the range of 3645  $\text{cm}^{-1}$  and for bending vibration N—H at 1510  $\text{cm}^{-1}$  (RCONHR'). This may indicate the presence of protein destruction products. The nitrogen content in the separated deposit 1 is 2.29%, deposit 2 – 5.45% and indicates the presence of about 12.5 and 29.5% of protein destruction products respectively, confirming at the same time the results of IR spectroscopy.

### Measurement of particle size

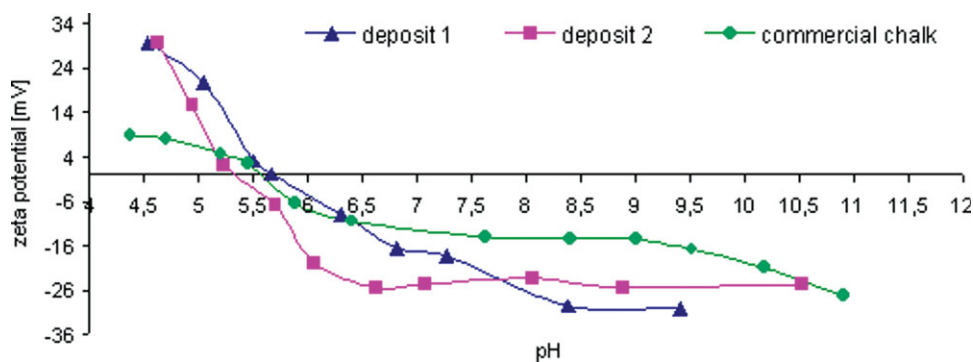
One of the most important parameters that decide about the filler behavior in polymers is the size of its particles. If the particles are too small, their dispersion may be difficult as they can form agglomerates that behave as large particles. Too large particles may concentrate stresses and consequently decrease the strength and hardness of the material under investigation. An appropriate size of particles depends on the type of polymer and its



**Figure 2** The average size of particles—Deposit 1. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** The average size of particle—Deposit 2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** The zeta potential of water dispersions of Deposits 1 and 2 in function pH (concentration 0.1 g/L). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

application.<sup>12</sup> The effects of particle size measurements are given in Figures 2 and 3. From the diagrams it follows that deposit 2 has both lower particle dimensions (92–130 nm) and lower particle size polydispersion as compared to those of deposit 1 (165–262 nm). From the performed measurements it follows that the precipitates separated from the effluents can be a filler for thermoplastics since the fillers used in those compounds show dimensions from 100 to 500 nm.

### Zeta potential

The dependence of quantity electric charge accumulated on particles—zeta potential of deposits 1 and 2 from pH is shown in Figure 4. From Figure 4, it follows that the behaviors of deposit 1 and commercial chalk in an elastomer medium will be similar as the pH values of their isoelectric points are very close to each other. The isoelectric point of deposit 2 precipitated from white liming liquors is at pH 5.3, which indicates a more acidic character of this deposit and consequently better donor properties as compared to those of commercial chalk.

### The SEM micrographs

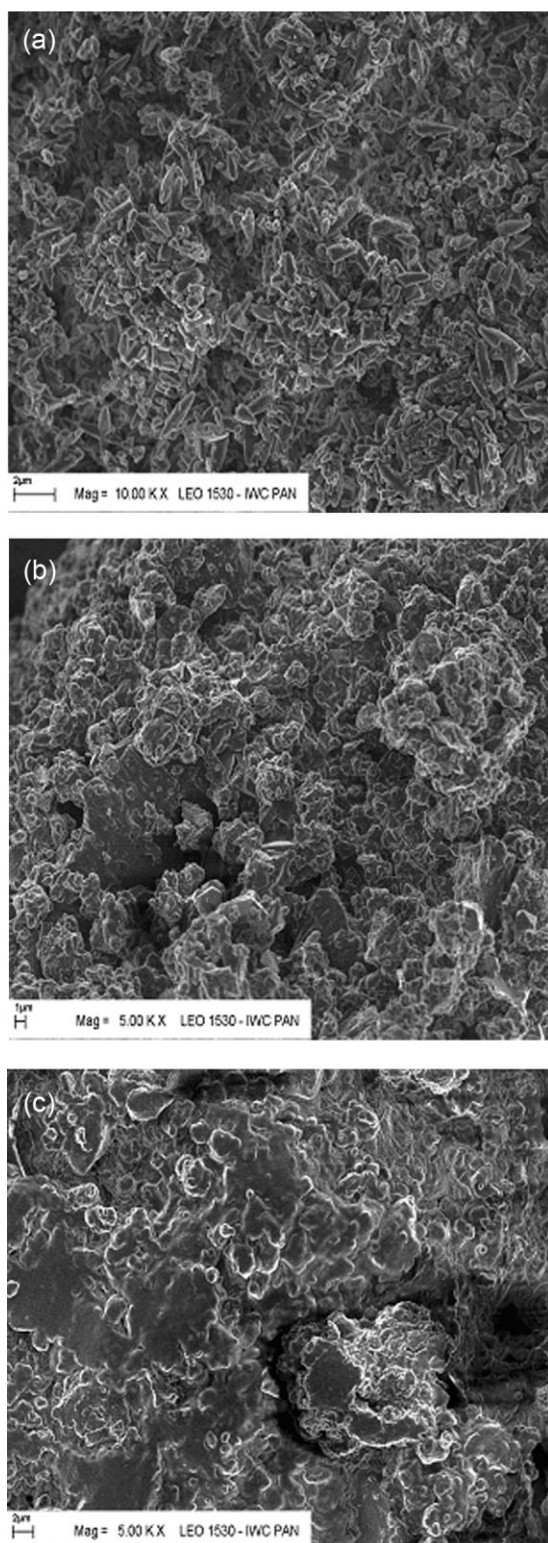
SEM micrographs commercial chalk and deposits 1 and 2 are given in Figure 5 from which it results that structure of precipitates is similar to commercial chalk.

### The influence obtained deposits on properties vulcanizates

To butadiene-acrylonitrile rubber (NBR) mixes 30 parts by wt. of commercial chalk (a reference) were added and in the remaining mixes the chalk was replaced with 30 parts by wt. of the obtained deposits 1 and 2. The compositions and properties of the prepared mixes and vulcanizates are given in Table II. The replacement of the typical filler – commercial

chalk – with the obtained chalk-protein deposits significant influence on the increment of torque  $\Delta L$  but the vulcanization time  $\tau_{90}$  is considerably shortened. This may indicate an interaction with the accelerating agent, which prevents the breakdown of cross-links being formed. Thus, the obtained deposits can be an activator of the cross-linking group due to the presence of  $-\text{OH}$  and  $-\text{COOH}$  groups. The increase in moduli 100, 200, and 300% is connected with the increased cross-linking density and the hydrodynamic effect of precipitate particles. In the presence of deposits particles as fillers, probably the capability to crystallize increased. Therefore, the tensile strength is higher. One should notice, that the growth of the tensile strength is larger, when was added deposit 1.

The separated chalk-protein deposits from the effluents were used as fillers for XNBR rubber mixes. The compositions and properties of the prepared mixes and vulcanizates are given in Table III. From the data listed in Table III it follows that the lowest torque increment and the longest optimal vulcanization time are shown by the XNBR rubber mix filled with commercial chalk. The incorporation of deposit 1 or 2 as well as the mixture of deposits 1 and 2 into this rubber mix has brought about not only torque increment, but also the shortening of the optimal vulcanization time. XNBR vulcanizates filled with chalk-protein deposits 5, 6, and 7 show a high tensile strength because of the possibility of crystallization due to deformation. This results from the very good orientation of rubber macromolecules due to the applied stress. These vulcanizates have higher cross-linking density than vulcanizate 4 filled with commercial chalk. They also contain a higher number of ionic nodes that decompose under the influence of ammonia vapor. This is confirmed by the obtained values of coefficient A. Comparing the mechanical properties of vulcanizates before and after accelerated thermal aging, it turns out that the aging coefficient S of vulcanizates 5, 6, and 7 have higher values than that of the reference vulcanizate 4. Thus,



**Figure 5** The SEM micrographs: a: commercial chalk; b: Deposit 1; c: Deposit 2.

the obtained deposits show properties of an anti-aging filler. From the data given in Table III it follows that all the vulcanizates containing the chalk-protein deposits in their compositions show higher values of the equilibrium swelling in water than

**TABLE II**  
Properties of NBR Rubber Mixes and Vulcanizates

Number of rubber mixes	1	2	3
Composition	Parts by wt.		
NBR rubber	100	100	100
Commercial chalk	30	–	–
Deposit 1	–	30	–
Deposit 2	–	–	30
The increase in the torque moment $\Delta L$ [dNm]	28	45.9	35.7
Optimal vulcanization time $\tau_{90}$ [min]	16	11	11
The stress at extension 100, 200, 300 [MPa]:			
$S_{100}$	1.00	1.86	1.44
$S_{200}$	1.30	2.60	1.99
$S_{300}$	1.62	3.56	2.78
Tensile strength $TS_b$ [MPa]	4.48	6.10	5.05
Elongation at break $E_b$ [%]	538.4	441.6	428.7

Other components of mixes: Zinc oxide 5; Sulfur 2.5; MBTS 0.5; Polnox N 1; Stearic acid 1; Ethylene glycol 1.5.

**TABLE III**  
Properties of XNBR Rubber Mixes and Vulcanizates

Number of rubber mixes	4	5	6	7
Composition	Parts by wt.			
XNBR rubber	100	100	100	100
Commercial chalk	30	–	–	–
Deposit 1	–	30	–	15
Deposit 2	–	–	30	15
The increase in the torque moment $\Delta L$ [dNm]	59.4	65.4	78.1	79.3
Optimal vulcanization time $\tau_{90}$ [min]	22	17	12	22
The stress at extension 100, 200, 300 [MPa]:				
$S_{100}$	2.26	4.47	7.20	7.84
$S_{200}$	3.95	6.77	11.25	12.62
$S_{300}$	8.67	10.43	14.46	16.92
Tensile strength $TS_b$ [MPa]	17.35	17.55	19.30	22.50
Elongation at break $E_b$ [%]	454.8	405.8	323.9	354.1
Crosslink density $V_f$ , concentration of the ion lattice points decomposing under the influence of ammonia $\Delta V_{NH_3}$ , percentage content of the ion lattice points decomposing under the influence of ammonia $A$ :				

$V_f \times 10^5$ [mol/cm <sup>3</sup> ]	2.1559	2.3397	3.5276	4.0628
$\Delta V_{NH_3}$ [mol/cm <sup>3</sup> ]	0.7832	1.0722	1.5474	1.9768
$A$ [%]	36.3	45.8	43.7	48.7
Aging coefficient $S$	0.55	0.56	0.64	0.73
Water absorption $Q$ [mg/mg]	0.075	0.289	0.276	0.389

Other components of mixes: Zinc oxide 5; Sulfur 2.5; MBTS 0.5; Polnox N 1; Stearic acid 1; Limanol PEV 1.5.

vulcanizates filled with commercial chalk. The presence of hydrophilic protein in deposits 1 and 2 causes increment their capability to absorb water and consequently makes it possible to transport enzymes, which means that the vulcanizates filled with the nanometersized chalk-protein deposits under investigation will be easier biologically degraded after their service life.

### CONCLUSION

1. Nano-sized deposits, containing calcium carbonate, protein destruction products and fats, can be separated from strongly polluted tannery effluents from cow hide liming processes combined with unhairing resulting in hair structure destruction and effluents from additional hide liming.
2. The obtained chalk-protein deposits can be filler for XNBR and NBR rubber that are filled generally with commercial chalk.
3. The vulcanizates filled with deposit 1 or 2 show very good mechanical properties, good resistant to thermal aging and increment their capability

to absorb water and consequently makes it possible to transport enzymes then facilitates their biologically degraded after their service life.

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