Tannery wastewater sludge ash for the production of waterproofing membrane: a technical and environmental feasibility study

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Abstract: Sludge from tannery effluent treatment processes is a by-product of leather-making industry, in which chrome compounds are the most common used materials. The objective of this work was to investigate the effects and feasibility in the use of tannery sludge ash as a partial or total replacement of usual mineral filler such as in manufacture of waterproofing membranes. The effects of sludge ash on the morphology and mechanical properties of membranes were investigated. Leaching tests were carried out in order to guarantee that the fulfilment of "filler function" was done in respect with environmental criteria. Besides, a Life Cycle Assessment (LCA) analysis was performed in order to assess the environmental performances of the waterproofing membrane filled by tannery sludge ash in comparison with the conventionally filled membrane. The performances of the membranes and the results of environmental assessment indicate that tannery sludge ash may be used as total replacement of $CaCO_3$ for waterproofing membranes.

Keywords: tannery sludge ash, bituminous waterproofing membrane, environmental performance

1 Introduction

Studies to minimize the amount of tannery waste and on the treatment and possible use of waste products are very important. In Santa Croce sull'Arno tanning district, Pisa (Italy), tannery wastewater sludge is thermally treated in a centralised plant sited inside the district area. This process generates a solid residue constituted by the tannery sludge ash (TSA) that must be disposed of. Several works were published in literature [1-4], focusing on the use of incinerated tannery sludge residues into cement agglomerates and ceramic products. However, no data on the utilization of tannery sludge ash in bituminous membranes have been reported.

Typically, bituminous membranes are composed by the following items: a bituminous compound (i.e. bitumen, mix of polymers and a mineral filler, usually calcium carbonate) that has to guarantee chemico-physical properties as barrier properties and good resistance to fracture; a shield (i.e. web of glass-fibers

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or nonwoven fabric) that relies with the function of support of the compound; a protective layer (i.e. typically talc, slate or sand) that act as UV-shield and prevent any occasionally abrasion.

Bitumen, widely used in road paving because of its good adhesion to mineral aggregates and its viscoelastic properties, has applications also in roofing membranes. In order to improve their performance, bitumen is often modified by the addition of polymers. Polymer-modified bitumen shows reduced thermal susceptibility and permanent deformation and has enhanced resistance to low-temperature cracking in comparison with the base bitumen. In waterproofing applications mixes of plastomers like atactic polypropylene (aPP), isotactic polypropylene (iPP) and polyethylene (PE) are usually used for bitumen modification as in this work.

The aim of this study was to investigate the technical applicability of TSA in waterproofing membrane manufacturing as a partial or total replacement of conventional mineral filler material, such as $CaCO_3$; the consequences due to the addition of sludge ash on the morphology and on the main mechanical and physical properties of the bituminous membranes were investigated; leaching tests were moreover carried out in order to evaluate the environmental compatibility of the final product.

The environmental impacts due to the waterproofing membrane filled by tannery sludge ash were finally assessed according to the Life Cycle Assessment (LCA) methodology and compared to the ones due to a conventional filled membrane.

LCA is an internationally standardized method for assessing the environmental performances of a product and/or a process over its life cycle [5]. The basic concept is that the environmental impacts of an item does not depend exclusively on the manufacturing process, but begins with its design and ends with its final disposal. For this reason, all the inputs (i.e. energy, material, etc.) and the outputs (i.e. products, waste materials, emissions, etc.) exchanged between a product/process system and the environment must be identified and quantified at each stage of its life cycle. According to the international standard ISO 14040, the structure of an LCA study is composed of four sequential steps: (1) *goal and scope definition*; (2) *Life Cycle Inventory*, i.e. the collection of all the input/output data; (3) *Life Cycle Impact Assessment*, i.e. the selection and quantification of appropriate performance indicators; (4) *interpretation*, with the discussion of the results and the outcomes of the study

2 Materials and methods

2.1 Materials

The sample of tannery sludge ash (TSA) used in this work was produced in a plant located in Santa Croce, Pisa (Italy), which produces about 8000 tons of ash per year. In this plant the tannery sludge (filter pressed to a 25 % total solids content) coming from centralised tannery wastewater treatment plants is thermally treated at a temperature of 900-950 °C in two rotary kilns in series in absence of oxygen. In the first kiln the sludge is dehydrated, and then it is decomposed in the second kiln with formation of volatile products and a solid residue. This solid residue is quenched by direct contact with water in order to

prevent the conversion of Cr^{+3} to Cr^{6+} in atmosphere before storage. According to the Council Directive 2000/532/EC this residue is classified as special and non-hazardous waste. Its main use in Italy is actually as mineral filler replacement in concrete and in asphaltic paving mixes.

The as-received TSA and a $CaCO_3$ powder, used as control filler, were dried in a laboratory oven at 105°C until the net weight was constant, and then sieved to a particle size below 75 µm. In fact, at least 80 wt % of the sample has to be less than 75 µm in accordance with the standard specifications for filler used in the preparation of waterproofing membranes (Bitumen Waterproofing Association).

Two bitumen samples with a 160/220 penetration grade, i.e. Bitumen 1 and Bitumen 2, were provided from an Italian refinery. The properties of the bituminous binders were evaluated by the penetration at 25°C (EN 1426) and the ring and ball softening temperature (TRB) (ASTM D36-76) (see Table 1).

The polymers used as modifying agents were the followings: Atactic Polypropylene (aPP) purchased from Degussa™ (trade name Vestoplast® 891); Isotactic Polypropylene (iPP) purchased from Basell™ (trade name Moplen® HF 500); and low density polyethylene (LDPE) supplied by Polimeri Europa™ (trade name Riblene® FF 20). All the three polymers were supplied in form of pellets and some their properties are reported in Table 2.

2.2 Preparation and characterization of polymer modified compounds (PMC)

In this work, two different formulations were realized: PMC with high polymer content (18 wt% of the base bitumen content) and low filler content (10 wt% of base bitumen content) that should be able to meet high performance criteria and PMC with low polymer content (8 wt%) and high filler content (30 wt%) that should match basic criteria of water insulation and low costs. The use of these concentrations and the composition of the polymer mixes used are based on information gained from waterproofing membrane manufacturers (Bitumen Waterproofing Association). The PMC samples prepared in this study are reported in Table 3. Mix of TSA/$CaCO_3$ with weight ratio of 1/1 was also used as filler.

Aluminum cans of approximately 500 cm^3 volume were filled with 250 g of bitumen and put in an electric heater where the base bitumen was heated to fluid condition (190°C). Then, a high shear mixer was dipped into the can and set to 5000 rpm. The polymers were then added gradually to the bitumen (5 g/min). At the end of polymer addition, the mixing process continued for 25 min until a homogeneous mixture was obtained. After that, filler was gradually added (10 g/min) to the mixture. After filler addition the mixing continued for 45 min. During polymer and filler addition and mixing, the temperature was kept constant at 190 °C. After completion, the PMC sample was split into appropriate containers, cooled at room temperature and stored at -20 °C for testing.

The PMCs were subjected to the following conventional tests: penetration at 25 and 60°C (EN 1426) and the ring and ball softening temperature (TRB) (ASTM D36-76). In addition, the temperature susceptibility of the bituminous compounds has been calculated in terms of penetration index (PI) using

the results obtained from penetration and softening point tests according to the following equation (Whiteoak, 2003):

$$PI = \frac{1952 - 500 \cdot \log(Pen_{25}) - 20 \cdot T_{RB}}{50 \cdot \log(Pen_{25}) - T_{RB} - 120}$$

Where Pen_{25} is the penetration at 25°C in dmm and TRB is the softening temperature in °C of the PMC.

Tab. 1 Properties of the bitumen samples

Sample	T_{RB} (°C)	Pen_{25} (dmm)	PI
Bitumen 1	44	127	- 0.34
Bitumen 2	43	146	- 0.18

Tab. 2 Properties of the polymers

Property	aPP	iPP	LDPE
melting point, °C	159.2	163.4	110.9
crystallization point, °C	94.2	122.9	96.6
melt flow rate*, g/10min	14.1	0.6	0.6

*ASTM D 1238

Further, a fluorescent microscopy has been used to investigate the morphology of the PMC before and after filler addition, by determining the grade of dispersion of the polymer within the base bitumen, and the effect of the filler (no detectable because no fluorescence phenomena occur) on the polymer dispersion, as well as to characterize the nature of continuous and discontinuous phases. Fluorescent microscopy is based on the principle that polymers swell due to the absorption of some of the constituents of the base bitumen as well as due to the fluorescent effect (Airey, 2002). The bitumen and filler rich phase appears dark or black, whereas the polymer rich phase appears light. For this morphological analysis, sample of each bituminous compound were taken directly from the mixing can, were poured into small cylindrical moulds (10 mm inside diameter, 20 mm height), preheated to the mixing temperature, and gradually cooled to room temperature and then chilled to -30°C. The cold samples were then fractured, and the fracture surfaces were examined at room temperature under a Leica DM LB fluorescence microscope at magnification level of 100x.

Tab. 3 PMC samples

Sample	total polymer wt %*	polymer mix composition wt %*			base bitumen	filler	filler wt %*
		aPP	iPP	LDPE			
AH1	18	12	5	1	1	TSA	10
AL1	8	4	3	1	1	TSA	30
CH1	18	12	5	1	1	$CaCO_3$	10
CL1	8	4	3	1	1	$CaCO_3$	30
mixH1	18	12	5	1	1	Mix**	10
mixL1	8	4	3	1	1	Mix**	30
AH2	18	12	5	1	2	TSA	10

AL2	8	4	3	1	2	TSA	30
CH2	18	12	5	1	2	$CaCO_3$	10
CL2	8	4	3	1	2	$CaCO_3$	30

* Weight percentage with respect to the base bitumen content; ** weight ratio TSA/$CaCO_3$ = 1

2.3 Preparation and characterization of waterproofing membranes

At the end of mixing process, the bituminous compound was poured into wood moulds in which previously a glass fiber shield was applied on the mould bottom, and subjected to a low shear process to ensure that the prepared membranes had constant width (140±1 mm x 50±1 mm) and thickness (3 mm±0.2).

The membranes were characterized by cold flexibility performance according to EN 1109/2002 method: this test has the purpose, using proper cooling medium and well defined conditioning time and stress levels, to identify the lower temperature, T_{cf}, at which no cold fracture occurs in the membrane.
In addition, leaching tests were performed on the membrane sample containing the highest amount of TSA filler (sample AL1) since this is the most critical condition. Because an internationally accepted and specific leachability test is not available for bituminous membranes, the membrane sample was tested in accordance with the waste leaching procedure reported in the Italian specification of wastes (Decreto Ministeriale 05/02/1998). The membrane sample was brought into contact with deionized water for 16 days setting the liquid/solid ratio to 10 L/kg. After 2, 8, 24, 48, 72, 102, 168 and 384 h the water was renewed to provide fresh opportunity for leaching. Each eluate was passed through a 0.45 μm membrane filter using a pressure filtration device and the chromium, chloride and sulphate content analysed according to the EN 12506/04 methods. The sum of the eluate concentrations were compared to the limit values cited in the Italian waste specifications (Decreto Ministeriale 05/02/1998).

3 Experimental results and discussion

The effect of polymers on the properties of the base bitumen can be seen in Table 4 as a decrease in penetration and an increase in softening points as the polymer content increases. Polymer modification reduces temperature susceptibility of the bitumen. Higher values of PI indicate lower susceptibility. Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as to permanent deformation. According to the results in Table 5, the PMCs exhibit lower temperature susceptibility (higher PI values) than base bitumen and the effect is more relevant as the polymer content increases. In addition, PMCs containing TSA as filler showed slightly higher PI values (lower susceptibility) in comparison with the ones containing $CaCO_3$.

Fluorescent microscopy images of PMCs before and after the filler addition are presented in Figs. 1 and 2. In the images, the swollen polymer phase appears light while a dark colour corresponds to bitumen and filler. PMC samples with a high polymer content (18% of the base bitumen) without filler

show a continuous polymer phase with homogenously dispersed bitumen phase (Fig. 1), independently of the used base bitumen. An increase in the sizes of the bitumen globules uniformly dispersed in the polymer phase was detected after the filler adding (10% of base bitumen content). This may be attributed to an higher affinity of inorganic fillers with bitumen, that increases the size of the dark areas. A continuous bitumen phase with no homogeneously distributed polymer globules was observed in the PMCs with low polymer content and without filler. After filler addition (30 wt % of the base bitumen content) the polymer phase dispersion improved regardless of the filler that was used, indeed, smaller size polymer aggregates homogenously dispersed in the continuous bitumen phase were observed (Fig. 2). This may be due to the shear stress applied, during the mixing, by the inorganic filler particles on the polymer aggregates that led to reduce their size enhancing their dispersion.

Tab. 5 Properties of PMCs and membranes

Sample	Bituminous compounds				Membrane
	T_{RB} (°C)	Pen_{25} (dmm)	Pen_{60} (dmm)	PI	T_{cf} (°C)
Bitumen 1	44	127		- 0.34	
AH1	155	25	71	9.00	- 6
AL1	155	21	76	8.66	0
CH1	155	23	70	8.84	- 10
CL1	153	21	80	8.55	0
mixH1	155	25	72	9.00	n.v.
mixL1	154	22	74	8.70	n.v.
Bitumen 2	43	146		- 0.18	
AH2	156	23	72	8.89	n.v.
AL2	156	21	77	8.71	n.v.
CH2	156	24	73	8.98	n.v.
CL2	154	16	91	8.09	n.v.

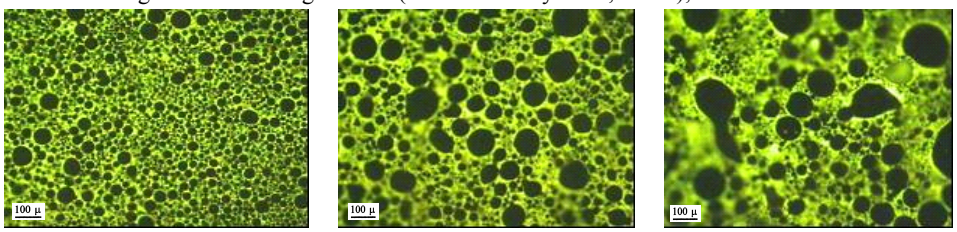
n.v. no valuated

The lower T_{cf} values were observed in the PMCs with higher polymer contents, independently of the filler type that was used. This may be attributable to the presence of a continuous polymer micro-network that extends throughout the composite, as observed by fluorescent microscopy images (Fig. 1), and that improves the resistance at low temperature of the base bitumen. The results of the leaching tests performed on the membrane based on the AL1 compound (with higher TSA content) are reported in Table 6 for total chromium, chloride and sulphate. As shown, the leaching of this product generates an eluate that does not exceed the limits cited in the Italian waste specifications.

Tab. 6 Chromium, chloride and sulphate concentrations in the eluates of membrane prepared with the AL1 compound (30% of tannery sludge ash)

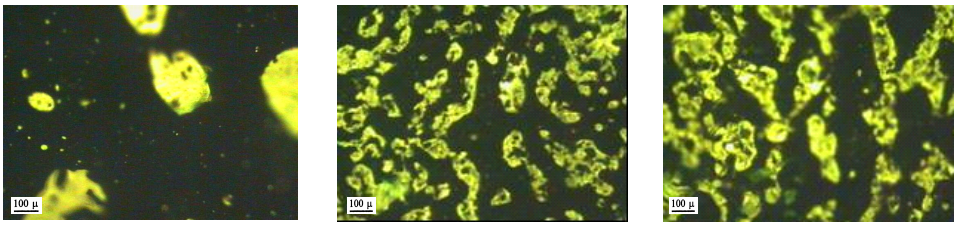
Leaching time, h	2	8	24	48	72	102	168	384	Sum	Limit value*	Method
Total chromium, µg/L	1.4	32.3	0.9	1.1	0.6	0.7	2.2	1.8	41	50	EN ISO 11885
Chloride, mg/L	12.4	21.3	14.2	10.6	14.2	10.6	7.1	1.8	92	200	ISO 92987
Sulphate, mg/L	8.9	9.0	9.2	10.2	11.1	n.r.	n.r.	8.4	57	250	EN ISO 10304

* Limit values according to the Italian regulations (DM 5 February 1998, All. 4); n.r. not relevable.



PMC without filler | *Sample AH1* with 10% TSA | *Sample CA1* with 10% $CaCO_3$

Fig. 1 Fluorescent images of PMC with base bitumen 1 at high polymer content/low filler content before and after filler addition



PMC without filler | *Sample AL1* with 30% TSA | *Sample CL1* with 30% $CaCO_3$

Fig. 2 Fluorescent images of PMC with base bitumen 1 at low polymer content/high filler content before and after filler addition

4 LCA Analysis

4.1 Goal and scope definition

No significant differences appeared between the properties of the TSA filled and $CaCO_3$ filled membranes. The LCA methodology was then applied in order to move the comparison to the analysis of their environmental performances.

The production and disposal of 1 m^2 of waterproofing membrane was selected as the reference unit (i.e. Functional Unit, in LCA language) for the expression of all the inputs and the outputs of the life

cycle. The extension of the study (i.e. the system boundaries) covered not only the manufacturing process but all the stages of the membrane life-cycle: from the extraction of the raw materials and the energy resources, to the final disposal of bituminous sheets.

4.2 Inventory analysis

The specific data about the waterproofing membrane production process were obtained from an Italian factory and are summarised in Table 4. In order to model the TSA process, the specific data about this system were obtained from the centralised plant located in Santa Croce sull'Arno in which the tannery sewage sludge treatment process is located. All the other pieces of information were obtained from database typically used in LCA analysis (e.g. the Ecoinvent database).

If the sludge were not used for the TSA production, an alternative disposal would be necessary. Therefore, in order to evaluate the actual environmental performances of the membrane with TSA, the material and energy flows needed for the common tannery sewage sludge treatment and disposal were considered as an avoided impact and discounted from the inventory.

4.3 Impact assessment

The potential effects caused by the input and output listed in the inventory was assessed with the CML 2 baseline 2000 method. The inventory items are assigned to well defined impact categories, representing specific environmental burdens. The selected method was developed by the Institute of Environmental Sciences of the University of Leiden (The Netherlands) and includes the followings impact categories: Abiotic depletion potential (ADP), Global warming potential (GWP), Ozone layer depletion potential (OLDP), Human toxicity potential (HTP), Fresh water aquatic ecotoxicity potential (FWAEP), Marine aquatic ecotoxicity potential (MAEP), Terrestrial ecotoxicity potential (TEP), Photochemical oxidation potential (POP), Acidification potential (AP), Eutrophication potential (EP).

The contribution of each inventory item to the corresponding impact categories is evaluated through a series of equivalence factors, which express effects due to an item in terms of reference parameters. For example, in the "climate change" impact category, CO_2 is the reference parameter and the equivalence factor is the Global Warming Potential based on a 100 years lifespan, whose value is 23 for CH_4 (i.e. the contribution of 1 kg of CH_4 to the global warming is equivalent to the emission of 23 kg of CO_2).

Tab. 4 Inputs and outputs of the waterproofing membrane production

Inputs		*Outputs*	
Bitumen	2.046 kg	*Atmospheric emission*	
PP	0.231 kg	CO_2 (fossil)	0.14 kg
LDPE	0.033 kg	water	0.12 kg
Filler	0.99 kg	*Solid waste*	
tissue-not tissue	0.14 kg	bitumen sheet	3.44 kg
Water	0.933 kg		

GPL	0.15 g
Diesel	0.0014 g
natural gas	2.6 MJ
Electricity	0.275 kWh

4.4 LCA results

The outcomes of the impact assessment are summarized in Table 7. Due to the thermal process of TSA production, the impact category scores associated to the TSA filled membranes resulted to be slightly higher than those associated to the conventional process. However, the indicators present the same order of magnitude to indicate that the environmental burdens due to the two life cycles are comparable. It is moreover worthy observing that when the materials and energy flows avoided for the tannery sewage sludge treatment and disposal were considered, the environmental burdens due to the TSA filled membranes resulted to be completely compensated.

Tab. 7 Results per impact categories

Impact categories	*Units*	*Membranes with $CaCO_3$*	*Membrane with TSA*	*Membrane with TSA and avoided impact*
abiotic depletion	kg Sb eq	$8.00 \cdot 10^{-2}$	$9.00 \cdot 10^{-2}$	$-9.20 \cdot 10^{-1}$
global warming	kg CO_2 eq	$1.26 \cdot 10^{1}$	$1.65 \cdot 10^{1}$	$-1.43 \cdot 10^{2}$
ozone layer depletion	kg CFC-11 eq	$9.59 \cdot 10^{-7}$	$1.01 \cdot 10^{-6}$	$-2.07 \cdot 10^{-5}$
human toxicity	kg 1,4-DB eq	$1.77 \cdot 10^{0}$	$2.12 \cdot 10^{0}$	$-1.82 \cdot 10^{1}$
fresh water aquatic ecotox.	kg 1,4-DB eq	$2.54 \cdot 10^{0}$	$2.59 \cdot 10^{0}$	$-1.04 \cdot 10^{1}$
marine aquatic ecotoxicity	kg 1,4-DB eq	$3.05 \cdot 10^{3}$	$5.02 \cdot 10^{3}$	$-1.86 \cdot 10^{4}$
terrestrial ecotoxicity	kg 1,4-DB eq	$9.15 \cdot 10^{-3}$	$1.00 \cdot 10^{-2}$	$-2.40 \cdot 10^{-1}$
photochemical oxidation	kg C_2H_4 eq	$1.99 \cdot 10^{-3}$	$2.57 \cdot 10^{-3}$	$-2.00 \cdot 10^{-2}$
acidification	kg SO_2 eq	$5.00 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	$-3.70 \cdot 10^{-1}$
eutrophication	kg PO_4^{3-} eq	$5.60 \cdot 10^{-3}$	$7.68 \cdot 10^{-3}$	$-4.00 \cdot 10^{-2}$

5 Conclusions

From the results and discussion presented above it can be concluded that the tannery sludge ash can be utilized as a good material in the bituminous membrane manufacture process in replacement of mineral fillers as $CaCO_3$. The technical feasibility in the use of this waste was demonstrated: the polymer modified compounds containing $CaCO_3$ or TSA showed comparable morphologies and properties in terms of penetration and softening temperature and the produced membranes showed similar cold flexibility independently of the filler used.

The results of the environmental impact assessment moreover showed that the use of TSA in replacement of $CaCO_3$ might lead to apparent environmental advantages in the waterproofing membrane

manufacturing if the avoided impact of treatment and disposal of tannery sewage sludge is taken into account.

As a consequence, the incorporation of tannery sludge ash into stable bituminous membranes can be a valuable alternative to dispose of this waste and it would allow an interesting and useful expansion of its current application field.

References

[1] T. Basegio; C. Haas; A. Pokorny, et al. J. Haz Mat., 2006, B137: 1156-1164.

[2] S. Swarnalatha; K. Ramani; A. Geetha Karthi, et al. Mat., 2006, B137: 304-313.

[3] J. Dweck; P.M. Buchler; A.C.V. Coelho, et al. J. Env. Sci. and Health: Part A, 2000, 35: 715-740.

[4] A. Filibeli; N. Buyukkamaci; N. Senol. Res. Cons. and Rec., 2000, 29: 251-261.

[5] H. Wenzel; M.Z. Hauschild; L. Alting. Environmental assessment of products, volume 1: Methodology, Tools and Case Studies in Product Development, Springer, 2000.