

LCA comparative analysis of different technologies for surface functionalisation

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ABSTRACT

Life Cycle Assessment (LCA) methodology is presented as the result of a project analysis applied to the specific context of hyperfunctional surfaces production. Nowadays, most of the processes used for surface functionalisation have a high environmental impact due to the use of large amounts of water, energy and chemical solutions. The aim of plasma technologies processing is to achieve the same, or even enhanced, surface functionalities, with respect to the traditional treatments, but providing an environmental friendly process. Surface functionalisation representative processes are considered for the treatment of thermo-sensitive and thermo-resistant substrates applied in the textile and food processing industry. Main plasma processes considered are Physical Vapour deposition (PVD), and Atmospheric Pressure Glow Dielectric Barrier Discharge (GDDBD). Innovative plasma processes are compared with wet processes for surface coating and treatment. The considered functionalities are wear-corrosion resistance, and oleophobicity. Moreover, Global Warming Potential dependence as a function of the different energy mix has been investigated for the specific processes analysed.

1. Physical Vapour Deposition , Chromium electroplating technologies and Duo-Plasmaline deposition of SiO_x

The main objective of this work is to calculate the energy and environmental burdens generated by ceramics Physical Vapour Deposition (PVD) , SiO_x Plasma and Chromium electroplating- coating technologies using different energy mixes.

PVD technology has the purpose of processing a wide variety of materials. The anti wear and anti corrosion functionality is obtained by of a thin single/multi-layer coating of nitrides, carbo-nitrides, carbides, sulphides, borides and oxides on the surface of the .Coating materials are produced in a vacuum chamber by means of different appropriate energy sources. The second system considered, Chromium electroplating process, is used extensively for decorative, engineering and electroforming purposes. The third system considered, plasma SiO_x deposition, is used extensively with the objective to improve surface finish, corrosion resistance and wear resistance of the materials . In these cases coatings were deposited on the 100Cr6 Chromium substrates of different thicknesses to obtain the same functionality.

1.1 The System and system boundaries

The boundaries of the considered systems include all phases from raw material extraction to the production and coating of a generic product. Product life durability and end of life have not been taken into account in this analysis .Due to the shape and quality variability of the products managed in the two processes analysed, it was decided to express the results in terms of 1 m² x 1 μm of coated surface for PVD and SiO_x since this F.U represents the reference unit that gives the same performance of the treated surface. For Chromium electroplating the reference unit is 1 m² x 3 μm, which is the unit that is equivalent in terms of performance for this treatment to the unit that has been used for the other two treatments.

In the case of PVD, two coatings widely-used in engineering applications have been studied: TiCN and TiN.

Furthermore, the analysis does not take into consideration the production and the transport of the substrate

materials, the production and the end-of-life of the plants (PVD and chromed plating) nor the end-of-life of the coated products.

1.2 LCI data inventory and hypothesis

Reference data for Chromium electroplating process considered Nickel and Chromium VI layers. Since these coatings do not contain Nickel, all Nickel compounds as raw materials have been eliminated by the analysis and assessment of the process environmental burden.

The inventory analysis provides a catalogue and quantification of the energy and material use as well as environmental releases associated with the processes included in the system boundaries

Three different scenarios have been taken into account to determine how the origin of the energy (production, transport, efficiencies) may affect the environmental burden in the same process: Italy energy mix, Europe energy mix and France energy mix.

For each scenario the model uses different amounts in terms of percentages of the origin of the energy depending on the reality of each country (Table 1.1)

Table 1.1 – Summary of energy origin for each energy mix to produce 1MJ of electricity.

	Italy mix	Europe mix	France mix
Coal	12%	27%	7%
Oil	34%	8%	2%
Gas	34%	16%	1%
Hydro	10%	6%	7%
Nuclear	9%	39%	82%
Other	1%	2%	1%

As far as data collection is concerned, it is important to put in evidence that each energy and mass flow of the plants has been allocated according to the Functional Units previously declared.

Data and information used in LCA studies can be divided into two main categories:

- *Primary data* are data collected directly from the plant and, therefore, guarantee an high level of accuracy.
- *Secondary data* are data obtained from databases, other previously carried out analysis or published reports [1] ,[2],[3], [4] and [5]and from the Boustead Model_V (www.boustead-consulting.co.uk) and refer to three different energy mixes

1.3 Results and comments

Main results regarding the Gross Energy Requirement are reported below (Table 1.2)

Table 1.2 GER for each treatment/energy mix (data in MJ/F.U)

Treatment	Production energy	Energy Use	Transport energy	Feedstock energy	Total energy
PVD –TiCN/ TiN Italy mix	255	124	2	0,0	381
PVD –TiCN /TiN Europe mix	255	124	2	1	381
PVD –TiCN/ TiN France mix	255	124	2	1	381
Cr VI- Galvanic coating Italy mix	187,3	115	2,5	0,9	306
Cr VI- Galvanic coating Europe mix	182,3	115	2,5	0,9	300
Cr VI- Galvanic coating France mix	187,3	115	2,5	0,9	306
SiOx plasma deposition Italy mix	607	348	6	41	1002
SiOx plasma deposition Europe mix	587	348	6	41	982
SiOx plasma deposition France mix	607	348	6	41	1002

In Table 1.3 are reported the values of the main environmental parameters for each treatment and energy mix

Table 1.3 Main environmental parameters values for each treatment/energy mix

Treatment	GWP (kg CO2)	AP (g eq SO2)	POPC (g CH4)	EU (g PO43-)
PVD – TiCN/ TiN Italy Mix	23,53	276,79	32,75	8,76
PVD – TiCN/TiN Europe Mix	17,36	140,63	15,32	5,98
PVD - TiCN /TiN France Mix	4,19	38,88	7,45	1,71
CrVI Galvanic coating Italy mix	18.93	210.52	22.44	6.92
CrVI Galvanic coating Europe mix	14.38	110.13	9.59	4.86
CrVI Galvanic coating France mix	4.76	35.68	3.60	1.73
SiOx plasma- Italy mix	59,78	718,75	75,99	22,92
SiOx plasma- Europe mix	46,21	419,44	37,66	16,8
SiOx plasma-France mix	17,38	197,35	20,54	7,46

General considerations regarding the wealth of data provided prove that Chromium plating process determines a huge local environmental burden while PVD and plasma deposition of SiOx determine a greater environmental burden on global scale. In general, the energy mix does not affect significantly the energy consumption for the same process. The energy mix to produce electricity is therefore relevant to define the environmental burden of the two systems. In particular, in the case of plasma treatments, the use of renewable electricity sources (as photovoltaic systems) and the increment of the process efficiency could be a good way to improve the environmental performances. Actually the environmental burden in terms of GWP is significantly different when applying different mixes. On the contrary, dramatic differences can be noted taking into account the environmental parameters that have been listed before. The higher use of electricity of the PVD and SiOx plasma process is balanced by higher raw material consumption, direct solid, air emission and generation of exhaust solution of the galvanic Cr process.

Table 1.4 Average raw materials consumptions in mg/F.U

Raw material	TiCN/TiN coating	Cr coating	SiOx
S (elemental)	2300	25077	700
Cr	0	81000	16
O2	21400	42500	45500
Water (total) (l/F.U)	5	8,5	51,1

Table 1.4 Average water emissions mg/F.U

Substances	TiCN/TiN coating	Cr coating	SiOx
COD	57	40	306
BOD	9	6	66
suspended solids	363	38800	6023
Cr ^{VI}	0	859	0
Zn+	0	217	1

2. Atmospheric pressure plasma deposition. Oleophobic properties on textile surfaces

This second case study reports a comparative LCA analysis between traditional and plasma processes for PET textile substrates to obtain oleophobic properties. The plasma process analysed corresponds to non wet atmospheric plasma technology working with Dielectric Barrier Discharge (DBD) tool, using chemical fluorocarbons compounds in gas phase. The equivalent traditional wet process consists in submerge the textile in a chemical bath solution containing fluorocarbons compounds. For both technologies a cleaning wet pre-treatment should be applied in order to remove unwanted surface oil on the fabric.

2.1 The System and system boundaries

Traditional technology includes an initial wet surface cleaning process (de-oiling) and a second chemical wet process that activates the surface mainly using fluoro-resin compounds. Plasma technology is based on a first surface wet cleaning process followed by an atmospheric plasma process using fluorinated gases. As energy sources, plasma treatment uses net electricity, while traditional process uses electricity and natural gas to heat the chemical bath solution. The F.U that has been chosen is 1 kg of treated material. The studied system contains the cleaning processes (de-oiling or de-sizing) and the functionalisation treatment to achieve the desired property. Environmental burdens caused by the production of the substrates, or machinery and tools used during the processes have not been taken into account. The following flow chart represents the system boundaries considered as well as the material and energy exchange with the outer environment. (see fig 2.1)

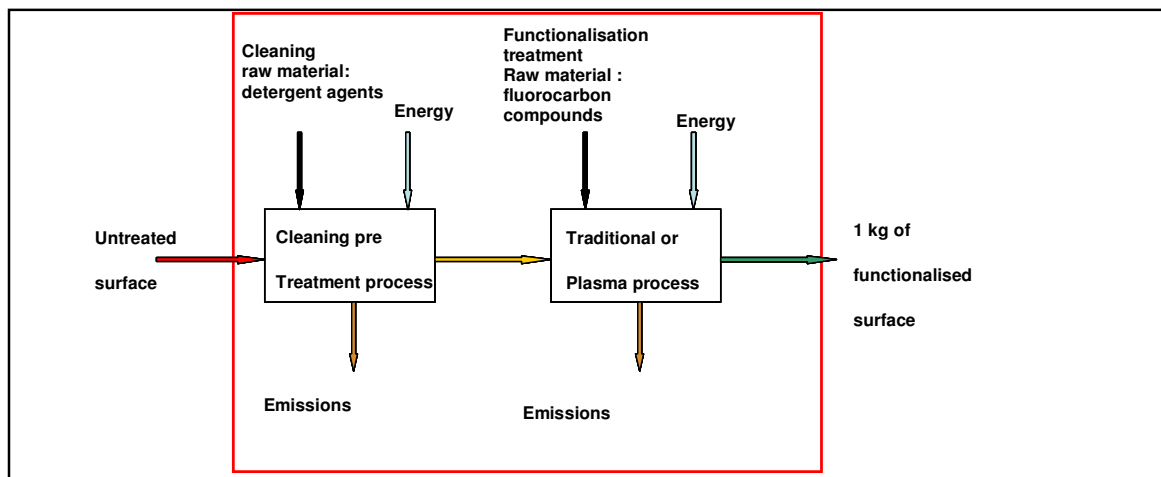


Figure 2.1 System Boundaries for Traditional and Plasma entire process: oleophoby on PET fabric

2.2 LCI inventory data and hypothesis

Data and information used in LCA studies can be divided into two main categories, *primary data* and *secondary data*:

- *Primary data* are data collected directly from the plant and, therefore, guarantee an high level of accuracy.
- *Secondary data* are data obtained from databases, other previously carried out analysis or published reports [1], [2] and [4] and from the Boustead Model_V

The processes described use materials and chemical composition that are restricted and its composition is protected by patents. In this case and in order to go forward with the analysis it has been decided to set specific hypotheses about general chemical compositions available for computation. These reference compounds are assumed to have equivalent performances with respect to the reference ones.

In addition, the LCA software used for the analysis library, despite its completeness, does not contain all the specified chemical compounds used in these processes. For instance, it has been particularly difficult to find data regarding CF_4 and similar PFC gases that are used as precursors in plasma processes as these gases are not included as a possible input material in Boustead library, (commonly these gases are a by-product of several industrial processes, but they are not employed as input raw materials). In order to cope with this situation, it has been decided to add these gases energy contribution to the total Gross Energy Requirement (GER) of the whole

process. This value has been added to the total GER applying 19 MJ/ kg [6],[7] concerning to the approximate value found in literature for the production of 1 kg of fluorocompounds

As emissions, it is important to mark out that plasma treatment has only air emissions, consisting in by-products coming from the chemical reaction of the fluorocompounds and the surface, while wet traditional treatment has mainly water emissions. These compounds (both used as fluoro-resin gas as raw material) have been treated as a generic PFC gas, with no GWP contribution. This point will be discussed next. Moreover, they have been considered the rest of the emissions as per the LCA analysis, assuming, where the value was not possible to evaluate, the maximum value permitted by the European Commission [8]

2.3 Results and comments

Table 2.1 reports the Gross Energy Requirements for each process, taking into account the GER contribution of fluoro-resins as raw material .

Table 2.1- GER for plasma and traditional wet process. [MJ/F.U.]

Process	Production energy	Process energy	Transport energy	Feedstock energy	Total energy [MJ/F.U]
Traditional process	2	23	0	0	25+0.703
Plasma process	2	5	0	0	7+0.077

As relevant data, it can be noticed that traditional processes have a water consumption definitely higher than plasma process (wet processes employing 35 litres per F.U and plasma process employing 5 litres per F.U). Moreover, the highest need of water employed in traditional processes cause that a larger amount of water needs to be treated before being emitted in the environment. As far as air emissions are concerned, again the results show that values that are found for plasma process come from the production of electricity and not from the process itself, due to the fact that pollutant substances emitted during the process are negligible. Furthermore, pollutant emissions for plasma processes are in any case lower compared to traditional process, above all for CO, CO₂ and NO_x. Dramatically lower are PM10 emissions for plasma process. Same comment should be said for the water emissions.(Table 2.2)

Table 2.2- Main air and water emissions for plasma and traditional wet process. [mg/F.U.]

Substances-air emissions	Oleophoby traditional PET	Oleophoby Plasma PET
dust (PM10)	1060	218
CO	1785	421
CO2	1388492	342863
SOX as SO2	758	689
NOX as NO2	2906	0
perfluorocarbons (PFC)	0	3770
Water emisions	Oleophoby traditional PET	Oleophoby Plasma PET
COD	17200	1751
BOD	4000	126
suspended solids	4694	77

In general, table 2.3 sums up the values of the main environmental parameters for each process.

Table 2.3- Main environmental parameters for plasma and traditional wet process.

Treatment	GWP (kg CO ₂)	AP (g eq SO ₂)	POPC (g C ₂ H ₄)	EU (g PO ₄ ³⁻)
Traditional Oleophobic PET	0.4	1.22	0.19	0.26
Plasma Oleophobic PET	1.67	2.36	2.81	0.76

The hypothesis taken into account relative to plasma PFC gas emissions deserves, however, a further comment. This hypothesis states that PFC gas emitted during the plasma functionalisation process was a generic PFC gas, non GWP contributor. This assumption, confirmed by further inspections among plasma processes providers, is quite relevant as it is well known the effects of PFC gas on the greenhouse effect. In order to compare results deriving from employing a generic PFC and those deriving from a specific PFC forcing an higher environmental impact, CF₄ (tetrafluoromethane) gas has been considered. This assumption is supported by the fact that in some plasma processes (not involving the processes analysed in the present work) CF₄ is effectively used. This gas has a GWP potential equivalent to 5700. The table 2.4 summarise the possible effect on the GWP of this CF₄

Table 2.4- Main environmental parameters for plasma and traditional wet process.

GAS	GWP 100 Potential	Gas emitted quantity (kg)	GWP gas contribution (kg CO ₂ eq)	Total GWP (kg CO ₂ eq)
Unspecified PFC	0	0,00377	0	0,4
CF ₄	5700	0,00377	21,489	21,889

3. Final considerations

All the reported results and specific comments are valid as long as all the initial hypothesis are satisfied. It has also to be pointed out that the environmental burdens of the different systems are strictly dependent on the electricity consumption and the chemistry of the exhaust gas, especially in case of use of PFC precursors in plasma processes; indeed the contribution of other raw materials is negligible. According to the LCA outcomes, especially for the second considered case, comparing on the basis of the same surface functional specifications, we may state that the plasma surface processing offer a clear environmental advantage on traditional technologies, above all if considering energy consumptions and use of water resources. In turn this has also a positive effect at local scale. In future investigations refinement of input data especially for what pertaining raw materials (chemical compounds and plasma precursors) is recommended to further reduce the level of uncertainty of results. However, since the aim is to perform a comparative analysis, application of sensitivity analysis criteria, that take into account also error (uncertainty) propagation through all numerical computations, would clearly prove the non-overlapping of compared average values considered in the LCA. Sensitivity analysis of the considered cases is a work in progress. This study has been supported by European 6th Framework Programme ACTECO project (Contract n° 515859).

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