# Improving Electrical Conductivity of Leather Surface: The Newest Technologies for the Newest Industrial Applications

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**Abstract**

A former branch of studies of the materials and of the technical procedures able to provide an improvement of the electrical conductivity of the leather surface has been carried out, in the past years, mainly with the aim of avoid the unpleasant accumulation of electrostatic charge on it, with possible serious consequences on human health. These studies have been carried out, for the most, using very rough technologies.
The present study takes into account the consumer requirement of an even more massive use of touch screen devices, where the leather have to compete with the modern textile fibers in terms of technological performances, with particular reference to the newest technologies for the production of conductive gloves and other kind of conductive goods, as shoes, garments and others.
Most of known technologies able to provide to some materials the unique ability to discharge static electricity and definitely to have a conductivity comparable to the one exhibited by human body, concern textile fibers. Some of the most common of these technologies have been already tested on leather matrix, merely by analogy with treatments on textile fibers. On the other hand, the goal of the present work is just to delve into the application of these technologies to leather matrix, with particular reference to the use of carbon-based nanomaterials, with opportune evaluation of cumulative/annihilation effects, environmental aspects and of possible economic and/or practical disadvantages.

**Keywords:** electrical conductivity, leather surface treatments, nanomaterials, carbon nanotubes, graphene nanoribbons, conductive polymers.

## 1. Introduction

The prominent role of touch screen technologies is mainly due to the possibility of enable human interface with the modern electronic devices without need of any keyboard, mouse or stylus and without need of any coupling with human skin.

Examples of the most used touch screen devices are the newest generations of PDAs (personal digital assistants), smartphones, well known Apple Computer's goods, as iPhone and iPad, but touch screen technology concern also cash point machines (ATMs), satellite navigation devices, beside a wide set of specific electrical tools used, for example, in automotive, aviation and aerospace industry.

Through the edges, the growing concern of leather market for the newest technological fields of applications, together with a growing environmental awareness, concurred to improve the knowledge of the leather scientists on this topic.

Leather itself may have a variable electrical conductivity, depending on its humidity degree, on the electrolytic content deriving from the chemicals used in the tanning process but, overall, on the

kind of finishing applied. Anyway, the production of leather goods characterized by an high performance in touch screen applications does need further appropriate treatments.

The newest technologies, mainly applied to textile fibers, include the use of conductive agents, as small sized metal particles, metal fibers, carbon fiber chains, carbon-based nanocompounds and conductive polymers, with particular reference to conjugates polymers converted into electrically conductive polymers, by treatments with opportune dopant agents.

In the present work, the application of some of this technologies to leather has been considered, taking into account all the peculiar technical problematic, concerning the compatibility between leather/leather finishing, conductive agents and chemical/physical processes to be adopted.

The average surface electrical resistance, exhibited by human skin, is estimated to be of about $10^5\Omega$, while leather surface resistance normally vary from about $10^9\Omega$ to $10^{10}\Omega$, depending on the kind of chemicals and technologies used in leather production, whose effects among the traditional tanning processes have been studied (Jiangen Wang et al., 2011). Electrical conduction improving of leather can be provided both by wet-phases or surface treatments, where we chose the latter type, resulting more effective. More in detail, the approach we adopted was based on finishing treatments with a composite system, where some carbon-based fillers have been inserted in a polymeric matrix.

## 1.1 The choice of the polymeric matrix

The intrinsic conductive properties of many finishing polymers have been widely discussed in literature (Marsal et al. 1998) and have to be taken into account for the planning of adequate conductive treatments. On the other hand, in a composite system, there are other crucial parameters to be considered, with particular reference to the mechanical-physical properties of the polymers; thermoplastic rather than thermosetting nature of the polymeric matrix, for example can critically affect the final conduction mechanism, due to its influence on the dispersive effects towards the conductive fillers. In other terms, the connectivity between the fillers, related to their reciprocal distance and to their peculiar “percolation threshold” through the matrix is tightly joined to the mechanical-physical properties of the polymers. Polymeric glass transition temperature, likewise, can influence the goodness of fillers dispersion at room temperature. More in general, it is possible to assume that thermoplastic polymers, compared with the thermosetting ones, are able to produce a better and more homogeneous connection between the fillers, with consequent generation of a good conductive path (Zulfia et al. 2013), avoiding the formation of fillers agglomerates. The influence of the fillers dispersion on the conduction path, in a composite system, is shown in figure 1.

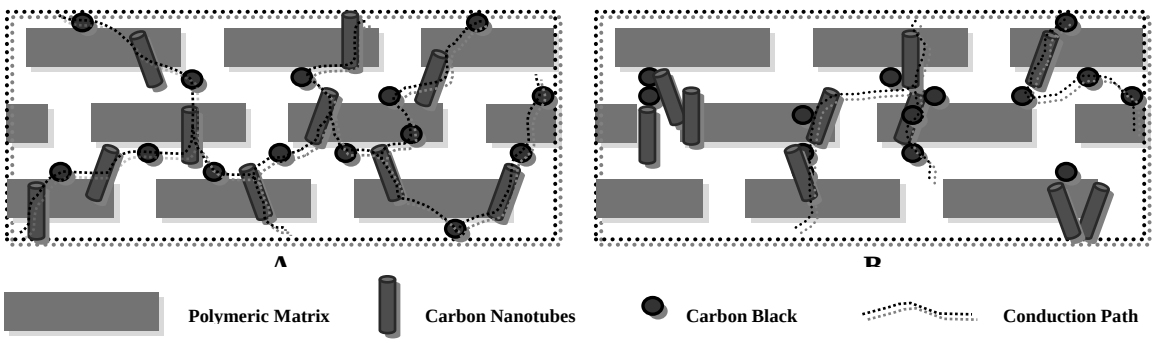


**Fig.1:** Scheme of the conduction path in a system with a good dispersion of the conductive fillers (A) and in a system with a worse dispersion of the conductive fillers (B)

The polymeric crystalline degree can also affect the goodness of the conduction path, so that, a low crystalline degree ensure a better conduction path, compared with an high crystalline degree. This effect is shown in figure 2.

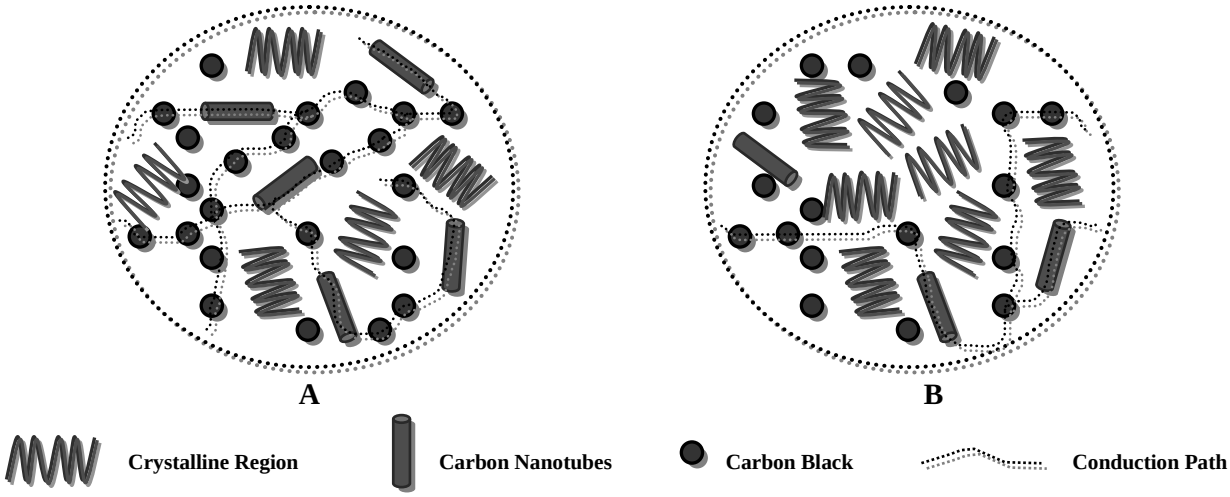


**Fig.2: Scheme of the conduction path in a system with a low crystalline content (A) and in a system with a high crystalline content (B)**

Furthermore, the choice of the most optimal polymeric matrix, has to be done according to other factors too, concerning the compatibility with leather surface and with the additives and solvents/dispersive agents utilized, further than concerning the possible influence of the operative conditions adopted in the production process of leather on the mechanical and chemical-physical properties of the polymers. SSIP research line of the last years has been mainly focused on these topics (Florio et al. 2009; Florio et al. 2010) where we reached many significant information on the crucial parameters able to affect the final finishing polymers properties.

Finally, the utilize of polymers characterized by an inner electrical conductivity as matrix, does not guarantee itself a good electrical conduction of the whole composite system; this could rather produce possible annihilative effects on the final conducive properties, especially when a different conduction mechanism is associated to the polymeric matrix and to the fillers; this could occur, indeed, when the main charge carrier is different, for example, when it is identifiable with electrons for the fillers and with ion diffusion for the matrix, so that the whole conductive system could be compromise (Wai-Kit Li and Yuen-Wah Wong, 2009).

### 1.2 The choice of the carbon-based fillers

The most common of carbon-based nanofillers can be identified with carbon black, nano-graphene and carbon nanotubes, but other, more unusual ones, could be used as, for example, modified-nanodiamonds. Since today the main possible application of conductive leather can be identifiable with the production of conductive gloves, our efforts were mainly focalized on an in depth study of nano carbon black fillers to use in leather

finishing, due to its lower cost. Then, the coupled use of both carbon black and other nanofillers, has been evaluated, with the particular aim of enhance more peculiar technologies for more sophisticated applications. The basic properties of carbon black and other carbon-based nanofillers have been widely discussed (Anyaporn Boonmahitthisud and Saowaroj Chuayjuljit, 2010; Silvain et al., 2007; Xinyu Yang et al. 2011; Xuefeng Lu et al., 2012), while utilize of CB in leather production has been mainly evaluated to avoid the accumulation of electrostatic charge on it (Marsal et al. 1995).

Carbon black (CB) is a material, made up of nano-sized particles (normally with average particle size of 50nm), produced by the incomplete combustion/thermal decomposition of heavy petroleum products, characterized by a good electrical conductivity. There are many types of carbon black, depending on the production process utilized, on the amount of impurities contained and on the size and granulometry of the particles. The most conductive types are characterized by a high surface/volume ratio.

Graphene, is one of the allotropic forms of carbon, with $sp^2$ hybridized atoms, organized in planar hexagonal cells. It exhibits a good electrical conductivity among the plans, while an insulating behavior is observed in a perpendicular direction. However it shows, by far, lower values of electrical conductivity compared with carbon black and, furthermore, the use of this material as filler, could seriously compromise the mechanical properties of the polymeric matrix. This is the reason why the use of graphene is not preferred for the treated applications.

Carbon nanotubes (CNTs) can be considered another allotropic form of carbon, characterized by a cylindrical nanostructure, where the walls are formed by one-atom-thick sheets of graphene. It is possible to have (CNTs) arranged as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). This kind of filler is characterized by a good electrical conductivity, where it is possible to get satisfying conductivity values with a lower amount of filler, compared with the amount carbon black needed. On the other hand, a disadvantage in using (CNTs) as conductive fillers is due to their higher cost, compared to CB.

## 2. Materials and methods

We started the study with applications to chrome tanned leather samples for gloves making.

- Surface electrical resistance was detected with multitension megohmmeter-GIGALAB-II- Mod.9265.043 - equipped with two probes: a concentric ring probe; a miniature square probe.
- IR leather surface/powders characterization has been carried out with a Spectrum One ATR-IR Spectrometer.
- Morphological studies and microanalysis have been carried out with a Zeiss EVO MA10 Scanning Electron Microscope equipped with a INCA X-act detector.
- Contact angle has been detected with a FIBRO System AB - Mod. PGX pocket goniometer.

- Thermal analysis of conductive fillers has been carried out with a STDQ600 TA Instrument equipped with a THERMOSTAR™ Mass Spectrometer.
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## 3. Results and discussion

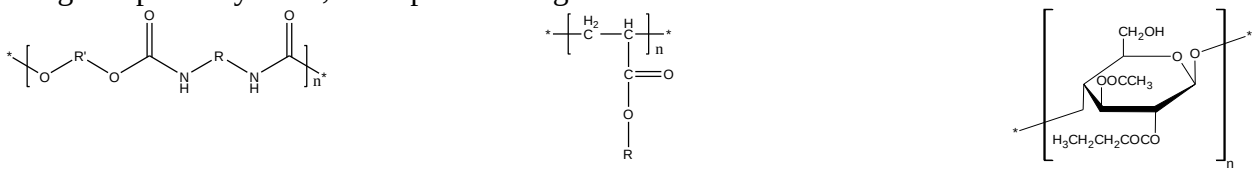
Although an effective surface electrical conductivity, for touch screen applications, is guarantied by surface electrical resistance values of about $10^5\Omega$, our efforts have been devoted to reach electrical resistance values deeply lower, in the range of $10^3\Omega$-$10^2\Omega$, in order to balance the eventual loss of conductivity due to usury effects. Surface treatments, indeed, could be affected by usury effects; we esteemed that 1600 cycles of Martindale abrasion was able to quadruplicate, on average, the electrical resistance values.

### 3.1 The polymeric matrix

Some of the most common finishing polymers have been tested as matrix for carbon fillers dispersion. The final choice has been done taking into account, beside the affinity with the fillers, also the affinity with leather grain, the more or less resistance to abrasion effects and their influence on some chemical-physical properties of leather surface, with particular reference to water permeability and surface hydrophily/hydrorepellency, were our objective was to reach a low water permeability (desirable for gloves production), without improving surface hydrorepellency; we found, indeed, that a better electrical conductivity was exhibited by samples characterized by a slight surface hydrophily.

Three different polymeric main layers has been applied to leather surface, were conductive fillers have been dispersed, for the most, in the basecoat or in both the basecoat and the middle finishing layer, depending on the kind of item to be released, particularly depending on its color.

Some of the main polymers, resulting the most effective for conductive leather production, using composite systems, are reported in figure 3:




**A** **B** **C**

**Fig.3:** Some of the main polymers utilized - general formula of: Polyurethanes - PU (A); Polyacrylates - PA (B); Cellulose Acetate Butyrate - CAB (C)

In figure 4, the IR-ATR spectrum of three finishing layers, containing this polymers, is reported. All the polymers utilized were cationic dispersions, due to the best results obtained, in terms of dispersive capability and of contribution to the final electrical conductivity of the leather samples.

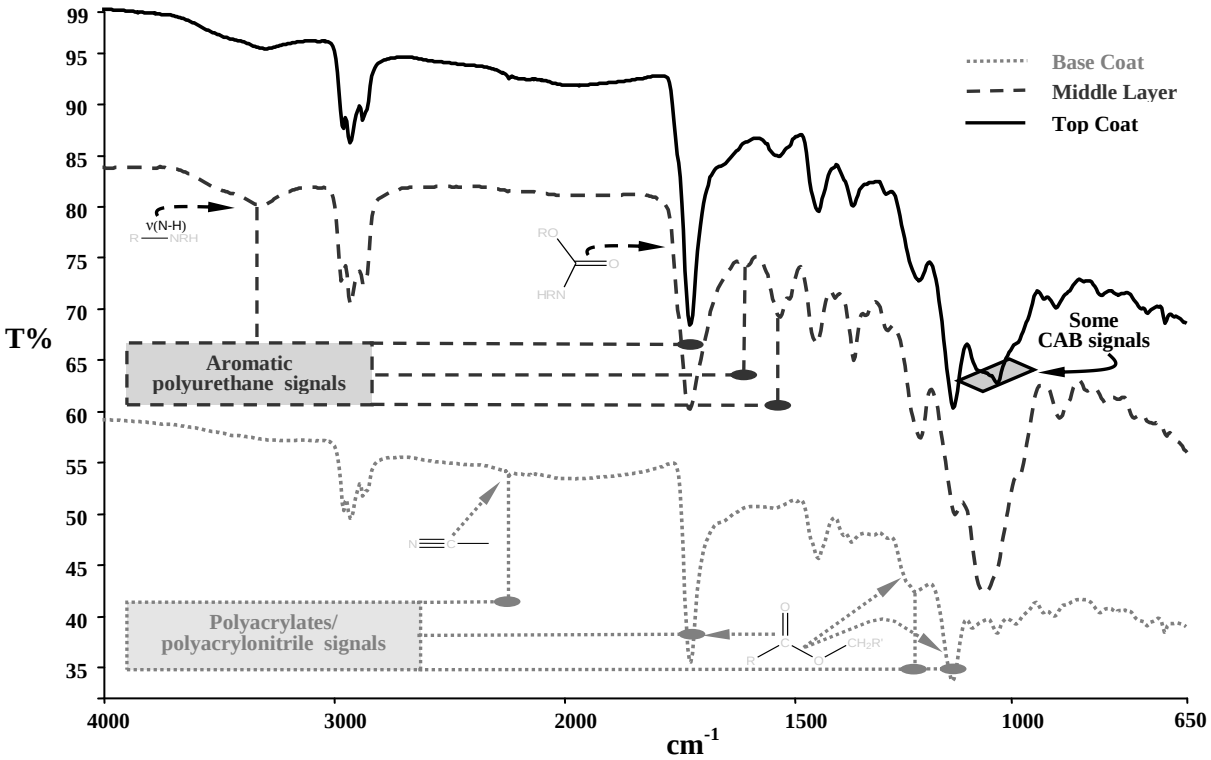



**Fig.4: IR spectra overlap of three different layers of a conductive leather sample**

### 3.2 The conductive fillers

Many types of CB have been analyzed, with different cost and produced by different suppliers, for which many technical features have been investigated, as the particles size and granulometry and the degree of impurities. We found that the main factor able to affect the final electrical conductivity of the leather samples was the particles granulometry.

As example, we reported the comparative study of two different types of CB, CB type 1 and CB type 2, where CB type 1 resulted to be more effective and more easily dispersible. The morphological study of the particles has been carried out with SEM microscopy, showing that the particles size was similar for the two types, but CB type 2 resulted more inclined to form very compact clusters and large beads (figure 5). On the other hand, CB type 1 resulted characterised by a more porous granulometry, with a lower tendency to form clusters.

A larger degree of impurities has been found for CB type 1, as resulted by SEM microanalysis, revealing a larger amount of oxygen content (figure 6) and by IR analysis, showing the possible presence of hydrocarbons. Furthermore, the presence of some IR signals, suggesting the presence of functional groups, as carbonyl and oxydryl ones has been considered too, as a possible factor able to allow a better dispersion in the polymeric matrix.

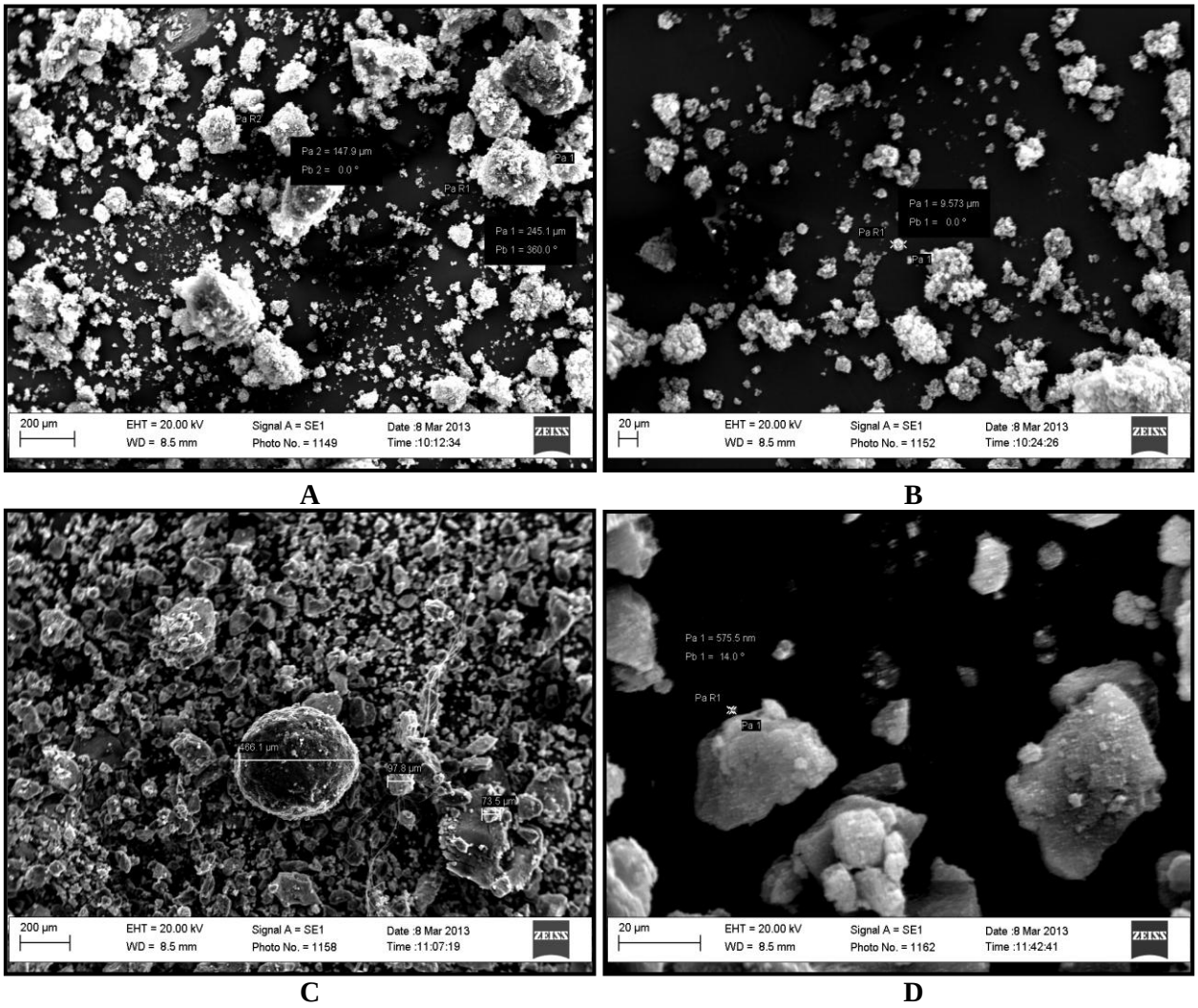
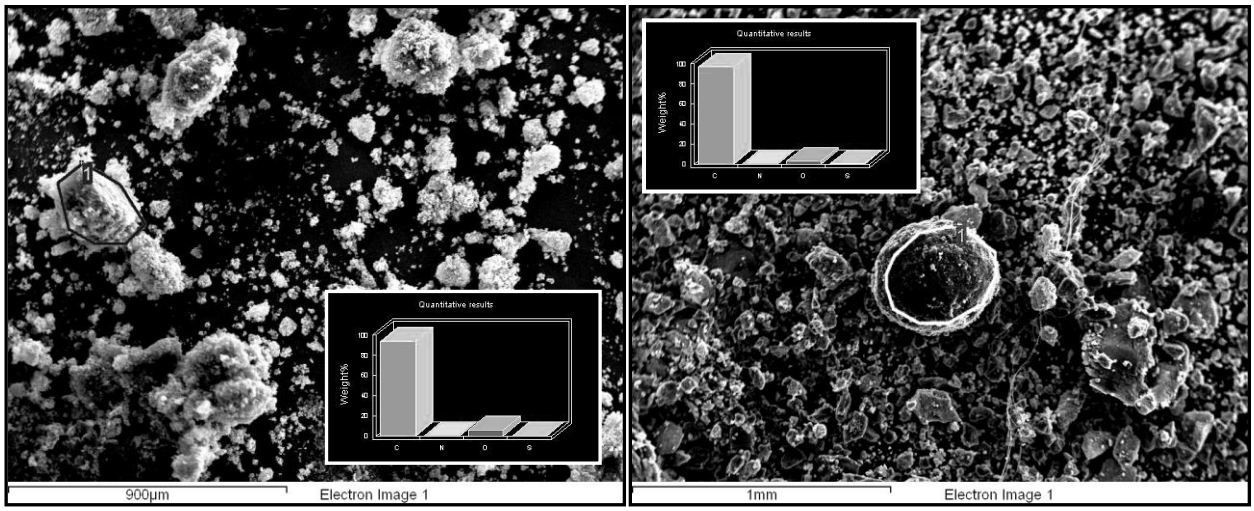



**Fig.5:** SEM images of CB Type 1 (A and B) and of CB Type 2 (C and D)

The presence of impurities has been investigated with Thermal Analysis/Mass Spectrometry too, where the possible presence of hydrocarbons has been confirmed; more in detail, a loss of mass 39, indicative of propargyl cation, $C_3H_3^+$, in the range of temperature of 400-450 °C has been found, as possible fragmentation of alkyne compounds. Furthermore, a loss of mass 43 has been found in the same range of temperature, were it is indicative propyl cation, $C_3H_7^+$ (related to alkane fragmentation), but also of $CH_3O^+$ cation (related to organic esters fragmentation). The loss of mass 44, indicative of $CH_2CHOH^+$ characteristic of McLafferty rearrangement of aldehydes and ketones, has been also found. Finally at 1200 °C a loss of mass 64 (possible loss of $SO_2$) has been detected too (figure 7).

Definitely we supposed that the best features exhibited by CB type 1, in spite of its higher impurities content, could be mainly related to its granulometry, with particular reference to its porosity, where particles could provide a larger surface area for the interaction between the filler and the matrix, allowing a better percolation threshold of CB type 1 through the matrix. Nevertheless, we noticed a decrease of the conductive effects, as the

amount of CB has been increased above the 5% w/w, due to the possible aggregation phenomena and to a worse dispersion leaded by an higher CB loading.
At the moment, the simultaneous effects of CB type 1 and CNTs are being evaluating, in an depth study, mainly finalized to the production of light colored items, were a very scant loading of CB is needed.




**A** **B**

**Fig.6:** SEM microanalysis of CB Type 1 (A) and CB Type 2 (B)

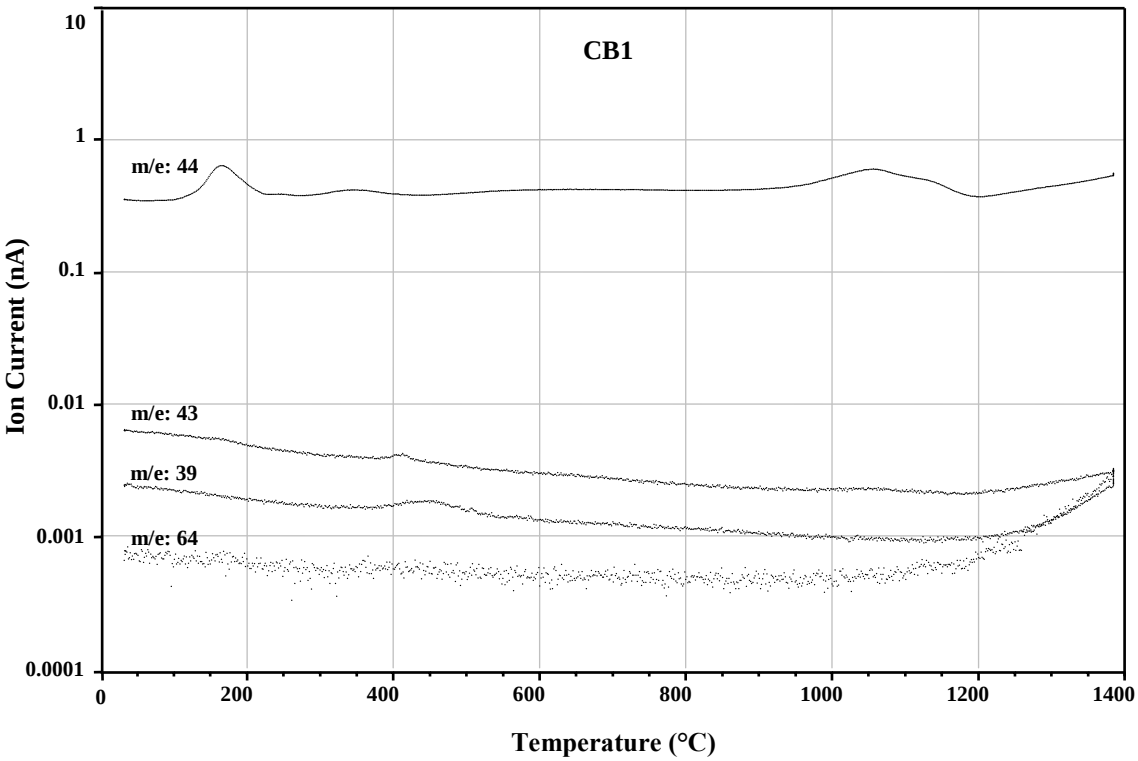



**Fig.7: Thermal analysis/MS detector of CB Type 1**

### 3.3 The conductive leather samples

Many leather samples have been produced and analyzed. A standard production process has been carried out, firstly, for the black colored samples; at a later stage, this procedure has been optimized for the production of differently colored items, were, more in detail, some modifications on the filler loading procedure and on the topcoat composition have been adopted.

The surface electrical resistance values varied from a minimum in the order of $10^2\Omega$ and a maximum in the order of $10^5\Omega$, with an average value of $8{,}56\times10^3\Omega$, depending on the kind of production process adopted. The samples utilized for gloves production have been selected according to the best surface electrical resistance values, but also according to the best commodities features exhibited, with particular reference to their appearance, their handle, some of their chemical-physical properties, as resistance to water permeability and some of their mechanical properties as resistance to abrasion.

SEM microanalysis has been widely employed as a crucial tool for the monitoring of the goodness of leather surface treatments (Florio et al. 2011);

The comparative microanalysis of two different samples is reported in figure 8, where the sample 1, made with a larger loading of CB (but within the 5%), resulted more conductive compared with the sample 2 and where both samples contained metal based pigments, showing that, in chrome tanned leather samples, treated with CB, the presence of conductive metals itself, does not affect significantly the final surface electrical conductivity, so that this has been only affected by CB content. Also if dyes and pigments, indeed, could include some conductive metals as copper, iron and others, on the other hand, the utilize of these metals to improve surface electrical conductivity contemplate the specific employment of metal fibers or ultra fine powders.

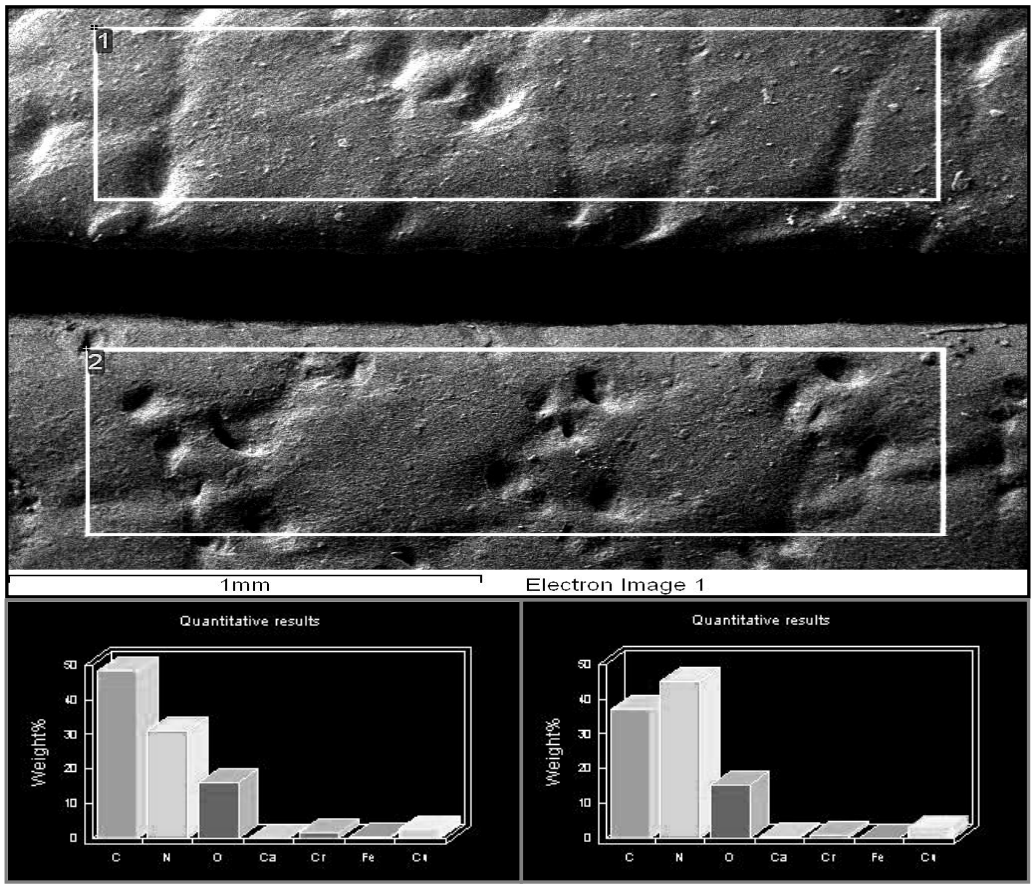
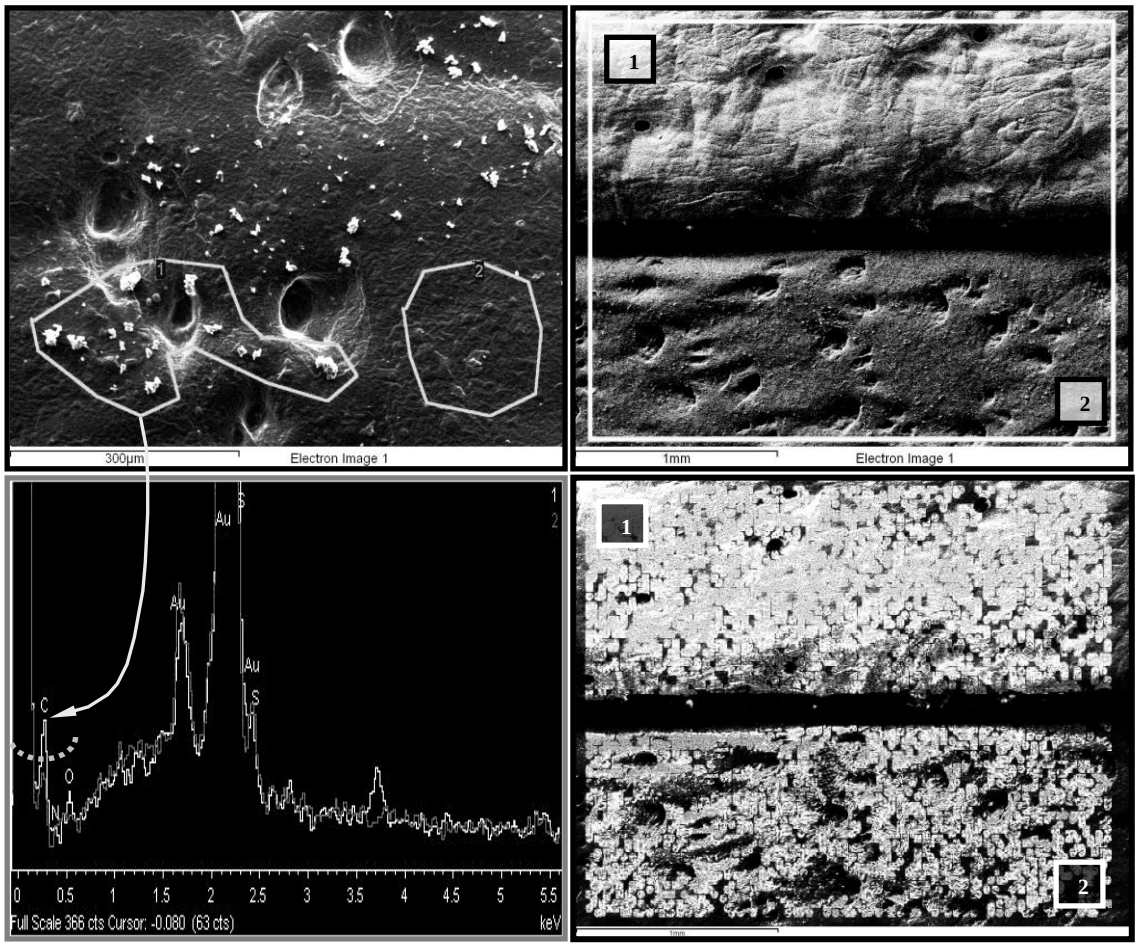



**Fig.8:** SEM X-ray microanalysis of two different black coloured samples

The presence of deposits, based on large sized clusters of CB on leather surface, has been identified when a non optimal dispersion has occurred (figure 9-A). The identification of this kind of failures allowed the planning of the most optimal operative conditions to be adopted for the fillers loading.

The monitoring of fillers distribution has been also gotten through the mapping of large portions of the samples surface. Figure 9-B shows the different distribution of carbon (white pixels in the picture) in samples, characterized by a different production procedure, where CB has been utilized as filler; SEM X-ray mapping showed that sample 1, characterized by a better surface electrical conduction, compared with sample 2, exhibited a better CB distribution too.

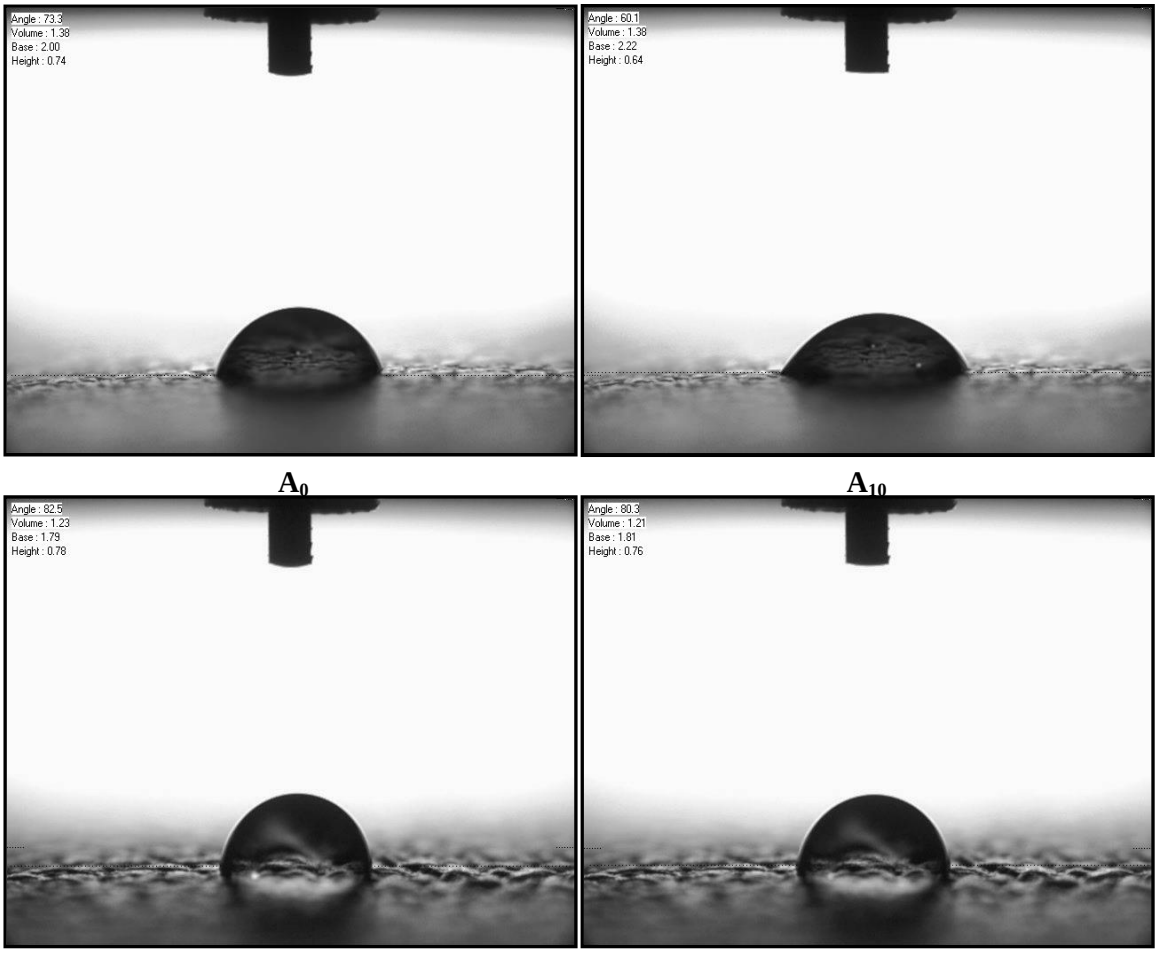



A B

**Fig.9:** SEM X-ray microanalysis: sample characterised by an inefficient CB dispersion (A) - **Carbon distribution in two red coloured samples treated with a different distribution of**

The contact angle of finished samples, has been esteemed too, showing that a better surface electrical conductivity was exhibited by samples characterized by a slight surface hydrophily.

More in detail, the study of the dynamic of water absorption allowed the selection of samples characterized by the opportune surface hydrophily. In figure 10, for example, the contact angle, the volume and the base esteem of water drops is reported for two different samples, at the impact time and after 10 seconds, where for the sample A, resulting more conductive than sample B, a lower contact angle, besides an higher base increase ratio has been detected, revealing an higher surface hydrophily for this sample.




**$A_0$** **$A_{10}$**

**$B_0$** **$B_{10}$**

**Fig.10**: Water drops on the surface of two different samples at the impact time and after 10 seconds

## 4. Conclusions

A significant improve of surface electrical conductivity of the treated samples has been gotten. The best results have been obtained using a particular type of CB, as conductive filler, characterized by an high porosity of the particles. Opportune combinations of CB and CNTs are being evaluating too.

The best combination of polymers, used as dispersive matrix, has been gotten taking into account their affinity with the fillers and with the leather grain, their resistance to abrasion and their surface chemical-physical properties.

The results obtained and the information collected from the experimental investigation encourage the industrial use of peculiar modern technologies to improve the electrical conductivity of leather surface and definitely allow to preserve the leather own and well known feature of being one the most comfortable material and, at the same time, to provide it the opportune properties to become one of the most hi-tech materials on the market.

Cold atmospheric plasma treatments will be evaluated too, in the near future, in order to get a satisfying surface functionalization for the fillers loading, avoiding a large utilization of chemicals and polymers.

Further developments of the studied technologies could be considered, in the near future, for an in depth study aimed at the utilization of these technologies in other possible fields, as their application to radio-frequencies technology, where appropriate electromagnetic interferences may be created by a suitable functionalization of leather surface.

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