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Improving electrical conductivity of leather surface: a new technology versus industrial applications

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Abstract

The present study takes into account the consumer requirement of an even more massive use of touch screen devices, where the leather has 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 kinds of conductive goods, like shoes, garments, and others. Most of the known technologies able to provide materials with a unique ability to discharge static electricity and conductivity comparable with the human body concern the use of textile fibers. On the other hand, the goal of the present work is to delve into the application of technologies for leather matrix, with particular reference to the use of carbon-based nanomaterials, and attention to economical and/or practical aspects.

1. Introduction

The prominent role of touch screen technologies is mainly due to the possibility of enabling human interface with modern electronic devices without the need for any keyboard, mouse or stylus and without the need for 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 cashpoint machines (ATMs), satellite navigation devices, besides a wide set of specific electrical tools used, for example, in automotive, aviation and aerospace industry.

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

The leather itself may have a variable electrical conductivity, depending on its humidity degree and electrolytic content from the chemicals used in the tanning process, but, overall, on the kind of finishing applied. Anyway, the production of leather characterized by a high performance in touch screen applications needs 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 nano-compounds, and conductive polymers, with particular reference to conjugates polymers converted into electrically conductive polymers by treatments with opportune dopant agents. The intrinsic conductive properties of many finishing polymers have been widely discussed in the literature [1] and have to be taken into account for the planning of adequate conductive treatments. Very few papers have been published on this topic [2], and some patents [3]. On the other hand, obtaining conductive leather gloves is still an open challenge. One possible approach can be related to the use of a
conductive filler to be incorporated in the finishing layer for improved conductivity. There are different crucial parameters to be considered in a composite system. Polymers’ mechanical and physical properties, thermoplastic rather than thermosetting nature can critically affect the final conduction mechanism, due to their influence on the dispersive effects towards the conductive fillers. In particular, 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 and 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 [4], avoiding the formation of fillers aggregates. In figure 1, the influence of the dispersion of the filler on the possible conduction path, in a composite system, is represented schematically.

The polymeric crystalline degree can also affect the goodness of the conduction path, so that, a low crystalline degree ensures a better conduction path, compared with a high crystalline degree. This effect is shown in figure 2. 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 [5, 6]. Finally, particular attention must be paid to the conduction mechanism of the matrix and filler, i.e., electrons for fillers and matrix or ions for filler and matrix [7].

Among additives, because of the electrical conductivity, carbon-based nanofillers can be identified, such as carbon black, nano-graphene, carbon nanotubes, and modified-nanodiamonds [8, 9]. Since today the main possible application of conductive leather can be identified with the production of conductive gloves, our efforts

**Figure 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).

**Figure 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).
were mainly focalized on an in-depth study of nanocarbon black fillers to use in leather finishing, due to its lower cost. The basic properties of carbon black and other carbon-based nanofillers have been widely discussed [10–13], while the utilization of carbon black (CB) in leather production has been mainly evaluated to avoid the accumulation of electrostatic charge on it [14].

Carbon black is a material, made up of nano-sized particles (normally with an average particle size of 50 nm), 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, the amount of impurities contained and the size and granulometry of the particles. The most conductive types are characterized by a high surface/volume ratio.

The average surface electrical resistance, exhibited by human skin, is estimated to be around $10^5$ $\Omega$, while leather surface resistance normally varies from about $10^9$ $\Omega$ to $10^{10}$ $\Omega$, depending on the kind of chemicals and technologies used in leather production [15]. Leather electrical conduction improvement can be provided by both wet-phases or surface treatments, where we chose the latter because it is more effective. More in detail, the approach we adopted, was based on finishing treatments by using a composite system containing carbon-based fillers.

Here we report a new approach for leather finishing, to make leather gloves suitable for use in touch screens. In particular, three polymeric composites layers: the basecoat, the middle and top layers were applied on the surface of chrome-tanned leather for gloves. The nanocomposites were based on the use of cheaper carbon black. Particular attention was devoted to the main technical challenges: compatibilization between leather/leather finishing, choice of conductive agents, and the chemical/physical processes to be adopted.

2. Materials and methods

2.1. Materials

2.1.1. The polymeric matrices

Three different polymeric layers were applied to the leather surface: the basecoat, the middle, and the top finishing layers. The conductive fillers were dispersed in both the basecoat and the middle finishing layer. The polymers used for conductive leather production, using composite systems: Polyurethanes - PU; Polyacrylates - PA; and, Cellulose Acetate Butyrate—CAB, for the basecoat, middle and top finishing layers, respectively, are shown in figure 3.

They are used as received and acquired by TFL. The choice of these materials was made in close collaboration with the R&D Department of the DMD tannery of the Solofra tanning sector, one of the three tanning Italy centers. In particular, the best materials used in the company, known for good commodities features: appearance, handling, chemical-physical properties, e.g., resistance to water permeability; mechanical properties, e.g., resistance to abrasion, were used.

The details of the preparation procedure are shown in table 1. For the preparation of the nanocarbons loaded suspension: a solution, aqueous base, of the different components at pH 7 was mixed with the nanofillers up to the desired amount under stirring at 40 $^\circ$C. To increase dispersion, in some cases, were indicated, Sodium dodecyl-benzenesulfonate (SDBS) was added as a surfactant. Indeed, the modification of the CB surfaces trough the use of SDBS, allows minimizing the electrostatic attraction of the particles and the consequent formation of clusters. After mixing for 3 h the suspensions were ready to be used. All the polymers utilized were cationic dispersions because of the best results in terms of dispersion and final electrical conductivity of the leather obtained. In figure 4, the IR-ATR spectra of three finishing layers (basecoat, middle, and top) are reported.
2.1.2. The conductive fillers

Many types of CB were analyzed, with different costs and produced by different suppliers, for which many technical features were investigated, such as the particle size and granulometry and the degree of impurities. In general, we found that the main factor affecting the final electrical conductivity of the leather samples was the particle granulometry.

In particular, in the following the comparative study of two different types of CB, CB type 1 and CB type 2, commercialized as Conductectex SC Ultra Beads—Columbian—IMCS UK Limited, and the results and discussions related to the best-identified candidate, are reported.

2.2. Composite preparation

Black colored leather samples were prepared with conductive fillers dispersed both in the basecoat and the middle finishing layer.

In particular, six different samples were obtained, adding CB1 and CB2 at three different loadings (5 wt%, 3 wt%, and 4 wt%). Three samples were prepared by adding CB1 and three samples by adding CB2, named: samples 1 containing a CB loading at 5 wt%; samples 2 were obtained with a lower amount of CB (3 wt%); finally, samples 3 was obtained by adding 4 wt% of CB.

2.3. Methods

Some analyses were performed:

- Surface electrical resistance was detected with multi-tension megohmmeter-GIGALAB-II- Mod.9265.043 - equipped with two probes: a concentric ring probe; a miniature square probe. For the measurements, leather samples, covered by the finishing layer, of 1 cm × 1 cm were tested. In calculation, a thickness of 20 μm, for the conductive layer, was considered.
IR leather surface/powders characterization was carried out with a Spectrum One ATR-IR Spectrometer.

Morphological studies and microanalysis were carried out with a Zeiss EVO MA10 Scanning Electron Microscope equipped with an INCA X-act detector.

The contact angle was detected with a FIBRO System AB - Mod. PGX pocket goniometer.

Thermal analysis of conductive fillers was carried out with a STDQ600 TA Instrument equipped with a THERMOSTAR™ Mass Spectrometer.

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

Figure 6. SEM microanalysis of CB Type 1 (A) and CB Type 2 (B).
3. Results and discussion

3.1. The conductive fillers

In the following an analysis of the two carbon fillers, CB type 1 and CB type 2, is reported.

The morphological study of the CB particles was carried out by using SEM microscopy. It shows that the particle size was similar for both CB1 and CB2. CB type 2 resulted more inclined to form very compact clusters and large beads, see figure 5. On the other hand, CB type 1 resulted characterized by a minor tendency to form aggregates.

Moreover, a larger degree of impurities was found for CB type 1, as evidenced by SEM microanalysis, revealing a larger amount of oxygen content (figure 6) and by IR analysis (not shown here), indicating the
possible presence of hydrocarbons. On the other hand, some carboxylic and oxodrylic moieties, evidence by IR signals, surely help the dispersion in the polymeric matrices. The presence of impurities was investigated by Thermal Analysis/Mass Spectrometry, too. The possible presence of hydrocarbons was confirmed. More in detail, a loss of mass 39, indicative of propargyl cation, C≡CH+ + , in the range of temperature of 400 °C–450 °C was found, as possible fragmentation of alkyn compounds. Furthermore, a loss of mass 43 was found in the same range of temperature, were it is indicative of propyl cation, CH3C≡CH+ (related to alkane fragmentation), but also of CH3O+ cation (related to organic esters fragmentation). The loss of mass 44 (possible loss of CO2), indicative of CH3CHOH+ characteristic of McLafferty rearrangement of aldehydes and ketones, was also found. Finally, at 1200 °C a loss of mass 64 (loss of SO2) was detected too (figure 7).

Table 2. Sample prepared and relative resistance values.

| Sample with CB1: electrical resistance values (KΩ) | Sample with CB2: electrical resistance values (KΩ) |
|-----------------------------------------------|-----------------------------------------------|
| Sample 1 | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 |
| 11,8     | 8,8     | 13,6     | 9,5     | 66,0     | 21,9     |
| 7,7      | 11,6    | 7,9      | 13,4    | 73,8     | 15,3     |
| 0,8      | 12,8    | 8,5      | 15,4    | 75,6     | 14,8     |
| 8,8      | 11,0    | 12,2     | 12,8    | 68,8     | 16,2     |
| 3,8      | 8,6     | 5,3      | 7,3     | 67,3     | 13,5     |
| 10,8     | 10,4    | 7,1      | 9,4     | 66,9     | 22,1     |
| Average  | 7,3     | 10,5     | 9,1     | Average  | 11,3     | 69,7     | 17,3     |
| St. Dev  | 4,2     | 1,6      | 3,2     | St. Dev  | 3,0      | 4,0      | 3,7      |

Figure 8. SEM and x-ray microanalysis of two different samples, obtained at two CB type 1 loading (CB1 addition at two different loadings, 5 wt% and 3 wt%, i.e., sample 1 and sample 2 with CB1), but in the absence of the surfactant.
3.2. The conductive leather samples

The surface electrical resistance values varied from a minimum in the order of $10^2 \, \Omega$ and a maximum in the order of $10^4 \, \Omega$ depending on the samples, see table 2. Nevertheless, we noticed a decrease in the conductive effects, as the amount of CB has been increased above the 5% w/w due to possible aggregation phenomena and worse dispersion.

![Figure 9. SEM x-ray microanalysis: sample characterized by an inefficient CB dispersion (A) - Carbon distribution in two samples treated with a different distribution of CB1 at 5 wt%: 1. after the addition of SDBS; 2. without SDBS addition (B).](image)

![Figure 10. The electrical conductivity of the prepared samples. *Electrical conductivity of sample 1 prepared in the presence of SDBS.](image)
The characteristics of the two carbon blacks: the lower tendency to aggregation and larger content of impurities for CB1 compared to CB2, result in a better dispersion behavior for CB1. Thus the following discussion is focused on CB1 based coating. SEM microanalysis has been widely employed as a crucial tool for the monitoring of the goodness of leather surface treatments [16]. The comparative microanalysis of two nano-coating, obtained at two CB type 1 loading (CB1 addition at two different loadings, 5 wt% and 3 wt%, i.e., sample 1 and sample 2 with CB1), but in the absence of the surfactant, is reported in figure 8. Although the two samples have different loading, they exhibit a very similar morphology. On the other hand, an optimization of the dispersion procedure was performed because of the presence of some deposits based on large-sized clusters of CB on the leather surface, see figure 9(A). The identification of this kind of failure allowed the planning for most optimal operative conditions to be adopted for the fillers loading, i.e., the addition of SDBS. The monitoring of fillers distribution was also obtained through the mapping of large portions of the surface of two samples, i.e., sample 1 obtained by adding CB1, with and without the use of SDBS. In particular, in figure 9(B), two different surfaces: 1 and 2, were compared through SEM images in the top right corner and by x-ray mapping in the bottom right corner. The bottom of figure 9(B) shows the different distribution of carbon (white pixels in the picture) in samples characterized by a different production procedure. The surface characterized by a better filler
distribution corresponds to sample 1 prepared in the optimized conditions, i.e. additive for improved
dispersion, which shows an even higher electrical conductivity (lower electrical resistance of 5.4 KΩ), also if
compared with sample 1 obtained with CB1 but in the absence of surfactant, see table 2.

In figure 10, the electrical conductivity of the different samples is shown. The values are very promising, also, if compared with other literature results [1, 2]. In figure 11, a SEM image of a leather coated sample is also shown, evidencing the substrate and the coating, and allowing to evaluate the thickness of the finishing layer, which is typically in the range 10–20 μm. Finally, a photo of a coated glove, obtained by adding 5 wt% of CB1 in the presence of SDBS, is shown in figure 12. It is worth noticing, that although an effective surface electrical conductivity, for touch screen applications, is guaranteed by surface electrical resistance values of about 10^5 Ω, our efforts were devoted to achieving electrical resistance values deeply lower, in the range of 10^3 Ω-10^2 Ω, 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 were able to quadruplicate, on average, the electrical resistance values.

For further evaluation, the contact angle on finished samples was estimated, too, showing that a better surface electrical conductivity was exhibited by samples characterized by slight surface hydrophilicity, see figure 13. In figure 13, the contact angle, the volume, and the base esteem of water drops are reported for two different samples, at the impact time and after 10 s, as an example. For sample A, (sample 1 with CB1), which is more conductive than sample B (sample 2 with CB1), a lower contact angle, besides a higher base increase ratio, was detected, revealing slightly higher surface hydrophilicity for this sample.

4. Conclusions

In summary, a significant improvement of the surface electrical conductivity was obtained for the treated samples. The best results were obtained using a particular type of CB, as conductive filler, characterized by a lower tendency to aggregate. It is worth noticing that although both samples contain metal-based pigments, they are not able to modify surface electrical conductivity, which requires CB content. Definitely, we can conclude that the best features exhibited by CB type 1, in spite of sample higher impurities content, could be mainly

Figure 13. Water drops on the surface of two different samples at the impact time and after 10 s.
related to its lower tendency to aggregate and larger surface area for interaction between the filler and the matrix, allowing a better percolation threshold of CB type 1 through the matrix.

The results obtained and the information collected from the experimental investigation encourage the industrial use of this approach to improve the electrical conductivity of leather surface preserving the leather and its well-known feature of being one of the most comfortable material, versus a hi-tech material for the market.

In order to obtain a satisfying surface functionalization, avoiding a large utilization of chemicals and polymers, cold atmospheric plasma treatments will be evaluated in the near future, too. Further developments of the studied approaches could be considered, in the near future, for the utilization of these technologies in other possible fields, e.g., radio-frequencies technology, where appropriate electromagnetic interferences may be created by a suitable functionalization of leather surface. Opportune combinations of CB and CNTs are under evaluation, too.

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