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ITALIAN LEATHER RESEARCH INSTITUTE
STAZIONE SPERIMENTALE PER L'INDUSTRIA DELLE PELLI E DELLE MATERIE CONCIANTI

SUSTAINABLE LEATHER FINISHING: OPTIMIZING THERMAL PROPERTIES WITH GRAPHENE NANOPLATELET-POLYURETHANE NANOCOMPOSITES

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Sustainable leather finishing: optimizing thermal properties with graphene nanoplatelet-polyurethane nanocomposites

Scope of the Research

Material and Methods

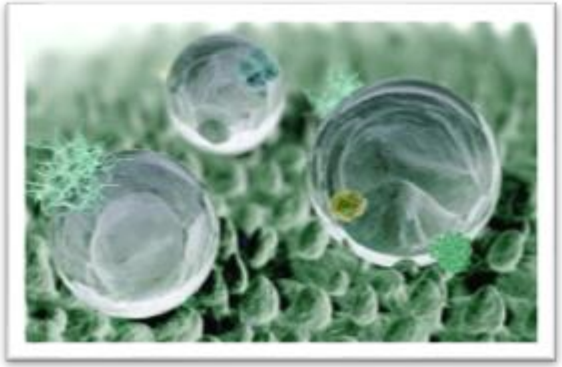
Discussion of Results

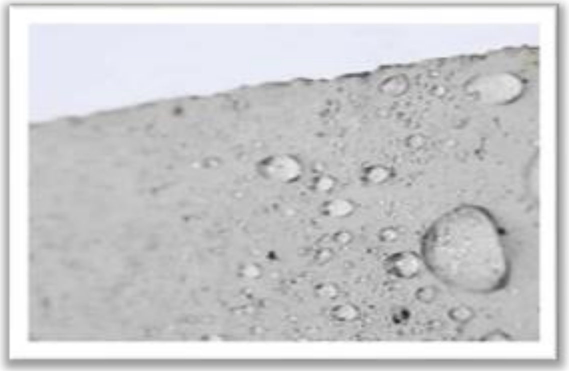
Scope of the Research

Nanotechnologies are widely used for surface functionalization, allowing to gain new or improved properties for coating materials.

Examples of applications include:

- **Antibacterial coatings** with silver or zinc oxide nanoparticles.
- **Self-cleaning surfaces** with TiO_2 nanoparticles.
- **Scratch and wear-resistant** protective surfaces with nanoceramics.
- **Barrier coatings** with nanoclays or graphene.
- **Optical coatings** with nanostructures for anti-reflection or special colors.





Scope of the Research

In **tanning industry**, nanotechnology has gained significant attention in all process phases.

Carbon-based and **graphene derivatives** offer outstanding potential for their high aspect ratio, superior thermal and electrical conductivity, and great mechanical reinforcement capabilities.

Graphene nanoplatelets (GNPs) are considered very suitable for industrial applications:

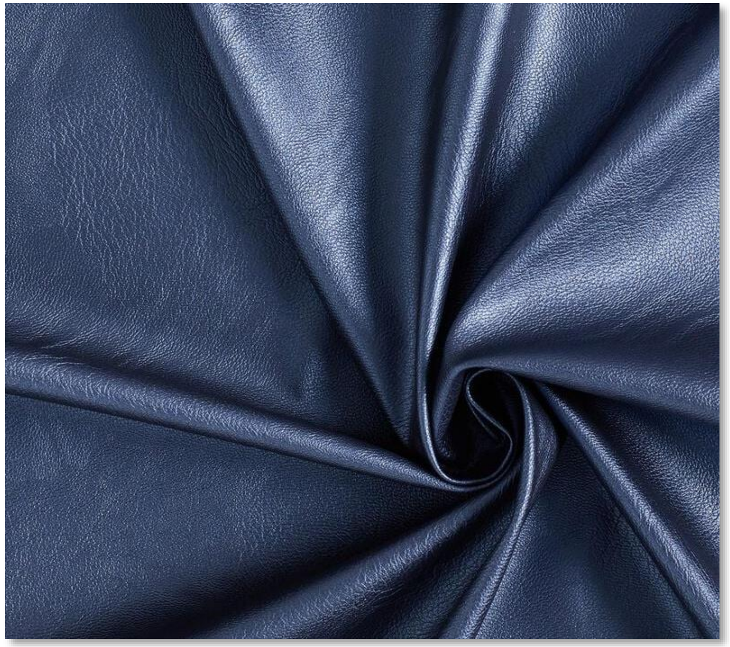
- They offer higher intrinsic **electrical and thermal** conductivity, fewer structural defects, and superior processability.
- Their **hydrophobic** nature promotes good **dispersion** within polymeric matrices.
- They are also significantly **more economical**, making them an attractive choice for large-scale use compared to graphene or graphene oxides.

Scope of the Research

These combined advantages make GNPs excellent candidates for **tanning industry** to produce **functionalized finishing** for leather, where enhanced performance are increasingly required.

In this work, two types of **GNPs** with different aspect ratios were used as fillers for finishing for automotive leather to develop a multilayer functional coating with:

- **enhanced mechanical performances**
- **improved thermal conductivity.**



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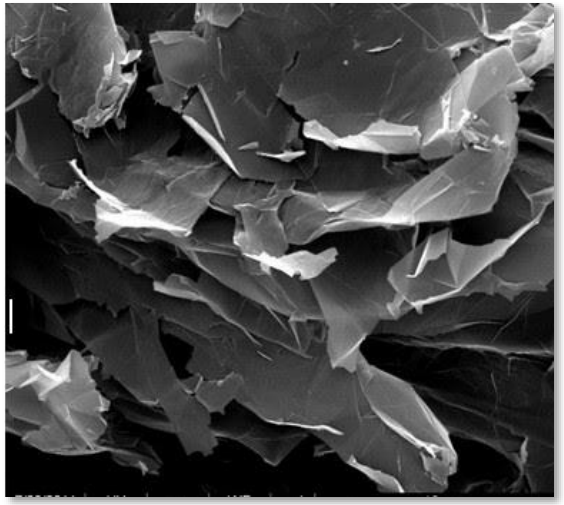
Material and Methods

Graphene Nano-Platelet

The properties of the two **graphene nanoplatelet (GNP)** used in the project (**G2NAN** and **G7NAN)** with different aspect ratios (1500 and 500) are reported below.

DESCRIPTION	G2NAN	G7NAN
Average lateral size	D59 = 25 μm	D90 = 16 μm; D50 = 7 μm
Aspect ratio	1,500	500
Average flake thickness	14 nm (42 layers)	21 nm (63 layers)
Bulk density (g/cm^3)	0.020 – 0.042	0.2
Carbon content (%)	> 97	> 65
State	Water paste	Powder



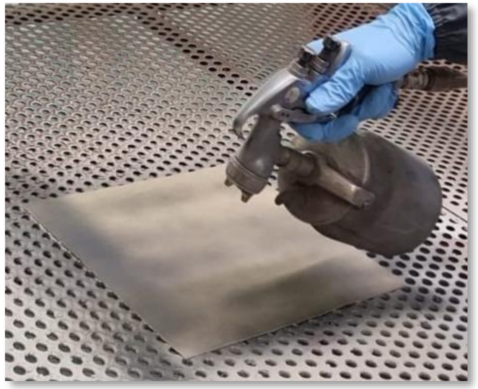
Aspect ratio and **lateral size** are the most important parameters influencing the final properties of the nano-composite, even in relation to their percentage composition into the matrix.

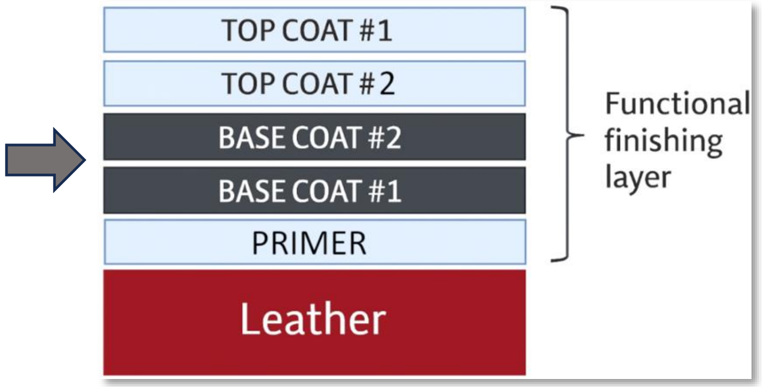
Material and Methods

Finishing Formulation

The **finishing** were prepared according to a Pasubio S.p.A. formulation, using a **polyurethane-based** base coat without pigments.

- GNPs has been **dispersed** into the chemicals through **ultra-sound sonication.**
- A laboratory-scale layer application using spray deposition was performed.
- The finishing consists of five layers applied sequentially.
- Only the **base coat** layers have been functionalized using **GNPs**.





Material and Methods

Finishing Formulation

To simulate industrial application, the viscosity of each layer was adjusted using a Ford Cup #5 to achieve a flow time of 20–25 seconds (viscosity between 100 cP and 120 cP).

Each layer has been dried in oven at 70 °C for 60 seconds to promote solvent evaporation and avoid interlayer defects before the subsequent coating was applied.

The amounts of GNPs used in the functionalized layers are reported. Quantities were selected according to the **electrical percolation threshold** of each GNPs type, providing sufficient nanoparticle networking within the coating matrix to potentially enhance electrical properties.

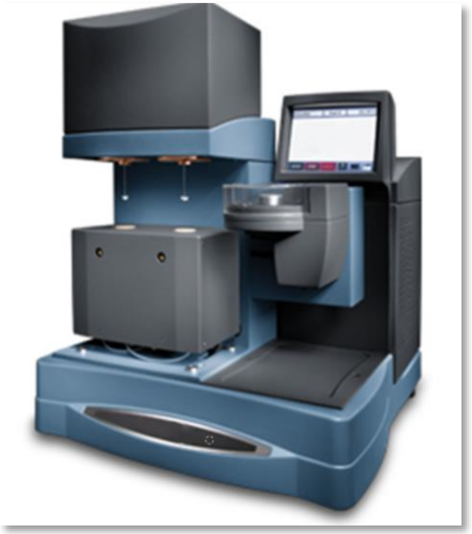
LAYER	COATING WEIGHT (g/m²)	G7Nan wt%	G2Nan wt%
TOPCOAT #2	27.5	–	–
TOPCOAT #1	27.5	–	–
BASE COAT #2	55.0	18.0	4.5
BASE COAT #1	55.0	18.0	4.5
PRIMER	33.0	–	–

Material and Methods

Multilayer Characterization

The multilayer coating were prepared by spray deposition onto silicon substrates to ensure the proper detachment of the film for subsequential characterization.

The following **tests** have been carried out **on neat and GNPs modified coating**:



TGA analysis in nitrogen at a rate of 10 °C/min up to 900 °C using a TA Q5000 (ASTM E 1131) to determine the thermal stability of the multilayer coating and the residual mass loss at 750 °C.

DSC analysis in nitrogen by means two heating/cooling cycles from − 50 °C to 280 °C at 10 °C/min using a TA DSC Q2000 to identify glass transition temperature (ASTM D 3418).

Material and Methods

Multilayer Characterization

Tensile tests were carried out to evaluate possible changes in the mechanical properties of the GNPs functionalized multilayer finishing.

- DMA techniques have been used by means of a TA Instruments Q850 in tension film mode.
- Rectangular test pieces measuring (20.0 ± 0.10 mm × 6.0 ± 0.10 mm) were tested in quasi-static conditions at displacement rate of 1 mm/min at two reference temperatures 23 °C and 60 °C.
- **Tensile strength**, **elongation at break** and **Young's Modulus** in the 0.05 % and 0.25 % of strain have been assessed.

Material and Methods

Functionalized leather

To assess the properties of functionalized leather, **crust** for automotive **finished** using G-NAN multilayer formulations has been analyzed by:

Nanoindentation tests using a NanoTest (Micro Materials Ltd):

- Performing the tests in force-controlled mode by applying a load in the range of 0.03 – 1.00 mN at a rate of 1 mN·s^{-1}.
- Applying a maximum indentation depth to less than 10 % of the sample thickness to minimize the subtrate effect.
- Recording for the results both the loading and unloading curves.

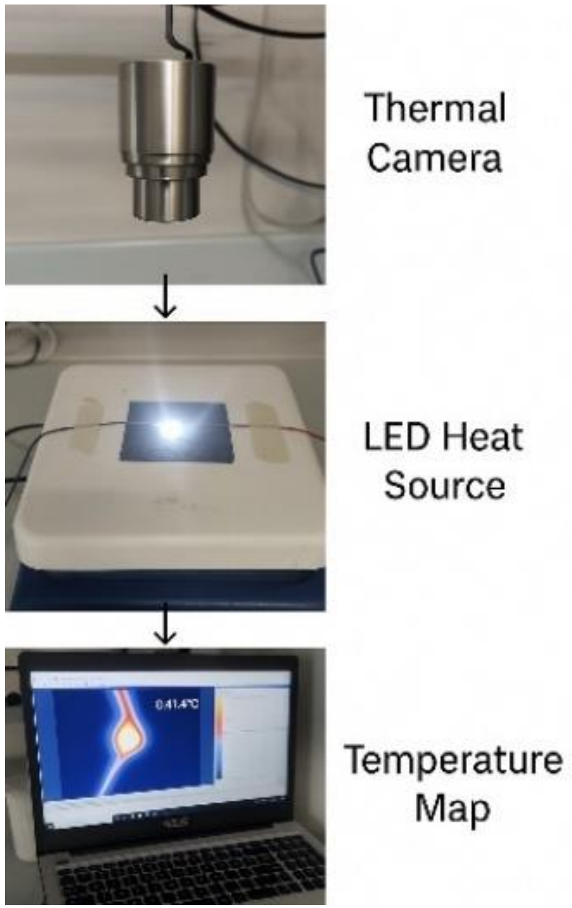
This test provides information on **surface changes** in terms of the final properties of a coated product

Material and Methods

Functionalized leather

A customized **Thermal diffusivity test** that provided the follow**:**

- A **Heat Source** has been applied by means of a **LED** powered at a voltage of 3.7 V to ensure constant and input **power of 1 W.**
- Samples were **fixed on a flat ceramic-insulated surface**.
- **LED** was placed **in contact** with the sample with a maximum duration of 4 min to achieve a stable thermal gradient.
- **Thermal imaging** was conducted using an IR camera (Optris Xi 400) measuring temperature distributions at regular intervals and enabling the thermal maps for heat diffusion analysis.



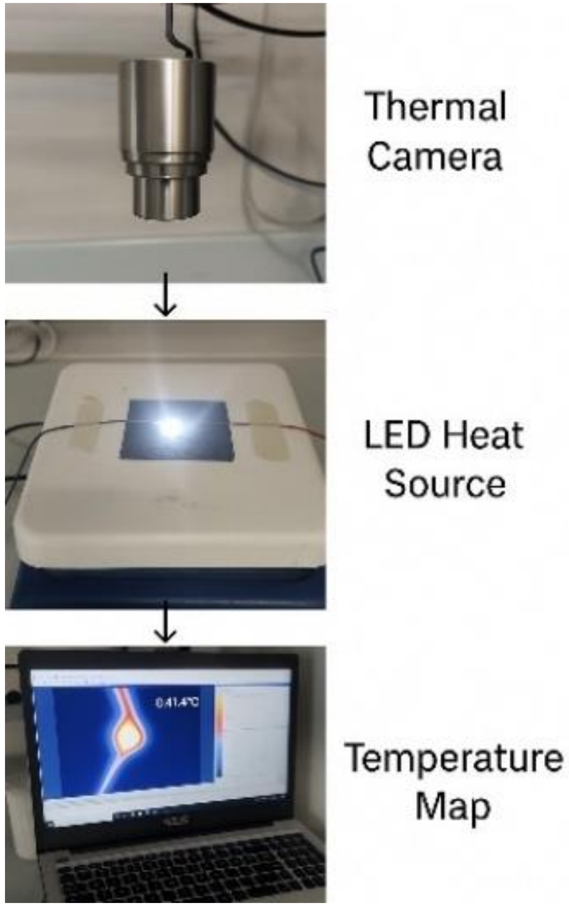
Discussion of Results

Functionalized leather

If a heat source is applied to a surface, the speed and the mode of heat transfer spatially depend on the thermal diffusivity. The thermal diffusion for the temperature *T(x, t)* along a distance x and as a function of time t is defined by:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

This model can be used to analyse the thermal behaviour by measuring the temperature distribution at successive times, allowing an **estimation** of the material's thermal diffusivity.



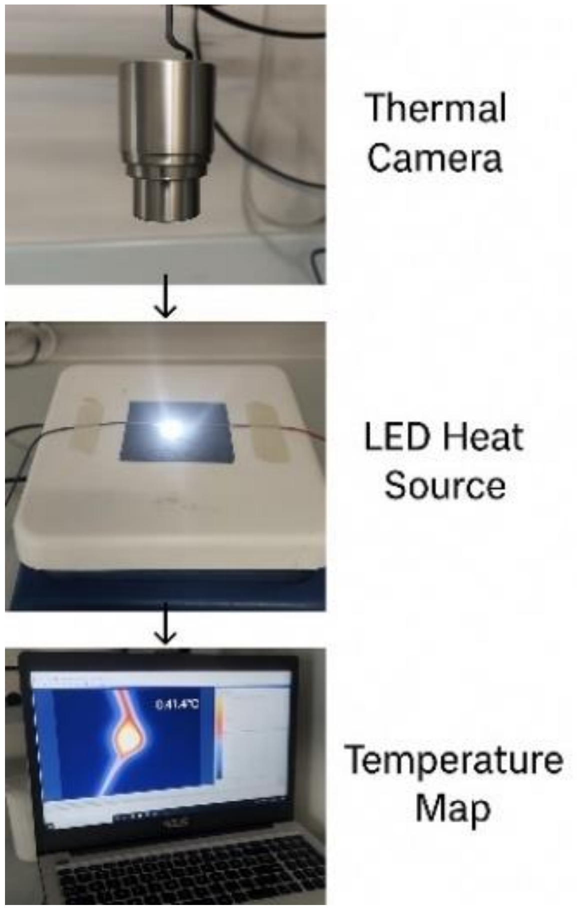
Material and Methods

Functionalized leather

Two configurations were tested to evaluate thermal diffusivity:

- **In-plane measures (Surface diffusivity):** heat source was placed on the finished surface, and temperatures were recorded on the same side.
- **Cross-plane measures (Bulk diffusivity)**: heat source was applied to the finished surface, and temperature was measured on the opposite side.

These tests provided data on heat distribution uniformity and rate, allowing indirect **estimation of thermal capacity and conductivity**.



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Scope of the Research

Material and Methods

Discussion of Results

TGA results define an average estimation of all the coating layers. The **actual GNP content** was determined by a correction of the dry residue with the value of neat multilayer at 750 °C.

The actual filler contents are in line with the expected filler content:

- For G7NAN-based film the filler content was measured 8.0 wt % versus the theoretical 8.6 wt %
- For G2NAN-based film the filler content was measured 2.2 wt % versus the theoretical 2.0 wt %

SAMPLE	NOMINAL FILLER (wt%)	RESIDUE (wt%)	FILLER CONTENT (wt%)	FILLER CONTENT (VOL%)	Tg_0 (°C)	Tg (°C)
Neat	0.0	7.4	0.0	0.0	-31.81	78.76
G2	4.0	9.5	2.2	1.0	-31.74	77.37
G7	18.0	14.8	8.0	4.6	-28.66	73.73

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Discussion of Results

Multilayer Thermal Analysis

DSC analysis revealed the presence of two distinct glass transition temperatures confirming the polyurethane nature of the coating: a **low-temperature transition** ($Tg_0 \approx -32$ °C) for the **soft segments** and a **higher transition** (Tg ≈ 78 °C) attributed to the **hard segment** domains.

The use of GNPs as filler determined only minor changes in the soft segment Tg_0, suggesting limited disruption of the flexible phase microstructure.

In contrast, the hard-segment Tg decreases with increasing GNP content and decreasing lateral size.

SAMPLE	NOMINAL FILLER (wt%)	RESIDUE (wt%)	FILLER CONTENT (wt%)	FILLER CONTENT (VOL%)	Tg_0 (°C)	Tg (°C)
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Discussion of Results

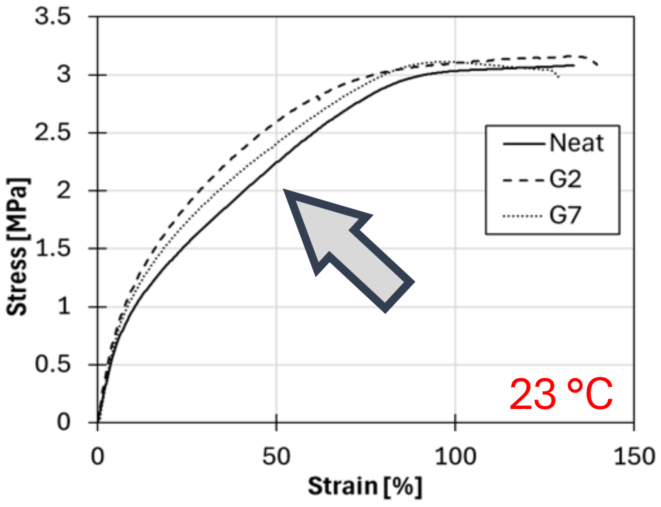
Multilayer Tensile Tests

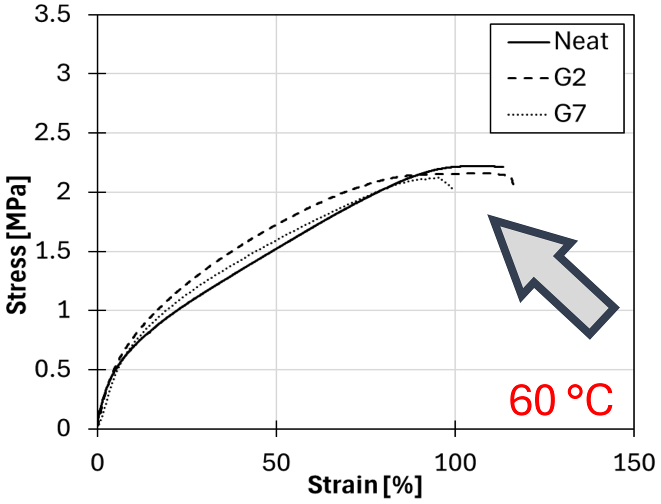
The stress–strain curves at 23 °C and 60 °C are reported in figures. They show an initial **quasi-linear elastic region**, followed by a progressive **plastic deformation** and a region before failure where the stress remains **nearly constant** due to strain-induced orientation of the soft segments.

At **23 °C**, the GNP filler determines an increase of coating stiffness and a slight increase of tensile strength using both GNPs.

At **60 °C** the GNP filler determines a slight increase of stiffness and a slide reduction of tensile strength.

In both cases, G2Nan determines a slight increase in elongation at break while G7Nan a slight decrease, more evident at higher temperatures.

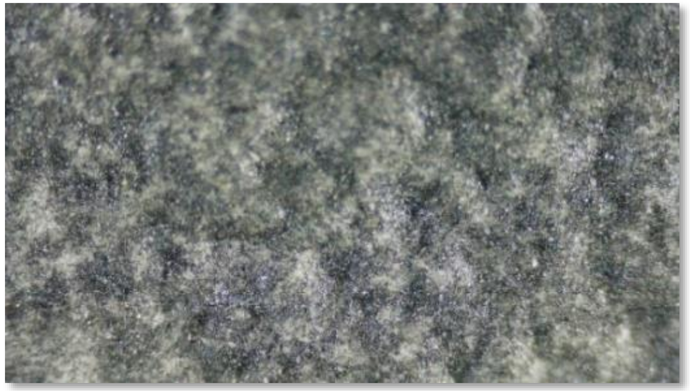




Discussion of Results

TESTS ON FINISHED LEATHERS

In the next slides, the results of tests carried out on automotive crust leather finished with modified GNPs functionalized coatings are summarized

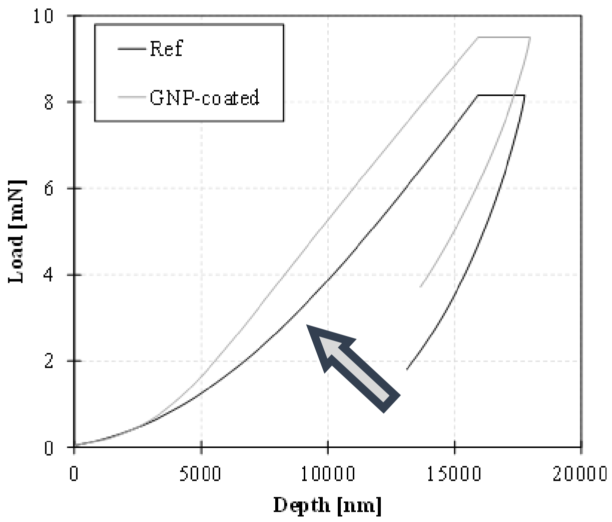


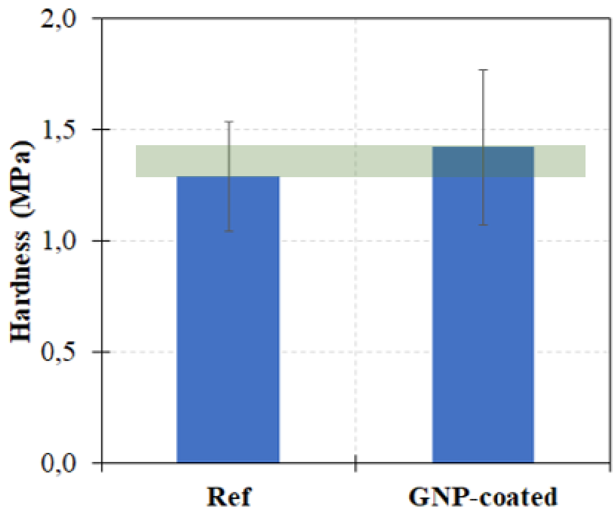
G2NAN finishing

G7NAN finishing

For brevity, only the tests on leather finished with the **G2NAN-functionalized** coating are reported

The results of nanoindentation tests on **leather finished** with G2NAN functionalized polymers are reported in comparison with the traditional finishing



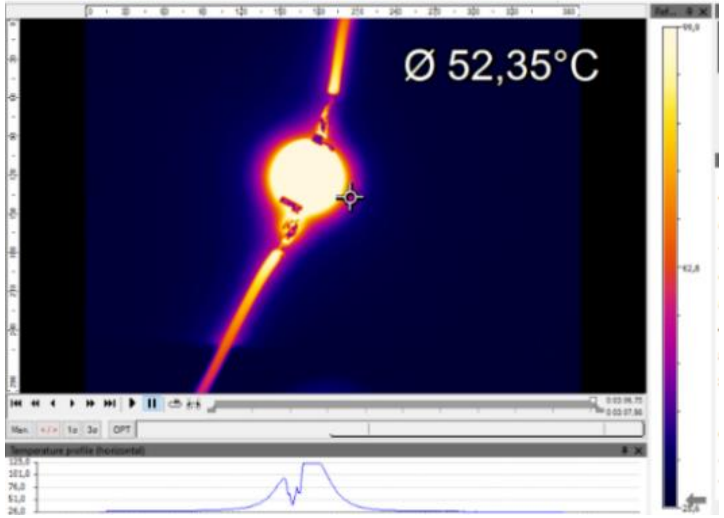


The Load-Depth curve shows that modified GNP finished leather resulted stiffer and harder than neat one, confirming the results of tensile tests

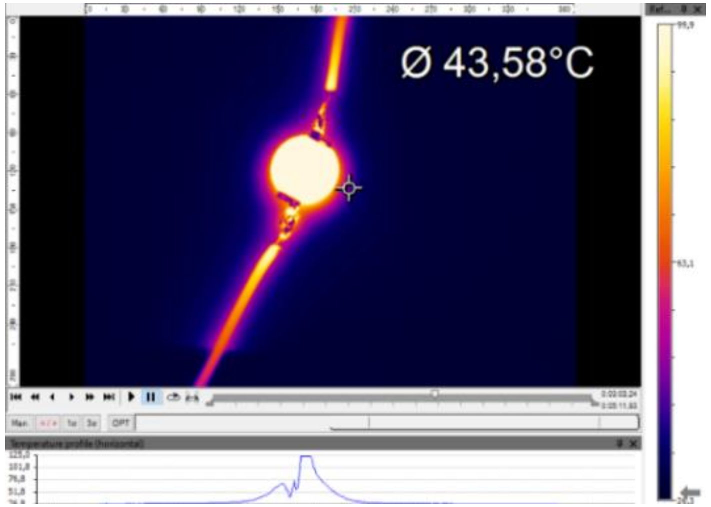
Discussion of Results

Test 1 – INPLANE TESTS

In **surface diffusivity tests** (in-plane measurements), temperature was measured 30 pixels far from the edge of the LED heat source after 3 seconds of application.



NEAT FINISHING



G2NAN FINISHING

52.35 °C

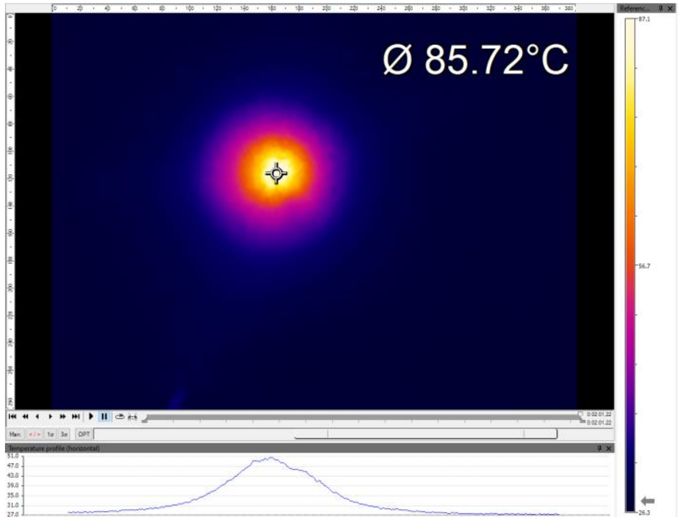
43,58 °C

For G2NAN functionalized finishing, temperature resulted about **8.5 °C lower** than neat finishing

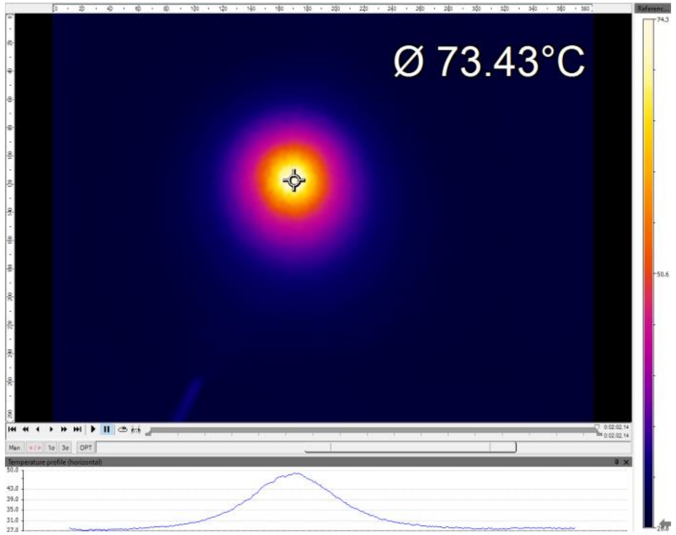
Discussion of Results

Test 2 – CROSS PLANE TESTS

In **bulk diffusivity tests** (cross-plane measurements), temperature was measured at the opposite surface in correspondence of the LED heat source after 3 seconds of application.



NEAT FINISHING



G2NAN FINISHING

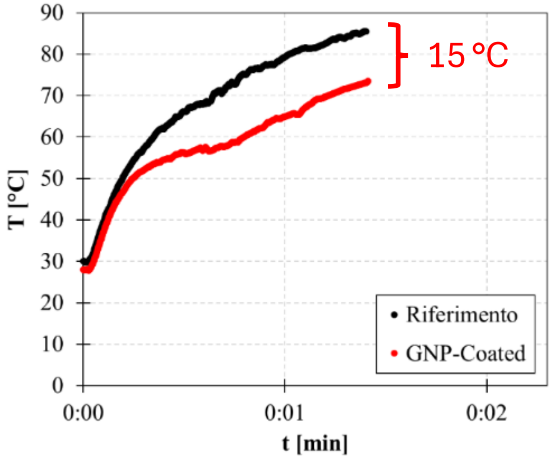
85.72 °C

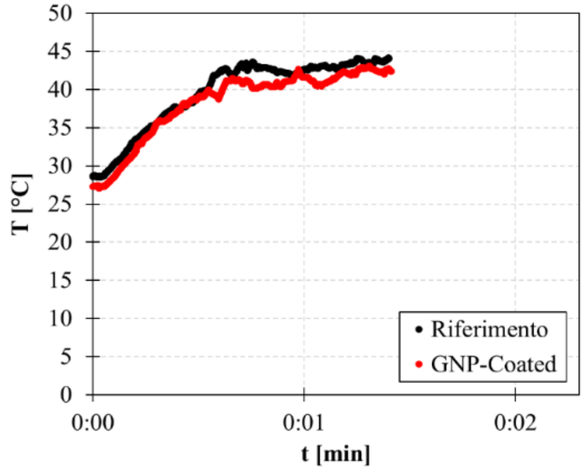
73,45 °C

For G2NAN functionalized finishing, temperature resulted about **12 °C lower** than neat finishing

Discussion of Results

Thermal Diffusivity Tests





For the **cross-plane configuration** the temperature evolution over time in two positions: in the centre of heat source and 30 pixels far from.

- In **central position** both temperatures (neat and G2NAN) initially increases at a rate of approximately 20 °C/min. Subsequently, the two profiles diverge, with the G2NAN coating reaching a temperature about 15 °C lower after 5 s.
- **At 30 pixels far** a similar trend is observed, although the G2NAN coating exhibits a slightly lower temperature than the neat one.

Thermal diffusivity of the material is **influenced** by the incorporation of **conductive GNP** nanofillers.

Conclusions

SUSTAINABLE LEATHER FINISHING: OPTIMIZING THERMAL PROPERTIES WITH GRAPHENE NANOPLATELET-POLYURETHANE NANOCOMPOSITES

Conclusions

- In this study, **two types of graphene nanoplatelets** (GNPs) with different aspect ratios (approximately 1500 and 500) were used as filler for PU-based finishing for automotive leather to create a multilayer functional coating.
- The proposed finishing system consists of a multilayer coating in which only the base coat was modified with a GNPs content selected to exceed the percolation threshold.
- GNPs **multilayers resulted stiffer** than neat finishing both at 23 °C and 60 °C.
- G2NAN (higher aspect ratio) determines a slight increase of tensile strength and elongation at break at 23° C, while G7NAN determines negligeable variations.
- **Leather** finished using GNP-modified coatings exhibited **increased surface hardness** and **indentation resistance**.

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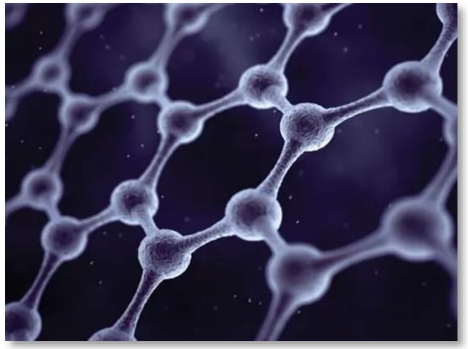
Conclusions

- A dedicated experimental setup was developed for non-destructive evaluation **of thermal diffusion**.
- A controlled-power LED source was applied in contact with the finished leather, revealing **a clear increase in thermal diffusivity** for the GNP-modified finishing layer compared to the neat system.



This increase in thermal diffusivity enables the potential application of GNP-based nanotechnologies in the automotive industry for the development of leather-upholstered seats with enhanced **thermal comfort properties**.

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THANK YOU FOR YOUR ATTENTION

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