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EMI shielding and conductive textiles functionalized with (Ti,Cu) nanomaterials for biomedical applications

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ABSTRACT

This study explores the potential of integrating thin film technology in the design of new and effective Electromagnetic Interference (EMI) shielding materials for textiles and wearables. This application is of particular interest to the textile industry as it can bring new functionalities to wearables and protect humans from prolonged exposure to EM radiation. Three different thin films of pure Ti, pure Cu and Ti-doped with Cu prepared by magnetron sputtering were used to functionalize textile knits based on cotton (code 39 F) and lyocell fibres (62 I). The films displayed different crystalline structures, morphologies, and topographies, which depended on their chemical compositions. The shielding effectiveness (SE) of the functionalized knits against EMI was evaluated in the frequency range of 2 GHz to 8 GHz. Also, the electrical response under stress was assessed since the electrical conductivity is closely related to the EMI shielding effectiveness. The results demonstrate the feasibility of using a thin conductive layer based on Cu to obtain shield textiles with great adhesion and low thickness, providing superior shielding efficiency for EMI by blocking the electrical waves.
Keywords: Ti-Cu thin films, Materials Design, Textile functionalization, EMI shielding, electromechanical response

1. INTRODUCTION

Wireless power transfer (WPT) has experienced, in recent years, significant technological innovations in distinct areas such as satellite or 5G communications, health-care treatments, or electrification of the automotive/transportation industry [1,2]. Based on the variation of electromagnetic fields, WPT systems are able to transfer low (microwatts up to milliwatts) or higher (few watts up to several kilowatts) power amounts, with no need for wires [1]. Due to the growing need for high-power transfer systems that function at increased frequencies and cover greater distances, electromagnetic radiation (EM) pollution has intensified, posing serious threats to human health [2]. As a result, developing high-performance EMI shielding materials to manage or alleviate the adverse effects of EM pollution on electronic devices, particularly on human health and other living organisms, has emerged as a crucial area of study [3,4].

Despite the recent advances in EMI shielding, the demand for low-weight protective wearables with outstanding mechanical properties (high ductility and low toughness) capable of protecting humans from harmful EM radiation/fields is still required [5,6]. The applicability of shielding wearables, used as Personal Protective Equipment (PPE), means a huge step in the medical field, especially for the imaging/diagnosis and (radio)therapy sectors, but also in the military or civilian domains. That is the reason why some authors have started to explore the modification and incorporation of metals into textiles to achieve effective EMI shielding structures [7,8]. However, the potentialities of thin film technology have hardly been explored for this purpose. Magnetron Sputtering is a versatile technology that enhances the growth of metals or metal alloys on the surface of almost any type of substrate, including textiles, making it ideal for producing smart surfaces with low weight or density, excellent electrical and mechanical properties, or high corrosion resistance. The use of thin films has been responsible so far for the functionalization of different materials in the biomedical field, such as temperature sensors [9–11], pressure sensors in prostheses [12,13] or biopotential dry-electrodes [14–18].
Metal-based materials (e.g. copper, aluminium, nickel) are preferred due to their high electrical conductivity, which is the primary factor determining the EMI shielding effectiveness (SE) [19,20]. However, their weight, high density, low flexibility and poor corrosion resistance restrict their large-scale use [4,20]. In turn, conductive polymer composites (CPCs) and flexible carbon fibre-based composites have been recognized as promising candidates for EMI shielding due to their high corrosion resistance, design flexibility, easy processing, low density and especially for high electromagnetic absorption [4,21,22]. More recently, MXene 2D materials based on hybrid systems with carbon-type conductive and magnetic particles, where M layers of early transition metals (III/IV element), are interleaved with n layers of X, representing either carbon or nitrogen, have gained relevance due to their inherent electrical conductivity and good mechanical properties [3,4] Zhao et al. [23] developed a rigid Ti$_3$C$_2$Tx porous framework templated with graphene oxide (GO), the epoxy nanocomposite showed a high electrical conductivity of 695.9 S.m$^{-1}$ and electromagnetic interference shielding effectiveness exceeding the 50 dB. In its turn, Li et al. [24] reported a hybrid hollow core-shell of reduced graphene oxide (RGO)/Ti$_3$C$_2$Tx foam fabricated by self-assembly and sacrificial template approaches, which exhibited a high effective absorption bandwidth (EAB) covering the whole X-band in its 3.2 mm of thickness. Also, Tong et al. [25] reported the development of a ternary TiO$_2$/Ti$_3$C$_2$Tx/RGO aerogel, exhibiting an EAB of 4.3 GHz with a maximum reflection loss of -65.3 dB at 2.5 mm thickness.

In this work, the Magnetron Sputtering technique was used to functionalize two types of knits/fabrics with three different metallic thin films: one pure titanium (Ti), one pure copper (Cu) and a copper-doped titanium (Ti-Cu) thin film. The functionalized textiles were characterized in terms of their chemical composition and (micro)structure. The electromagnetic properties as well as the electrical and mechanical response were studied through a wide range of experimental setups. The results demonstrated the potential of integrating thin film technology in the development of new and effective EMI shielding materials. This application is particularly interesting for the textile industry bringing new functionalities to textiles and wearables, able to protect humans from prolonged EM radiation exposure.

2. MATERIALS AND METHODS

2.1 FUNCTIONALIZATION OF THE TEXTILE STRUCTURES
In this work, we used circular knitted fabrics prepared by @Impetus, using 100% cotton yarns (reference code 39F) and 100% Lyocell Standard conventional yarns (reference code 62I). For the knit 39F, a Mayer gauge 34” circular knitting machine, with 28 needles per inch, was used to produce a single jersey structure, using a Ne 30/1 cotton yarn. For the knit 62I, it was also used a Mayer gauge 34” circular knitting machine with 28 needles per inch to produce a single jersey structure, using a Ne 30/1 Lyocell Standard conventional yarn.

Initially, the knits with $210 \times 148$ mm$^2$ dimensions were cleaned using an ultrasonic bath of water and ethanol for 30 min and dried. Afterwards and anticipating the low surface energy and hydrophobicity of textiles, the samples were submitted to low-pressure plasma treatments just prior to the deposition. The main objective was to enhance the adhesion strength at the interface textile/thin film [14,26,27]. The activation took place in a plasma cleaner system (Zepto, Diener electronic GmbH & Co. KG, Ebhausen, Germany) with a 13.56 MHz generator connected to a rotary pump working at a low base pressure of 20 Pa, whilst the working pressure never exceeded the 80 Pa. Different atmospheres: i) Argon (Ar), ii) Oxygen (O$_2$), iii) Nitrogen (N$_2$), iv) mix Ar + O$_2$ or, v) mix Ar + N$_2$, with high (50W) and low (12.5W) power energy for several exposure times (1 min, 3 min, 5 min, 15 min) were tested on the activation of both 39F and 62I textiles knits [17]. The textile surfaces’ affinity towards the thin films to be sputtered was evaluated, immediately after the plasma treatment, by measuring the contact angle (CA) with ultrapure water, and the most promising conditions were selected [14,17,27,28]. The CA was determined by the water droplet method using a contact angle goniometer (OCA 15, DataPhysics Instruments GmbH, Filderstadt, Germany). A minimum of 3 valid sessile drop repetitions were performed for each textile and plasma condition.

After activation, both textile knits were functionalized with Ti-, Cu- pure and intermetallic Ti-Cu thin films by DC Magnetron Sputtering, one of the more versatile Physical Vapour Deposition (PVD) techniques. All the depositions were carried out for base pressures lower than 2.0×10$^{-4}$ Pa, in a custom-made system [17,29]. A DC power supply (current density of 75 A/m$^2$) was used to generate the plasma in an Ar atmosphere. The gas flow rate was kept at 25 sccm, while the work pressure was set to 3.0×10$^{-1}$ Pa. The textile samples were centred inside the vacuum chamber (70 mm from the target) and grounded. To ensure the homogeneity of the as-deposited knits, the depositions were performed in a rotating mode (5.5 rpm) for 60 minutes. Ti and Cu targets, both with 99.99% purity and 200 mm × 100 mm × 6 mm dimensions, were used to deposit the pure Ti and Cu metallic thin films. For the deposition of the Ti-Cu
intermetallic thin film, a Ti target was modified with 25 pellets of pure Cu (area: 16 mm², thickness: 0.5 mm) glued with conductive silver paint over the erosion zone, as depicted in Fig. 1. All depositions were performed at room temperature for 60 min.

The chemical composition of the thin films used to functionalize both textile substrates was determined by Rutherford Backscattering Spectrometry (RBS) analysis. The experiments were conducted in a small chamber (RBS) of a 2.5 MeV Van der Graaf accelerator. For the analysis, two types of beams, 4He⁺ and 1H⁺, with energies ranging from 1.5-2 MeV and 2.3 MeV, respectively, were used. Inside the chamber, three detectors (one Si surface barrier and two pindiode detectors) were placed in different positions relative to the normal incidence of the beams. The IBA DataFurnace NDF v10.0b software [30] was used to simulate the in-depth composition profiles[31]. The accuracy of determining the atomic concentration of both Ti and Cu metals was approximately 0.5 at%.

![Figure 1- (a) Scheme of the Ti target doped with Cu pellets glued on the erosion track and (b) the target placed on the magnetron.](image)

The crystal features of the 3 different films deposited on both 39F and 62I knits were evaluated by X-ray diffraction (XRD) analysis using a Bruker D8 Discover diffractometer, operating with Cu–Kα radiation (λ = 1.5406 Å) in the Grazing Incidence X-ray diffraction (GIXRD). The corresponding structures were analyzed through the Inorganic Crystal Structure Database (ICSD).

The morphology and topographical characteristics of the functionalized textile were evaluated using a high-resolution Scanning Electron Microscope (SEM; FEI Nova NanoSEM 200) with
X-ray microanalysis and electron backscattered diffraction analysis, operating at 15 keV. The thickness estimation was obtained by analyzing the cross-section images collected at three different points.

2.2 ELECTROMECHANICAL AND ELECTROMAGNETIC MEASUREMENTS

The combined electromechanical behaviour of the functionalized knits was investigated by a homemade uniaxial tensile machine equipped with a 200 N load cell with a two-point probe geometry incorporated in the tensile straining grips, presented in Fig. 2 (a). The electrical resistance was measured as a function of the strain by using aluminium contacts placed directly over the sample on the opposite grips. The electrical isolation of the samples and the sample holder were achieved by using @Kapton tape (LINQTAPE™ PIT1A-Series). The two-point electrical resistance was measured using a Keithley 2700 multimeter. Both 39F and 62I textile knits functionalized with the (Ti,Cu) thin films were pulled in the same rolling direction to avoid mechanical anisotropies. Only the section of the sample that underwent tensile strain was used to measure the electrical resistance.

During the tensile tests, the samples were loaded continuously until fracture at a fixed displacement rate of 0.018 mm/s, the initial grip distance was kept at 45 mm, just as the strained area, which was 1 mm². Fourteen tests were conducted for each functionalized knit, consisting of seven tests loaded in the direction of the knit’s loop (longitudinal stretching) and seven tests loaded perpendicularly to the knit’s loop direction (normal stretching), as illustrated in Fig. 2 (b) and (c), respectively.

Figure 2 - (a) Schematic representation of the uniaxial tensile machine used to assess the electromechanical response of the textile-based electrodes functionalized with the (Ti,Cu) thin films. (b) Normal Stretch direction. (c) Longitudinal stretch direction.

The electromagnetic interference (EMI) measurements were carried out using a Keysight Vector Network Analyzer (VNA), model ENA E5071C. Two Broadband SMA Waveguide
Horn Antennas, model PE9887-11, with a nominal gain of 11 dB, were connected to the VNA. These antennas enabled the simultaneous acquisition of both transmitted (S21) and reflected (S11) signals. Figure 3 depicts the experimental setup employed for the EMI measurements. The antennas (source and receptor) were separated by 30 cm, and the insulating acrylic sample holder was fixed in front of the receptor to prevent EM leakage. The functionalized and non-functionalized textiles were measured after calibrating the system without the textile using the empty sample holder.

Figure 3 - Experimental setup for EMI measurements. The antennas were fixed 30 cm apart while the sample holder was fixed at the front of the receptor. The measurements were performed for both knits functionalized with (Ti,Cu) thin films, using the original knitted fabrics (39F and 62I) as references.

Theoretically, the shielding effectiveness (SE) measures the material’s ability to attenuate electromagnetic interference, usually expressed in decibels (dB). SE is calculated based on the logarithmic ratio of incident power ($P_I$) to the transmitted power ($P_T$). In SE measurements, three mechanisms may be considered: absorption ($SE_A$), reflection ($SE_R$), and multiple reflections ($SE_{MR}$) [32]

$$SE = SE_A + SE_R + SE_{MR}$$

(1)

In a common approach, the $SE_{MR}$ mechanisms can be ignored if the absorption loss is higher than 10 dB.

The reflection and transmission coefficients are represented by the S11 (or S22) and S12 (or S21) parameters of the two-port network system, respectively. The analysis of the S parameters allows for the description of transmittance (T), reflectance (R), and absorbance (A) through the shielding material, as described in [32]:

$$T = \frac{P_T}{P_I} = |S_{12}|^2 = |S_{21}|^2$$

(2)

$$R = \frac{P_R}{P_I} = |S_{11}|^2 = |S_{22}|^2$$

(3)
\[ A = 1 - R - T. \]  
(4)

where \( P_R \) and \( P_T \) are the power reflected and transmitted, respectively. The shielding effectiveness contribution from absorption and reflection mechanisms can be obtained through [32]:

\[ SE_R = -10 \log(1 - R) \quad \text{(dB)}, \]  
(5)

\[ SE_A = -10 \log\left( \frac{T}{1-R} \right) \quad \text{(dB)}, \]  
(6)

\[ SE = -10 \log(T) \quad \text{(dB)}. \]  
(7)

In our case, the experimental setup allows us to minimize this contribution. Nevertheless, if the SE\(_{MR}\) cannot be neglected, the earlier relations are not valid and further analysis of the S parameters is required.

### 3. RESULTS AND DISCUSSION

#### 3.1 TEXTILE STRUCTURES – PLASMA ACTIVATION

As described in section 2, plasma treatments were carried out to activate the surface of the textile knits and enhance the adhesion of the (Ti,Cu) thin films. Low-pressure plasma treatments induce several phenomena, including: i) cleaning the contaminant superficial layers, ii) surface etching, which changes the morphology and topography, and iii) activation through the generation of new reactive species, leading to the formation of new chemical groups, crosslinking and chain scission [14,17,28]. It is important to note, that despite the changes promoted on the knit’s surface, the fundamental properties of the textile material were not compromised [33,34]. Then, to assess the changes/activation promoted on the treated knits, which strongly influence the adhesion at the textile/thin film interface, the surface wettability was measured [14,17,28]. Figure 4 illustrates the evolution of the water contact angle after activation for both the 39F and 62I knits, which were treated in their pristine form.
Figure 4 - Evolution of water contact angle (CA) on both textile knits. The photographs on the left show the shape of the water sessile drop on the surface of the 39F knit: (a₁) untreated and (a₂) treated in an Ar + O₂ atmosphere. The graphs on the right exhibit the variation of the CA on the (b) 39F and (c) 62I textile knits using different times and plasma atmospheres for (b₁ and c₁) 12.5 W and (b₂ and c₂) 50 W. The starting point of 0 min represents the pristine (non-activated) knits used as reference.

From the results presented, it is evident that was easier to obtain hydrophilic cellulose fibre-based textile samples (62I) than cotton-based textiles (39F). In fact, after 1 min of plasma treatment and regardless of the atmosphere or the power used, the 62I knits became completely hydrophilic. On the other hand, the textiles based on cotton (39F) showed better wettability for higher powers (50 W) evidencing a high dependence on the atmosphere used. While, for lower powers (12.5 W), the plasma treatment of Ar + O₂ showed the highest hydrophilic effect (CA = 0°, after 1 min). This gain in hydrophilicity combines, the existence of polar groups promoted by the reactive O₂ atmosphere and the roughness changes, achieved by the Ar etching effect. The hydrophilicity of cotton treated in pure Ar or O₂ plasmas has already been reported in other works [35,36]. Cotton is mainly composed of cellulose mixed with hydrophobic impurities in the cuticle layer. When submitted to a mixed Ar + O₂ plasma atmosphere, the Ar becomes responsible to etch/destroy the non-cellulosic impurities present in the outermost layers of the cotton fibres, while O₂ facilitates the etching process and the formation of new chemical polar groups (e.g hydroxyl or carboxylic groups) [35,36]. The combined effects enhance the knit’s activation, even for lower powers.
3.2 CHEMICAL AND STRUCTURAL CHARACTERIZATION

The chemical composition of the (Ti,Cu) thin films gives a measure of the atomic concentration (at%) of each element in the three films prepared. The RBS spectra analysis revealed residual contamination by oxygen (less than 3 at.%) present in the remaining atmosphere [37]. Therefore, for the pure Ti and pure Cu metallic films, the atomic concentration of each element is nearly 100 %, while for the film prepared with a Ti target doped with Cu, the atomic concentration in Ti was approximately 74.4 % and in Cu ≈ 25.6 %, labelled from now has TiCu$_{0.34}$ according to the Cu/Ti ratio.

The thin films deposited on the textile knits were then evaluated for their crystalline structure, using the Grazing Incidence XRD technique, to increase the sensitivity to the films and minimize the substrate contribution [38]. Both substrates (39F and 62I) were considered, as well as Si substrates with (100) orientation, the latter being used only for comparison purposes. The structural properties of the functionalized textile substrates are presented in Fig. 5.

Sputtering is a process that relies on the growth of ad-atoms, whereby the ejected material from the target replicates the textural features of the substrate surface [39–41]. Comparing the results, it is possible to observe that Cu thin films maintain their crystalline structure, even when deposited on highly porous structured substrates, such as knits. Nevertheless, the same is unclear for the Ti and TiCu$_{0.34}$ thin films. Deposited on textile substrates, the Ti thin films lose crystallinity, resulting in amorphous structures with minor traces of the (100) orientation (ICSD code #44872).

![Figure 5 - X-ray diffraction of the (Ti,Cu) thin films deposited on: a) boron-doped p-type crystalline silicon substrates with (100) orientation, (b) 39F cotton-based knit and (c) 62I lyocell-based knit.](image-url)
In addition, it is also evident that the pure Cu and Ti thin films typically exhibit polycrystalline structures, as evidenced by the films deposited on Si (Fig. 5a). For the Cu-pure thin film, the (111) preferential orientation growth (ICSD code #52256), along with the (200) growth, is quite evident and common to all the substrates used. While for the pure Ti film deposited on silicon, it is possible to observe the (002) preferential orientation growth at $2\theta \approx 38^\circ$ (ICSD code #44872), and minor traces of the orientations (100) and (101), respectively located at $2\theta \approx 35^\circ$ and $2\theta \approx 40^\circ$ (ICSD code #44872). When pure Ti was deposited on the knits, the characteristics of the pure film changed, and the (100) growth orientation became the preferential orientation.

Regarding the diffractograms of the TiCu$_{0.34}$ thin film deposited on the different substrates (e.g. silicon, Figure 5 (a) and textile knits, Figure 5 (b) and (c)) broad diffraction humps without any observable crystalline peaks can be observed, indicating an amorphous structure. This amorphous diffraction domain, located near $40^\circ$, can be indexed to different phases of intermetallic compounds, specifically Ti$_2$Cu (ICSD code #629388) or TiCu (ICSD code #629389). Though, based on the chemical composition of the film, the former phase is more likely. When the TiCu$_{0.34}$ thin film was deposited onto textile substrates, cotton-based knit (39F) and lyocell fibres (62I), different structural rearrangements were observed. In the 39F knit, it was possible to identify a mixture of phases of pure-Ti (101) and the intermetallic Ti$_2$Cu (002). However, for 62I, it was only possible to identify the broadband structure of the Ti$_2$Cu intermetallic phase. Structural characterization also highlights that the diffraction peak of the Ti-Cu intermetallic phases appears more defined in the coated lyocell fibres (62I) than in the cotton-based knit (39F). These results show the influence of the substrate porosity in the crystalline features developed by the film. Despite having the same composition, the use of different substrates led to distinct structural rearrangements, ultimately yielding different properties. Nevertheless, irrespective of the deposited thin film and employed textile, the effectiveness of the Magnetron Sputtering technique in the functionalization of textile knits can be verified.

**3.3 MORPHOLOGICAL EVALUATION**

The morphological analysis of the textile knits functionalized with the (Ti,Cu) thin films was conducted using different types of micrographs (Fig. 6). The adhesion and cohesion of three different thin films to the fibre, as well as the microstructure growth and surface texture, were evaluated and compared. To simplify the analysis, all images in Fig. 6 pertained to cotton-based substrates (39F textile) since the morphological features were similar for both knits.
The results also indicate that, despite utilizing the same deposition time, the (Ti,Cu) thin films exhibited distinct thicknesses, indicating different deposition rates as detailed in Table 1. The deposition rate is closely related to the complex process of magnetron sputtering and plays a main role in the morphological features of the films. Regardless of the error associated with the growth rate determination, it is evident that the films of pure Cu or Ti-doped with Cu are thicker than the pure Ti thin film.

Table 1: Details of the (Ti,Cu) thin films. The thickness was an average of several measurements obtained from SEM images, and the deposition rate was a measure of the amount of material deposited per unit of time.

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Thickness (nm)</th>
<th>Deposition Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-pure</td>
<td>309 ± 10</td>
<td>~5.1</td>
</tr>
<tr>
<td>TiCu$_{0.34}$</td>
<td>359 ± 10</td>
<td>~5.9</td>
</tr>
<tr>
<td>Cu-pure</td>
<td>316 ± 10</td>
<td>~5.3</td>
</tr>
</tbody>
</table>

For Ar$^+$ energies between 300 eV and 400 eV, the sputtering yield of a pure Ti target ranges between 0.307 - 0.394, while for a pure Cu target, it varies between 1.317 - 1.632. These values were based on the empirical Equations proposed by N. Matsunami et al [42], considering the values of target potential obtained in the experimental preparation of the Ti-and Cu-pure thin films. Therefore, higher ratios of sputtered atoms per incoming ion were expected for the pure Cu and TiCu$_{0.34}$ thin film prepared with 25 pellets of Cu onto the erosion zone of the Ti target. Nevertheless, the fibres coated by the TiCu$_{0.34}$ thin film exhibited higher deposition rates than pure Cu. This behaviour can be explained by the increased densification of the Cu-pure film microstructure, as observed in the micrograph presented in Fig. 6 - cii, while some traces of a columnar structure were noticed in the thick and dense microstructure of the TiCu$_{0.34}$ thin film (Fig. 6 - bii), corroborated by the amorphous crystalline structure mentioned earlier. Moreover, the sputtering of multicomponent targets depends significantly on the sputtering yields of each metal, their different masses and interactions as a compound.
The surface topography changes for the different films prepared are also illustrated by the images (iii) in Fig. 6. The TiCu$_{0.34}$ thin reveals a smoothed and featureless surface, typical of Thin Film Metallic Glasses (TFMGs) structures [15,17]. By comparison, pure Ti and Cu thin films reveal rougher surfaces with three-dimensional grain features with different crystallite sizes (lower for Ti than for Cu thin film).

The microstructural analysis revealed a good adhesion of the (Ti,Cu) films to both knits, as shown in Fig.6 (i), which demonstrated that the flux of the sputtered atoms reached homogeneously all the fibres despite their 3D geometry and the porosity among them. From the SEM images, it is possible to verify a complete insertion of the thin film on the fibre´s textile.

### 3.4 ELECTROMECHANICAL PERFORMANCE OF THE FUNCTIONALIZED TEXTILE STRUCTURES

To assess the electromechanical properties of the functionalized knits, mechanical tests were conducted, whilst the electrical resistivity was measured. The maximum strain achieved at the rupture of both knits (39F and 62I) functionalized with the thin films was determined and compared to the results obtained from the pristine textile knits without functionalization. The
longitudinal stretching (L) and normal stretching (N) to the orientation of the fibres were measured as previously shown in Fig. 2 (b) and (c). The average results of the maximum strain obtained from these tests are presented in Fig. 7

![Figure 7](image_url)

Figure 7 – Average results of the Maximum Strain at the rupture of 39F and 62I fabrics. The results were obtained from uniaxial strain tests conducted both parallel (Longitudinal stretching: L) and perpendicular (Normal stretching: N) to the knit's loop direction.

The elongation of the textile knits significantly improves after functionalization with Ti- and Cu-pure thin films (up to 75%). The exception is for the 62I knit functionalized with TiCu$_{0.34}$ thin films, where the reduction of the maximum strain at the fracture appears to be related to the formation of the Ti-Cu intermetallic compounds coexisting in different phases in a quasi-amorphous state, as suggested by the structural analysis (Section 3.2). However, the functionalized knit 62I results in withstands higher stresses in the longitudinal direction. Also, the 39F knits revealed a higher resistance to deformation after functionalization with any of the (Ti,Cu) thin films.

Moreover, the electrical resistivity response was registered during the mechanical measurements performed on the textile substrates, and the results are shown in Figs. 8 and 9, for 39F and 62I knits, respectively. The tests did not include the pristine knits as they are insulating and cannot be compared to the functionalized textiles.
The results reveal a common pattern for both knits (39F and 62I) functionalized with Ti thin films. It was impossible to acquire an electrical signal during the entire uniaxial strain. It appears that the columnar morphology of these films cannot follow up the high flexibility of the polymers. Although the tensile stress forced contact between the coated fibres, the electric current did not flow, resulting in highly resistive knits.

A completely different behaviour was presented by both types of knits functionalized with ductile and dense Cu-pure thin films. After stretching, the fibres in the knit start to establish new contacts, narrowing the loop, and decreasing the electrical resistivity for tens or hundreds of ohms. In fact, for strains up to 40% (normal stretching) and 80% (longitudinal stretching), the electrical resistance of the knits drops to very low values (high conductivity), see the video in the supplementary material.

Surprisingly, the 62I knits coated with the TiCu_{0.34} thin films became highly conductive after experiencing 10% (normal stretching) or 40% (longitudinal stretching) of strain. Despite the reduction in maximum strain registered for this specific type of knit, the Cu content in the film allied to the dense structure with smoothed and featureless surfaces (similar to TFMGs) was able to provide electrical conduction for a specific range of the fibre’s deformation. However, the 39F knits coated with the same film revealed an opposite behaviour similar to the 39F knits.
functionalized with Ti. Apart from the film’s influence, the structural characteristics of the fibres and the weaving process of the intertwined fibres play a significant role in the electromechanical behaviour of the fabrics.

Figure 9 – Electromechanical tests performed on the 62I knit functionalized with: (a,d) Ti-pure thin films, (b,e) TiCu$_{0.34}$ thin films and (c,f) Cu-pure thin films. The tests were conducted for (a-c) normal stretching and (d,f) longitudinal stretching.

3.5 EMI SHIELDING OF THE FUNCTIONALIZED TEXTILE STRUCTURES

Figure 10 shows the EMI shielding characteristics of the (Ti,Cu) thin film deposited on both 39F (Fig 10 (a)) and 62I knits (Fig. 10 (b)). These SE physical quantities provide practical information about the degree of contribution of the reflection and absorption to the total EMI. The insertion of metals onto textiles can considerably increase the EMI properties, even for low thickness values, as is the case of the (Ti,Cu) thin films. To calculate the EMI SE properties of the functionalized and non-functionalized textiles, Eqs. (1) - (7) were considered. Figures 10 (a) and (b), demonstrate the SE (dB) properties as a function of the frequency for all the functionalized knits, providing measurements from 2 GHz up to 8 GHz, which covers an interesting frequency range for real shield applications. It is important to point out that for these results, a moving-average analysis with a factor of 50 measurements was considered.

Initially, the non-functionalized knit textiles (pristine), were considered, which presents SE results near 0 dB, as expected. In contrast, for the 39F functionalized knit, it was observed a
significant increase in the SE (dB), reaching 10 dB for Ti, 14 dB for TiCu$_{0.34}$, and nearly 15 dB for the knits functionalized with Cu film. Regarding the 62I knits, although there is a substantial increase in shielding effectiveness, the efficiency remains constant for Ti and TiCu$_{0.34}$ at around 10 dB, while the Cu thin film reaches 15 dB. Moreover, the EMI shielding characteristics, as well as the EMI SE measured by using both knits, agree well with each other in the common frequency range and remains consistent in the extended frequency range up to 8 GHz.

Figures 10 (c) and (d) depict the SE (dB) as a function of the functionalized knits for fixed frequencies, for 39F and 62I knits, respectively. From the results, it is evident the increase of the SE (dB) behaviour with the textile functionalization, irrespectively of the film deposited. According to the results, Ti provides the lowest SE (dB) protection when compared to TiCu and Cu functionalized knits, which is particularly evident for the 62I knit. At the same time, Ti functionalization appears to provide the lowest shield protection, while the inclusion of Cu content leads to a significant increase in the SE (dB). Notably, the most effective protection occurs for 6 GHz and 8 GHz, regardless of the textile used. Specifically, values of 15.5 dB and 16.2 dB were observed for the textiles functionalized with Cu, measured at 6 GHz. It is important to point out that the studied system presents an interesting pathway to insert functionalization on the textile, with great adhesion end low thickness, which can explain the SE (dB) values observed when compared with other techniques employed to obtain shield textiles. These results demonstrate the validity of using a thin conductive layer based on Ti and Cu to provide superior shielding efficiency for EMI by blocking the electrical waves at low layers thickness.

Figure 10 – (a) EMI shielding characteristics as a function of frequency for pristine and functionalized 39F knit. (b) Similar EMI shielding plot for pristine and functionalized 62I knit. (c) EMI shielding as a function of
4. Conclusions

To conclude, the (Ti,Cu) thin film deposition on both 39F and 62I knits increased the EMI shielding properties, even for low thickness values, without compromising the textile characteristics. The SE (dB) properties showed a significant increase in shielding effectiveness with the functionalization of knits for the frequency range of 2 GHz up to 8 GHz, one of the most important regarding human protection from prolonged EM radiation exposure. The TiCu$_{0.34}$ and the Cu-pure films provided the greatest SE (dB) protection, reaching values near 16 dB at 6 GHz. The study demonstrated the validity of using a thin conductive layer based on Ti and Cu to provide superior EMI shielding efficiency. In agreement with the literature, those were the films that also exhibited the best electrical performance under mechanical stress. Both types of knits coated with Cu-pure film showed high conductivity through new contacts established by the fibres during stretching. Also, 62I knits coated with TiCu$_{0.34}$ films were shown to be highly conductive within a specific strain range, highlighting the influence of the film’s microstructure on the functionalized fabric. These findings demonstrate a promising pathway for the development of functionalized fabrics with high conductivity and superior EMI shielding efficiency in various fields, opening up new avenues for research in the field of wearable electronics.

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**Conflicts of interest**

There are no conflicts to declare.

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**References**


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