PVDF-based coatings with CNT additions for strain monitoring of mortar substrates subjected to bending

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Abstract. Sensing coatings are rapidly entering the field of non-destructive tests. While cement-based composites are proving an excellent interaction with new/recent structures, polymer-based coatings, already employed for structural retrofitting purposes, can provide a valuable alternative. This study investigated the production, application, and use of poly(vinylidene fluoride) (PVDF) coatings. A 10w/v% PVDF-to-solvent ratio became the best trade-off between electrical conductivity and bond strength with the substrate. Different concentrations of Carbon Nanotubes (CNT) were investigated: 0.05, 0.10, 0.25, 0.50, and 0.75% by weight of PVDF. The conductive PVDF-CNT composites were brushed on the casted mortar beams with screws embedded as electrodes. The mortar beams and attached polymer coatings were then subjected to bending stress. The Gauge Factor was obtained by comparing the substrate’s strain with the coating’s electric response. The sensing intervals in the Fractional Change of Resistance-strain curves varied in relation to the CNT concentration. For instance, adding 0.50w/v% of CNT gave the highest sensitivity up to 0.2‰ strain, followed by a lower – still sufficient – gauge factor. PVDF-based coatings with CNT additions of 0.25 and 0.75w/v% witnessed a comparable sensing performance in the same strain limits, abruptly increasing and finally stabilizing to a low gauge factor. In contrast, both 0.05 and 0.10w/v% resulted in a low monitoring potential overall. The varying sensing zones experienced by the coating were attributed to the microscopical behavior of CNT within the PVDF matrix. In conclusion, the results highlighted the potentiality of polymeric coatings for sensing, monitoring, and inspection of concrete structures.

1 Introduction

As most construction environments struggle to keep up with modern safety and performance requirements due to their age and technical limitations, their structural assessment and ongoing maintenance protocols are central to the construction process. Thus, strain/stress sensors are used to monitor the serviceability and safety levels of strategic infrastructures, within the field of Structural Health Monitoring (SHM) [1]. Despite the large use of conventional sensors, the field has progressively been moving towards cementitious and polymeric composites capable of providing physical insights for the system under study [2].

By adding functional fillers, both steel and carbon-based, the electrical properties of the system can be exploited to achieve safety and serviceability information [3]. The matrix + filler composite's conduction mechanism is consistent with the percolation theory [4]. As a result, the system's conductive process is divided into ionic, tunneling, or contact depending on the filler concentration [5].

Self-sensing concrete, although widely studied [6-8], is limited to the physical limitations of carbon-based composites and, therefore, cannot be used in existing structures. Polymer-based thin layers, on the other hand, can be easily applied on top of new and existing structures. The literature discussed the electrical properties of numerous polymer matrices with the addition of CNT (e.g., epoxy [9,10], polycarbonate/acylonitrile butadiene styrene [11], polylactic acid [12], ultrahigh molecular weight polyethylene [13]). However, since their employment in civil engineering is not frequent, this study investigated the strain sensitivity of poly(vinylidene fluoride) (PVDF) composites. Such polymeric resin is characterized by high mechanical properties, good chemical resistance, great hydrophobicity, and thermal stability [14]; moreover, it also presents a good piezoelectric performance with conductive additives [15]. Among the numerous carbon-based fillers, Carbon Nanotubes (CNT) were employed in this study given their numerous physical and theoretical applications in polymeric matrices [16].

2 Materials and methods

2.1 Materials

Thin multiwall carbon nanotubes, supplied by Nanocyl (NC7000TM series), were produced via Catalytic Chemical Vapor Deposition (CCVD) - properties shown in Table 1. Among the different organic solvents
suitable for PVDF, dimethyl sulfoxide (DMSO) – supplied by Sigma-Aldrich – was selected for its rate of dissolution and solution stability [17].

Table 1. CNT properties (from the manufacturer).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Method of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter [nm]</td>
<td>9.5</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Average length [μm]</td>
<td>1.5</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Carbon purity [%]</td>
<td>90</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Transition metal oxide [%]</td>
<td>&lt; 1</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>Surface area [m²/g]</td>
<td>250-300</td>
<td>BET surface area analysis</td>
</tr>
<tr>
<td>Volume resistivity [mΩ cm]</td>
<td>10</td>
<td>Resistivity on powder</td>
</tr>
</tbody>
</table>

The 40 mm x 40 mm x 160 mm mortar substrates were prepared in agreement with EN 169 -1 and composed of 3 parts standard silica sand, 1 part Portland cement (CEM II/N-LL 32.5 R), and 0.5 deionized water. Once poured, the samples were demolded after 24 hours and subsequently submerged in water where they were left to cure for 28 days.

2.2 Mix design

Four different PVDF-to-solvent ratios were designed and investigated in relation to conductivity and workability, i.e., 5.0, 7.5, 10.0, and 12.5 w/v%, with 1% of CNT by weight of PVDF. Once the optimal design was achieved, five percentages of CNT were added to the polymeric resin (i.e., 0.05, 0.10, 0.25, 0.50, 0.75% by weight of PVDF), as schematically represented in Table 2, to assess the electrical properties of the solution.

Table 2. Composition of the studied sensing coatings.

<table>
<thead>
<tr>
<th>Name</th>
<th>CNT0.05</th>
<th>CNT0.10</th>
<th>CNT0.25</th>
<th>CNT0.50</th>
<th>CNT0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding matrix</td>
<td>Polyvinylidene Fluoride (PVDF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>Dimethyl Sulfoxide (DMSO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solute-to-solvent ratio</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductive filler</td>
<td>Carbon Nanotubes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filler dimension</td>
<td>1D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>0.05</td>
<td>0.10</td>
<td>0.25</td>
<td>0.50</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Dispersion of CNT in solvent was carried out via a sonicator probe - 750 Watts @20%, at 20 kHz - for 10 minutes with a pulse of 2 seconds followed by 2 seconds of pause. This was chosen to avoid both temperature increase as well as CNT destruction in the solvent. Meanwhile, the PVDF solid particles were dissolved in DMSO, once the solvent reached 60 °C [17]. The obtained solution was subsequently stirred for approximately 15 minutes until a homogeneous composite was achieved. Then, the sonicated solution of CNT/DMSO was added to the PVDF/DMSO composite and the mixture was sonicated for additional 10 minutes. Once a fully homogeneous dispersion was achieved, the system was left to cool down for 30 minutes before being brushed on top of the mortar samples. The entire process is summarized in Fig. 1.

The composite was brushed onto the bottom surface of the mortar beam, i.e., the area subjected to tension. The horizontal dimensions of the coating were chosen as 20 mm x 120 mm, while the thickness was limited by applying 2 layers of polymeric resin onto the cementitious substrate (Fig. 2).

2.3 Experimental program

The produced film was observed via a Leica optical microscope. The Kinexus pro+ rheometer – supplied by Malvern – was used to test the viscosity of polymer composites at different shear rates and temperatures.
The electric characterization was conducted in Direct Current via an Agilent E612A Power supplier while a Hioki LCR meter 3533/01 was used for impedance measurements in Alternating Current at 1, 5, and 10 kHz. To achieve good electric interaction between the coating and the power supplier, screws (φ = 4 mm) were drilled 5 mm into the mortar samples before the polymeric coating was applied on top. The screws were embedded in the system in accordance with the 2-probe method [18] at a longitudinal distance of 80 mm (as shown in Fig. 3).

Finally, the 3-point bending tests on mortar samples were applied via a 50 kN load cell (Zwick Roell), at 480 N/min, to investigate the strain sensitivity of the polymeric coating. The maximum load was 800 N to avoid the ultimate failure of the system and to investigate the testing repeatability within the beam’s elastic regime. The strain at the bottom layer (tension zone) was obtained according to equation 1:

\[ \varepsilon = \frac{M_{z}}{EI} \]  

(1)

where \( M \) is the bending moment, \( z \) is the vertical distance between the neutral axis and the layer under maximum tension, \( E \) is the stiffness obtained via the displacement readings, and \( I \) is the moment of inertia of the prism [19]. Since the polymeric coating was a few microns thick, the authors decided not to affect any of the geometrical factors involved, thus approximating the system to a unique element rather than a composite (i.e., substrate + coating).

The electromechanical results were recorded via the LCR meter applying 1 V at 1 kHz. The Fractional Change of Resistance (FCR) is defined by equation 2:

\[ FCR = \frac{Z_{i} - Z_{0}}{Z_{0}} \cos \phi \]  

(2)

where \( Z_{0} \) is the impedance before any load is applied, \( Z_{i} \) is the impedance value corresponding to the \( i^{th} \) load step, and \( \phi \) is the phase angle [20].

Fig. 5 presents the microscopical rearrangement of carbon nanotubes when the PVDF matrix is elongated in tension and, thus, the new electrical pathway. In this case, under tension, the contact points between the CNTs are located at a higher distance and the impedance of the sample is expected to increase when testing.

The main goal of the experiment consisted of establishing the relationship between the measured impedance value (FCR, equation 2) and the actual strain experienced by the system in tension (\( \varepsilon \)). So, the Gauge Factor (\( \lambda \)) was defined as the ratio between these two parameters:

\[ \lambda = \frac{FCR}{\varepsilon} \]  

(3)

3 Results

3.1 Mix optimization

When producing the PVDF-based coating, electric conductivity and adhesion strength were the main variables in optimizing the mix. For what concerned the latter, preliminary results showed that a high solute-to-solvent ratio led to poor bonding between the coating and the cementitious substrate, i.e., the coating was easily detached with a spatula and/or ethanol treatment. At the same time, the composite system was investigated concerning its influence on electric conductivity. Fig. 6 shows how the electric resistance shifted in polymer resins when changing the ratio between the polymer and the solvent (i.e., 5.0, 7.5, 10.0, and 12.5 w/v%).
Apart from 5.0 w/v% that showed resistance values of 1 GΩ in DC and between 17.2 and 8.3 MΩ in AC, the other concentrations were characterized by a good conductive property. After progressively decreasing to ~1 MΩ (for composites with 10 w/v%), the system’s resistance slightly increased at 12.5 w/v%. Finally, 10.0 w/v% was chosen as the optimal ratio between the polymer (PVDF) and the solvent (DMSO). This performance was related to the inner structure of the system. As described in Section 3.2, a lower solute-to-solvent concentration led to more pores caused by solvent evaporation, which modified the network conductive path.

The following steps for optimizing the mix involved the fluidity and electrical assessment of varying CNT concentrations in the PVDF matrix. Thus, five percentages by weight of polymer were tested at 25 °C. Additionally, since the coating application process occurred while the solution was cooling down, the fluidity of the composite was assessed at 45 °C. Fig. 7 shows that the viscosity grew proportionally to the CNT concentration with respect to pure PVDF-based solutions up to CNT0.50.

When CNT was included in the solution, the composite experienced a viscosity reduction when the temperature reached 45 °C. However, polymeric solutions with no added filler did not present a viscosity variation related to temperature increase (i.e., 46 mPa.s for control samples at both 25 and 45 °C). This proved that the temperature change affected exclusively the dispersion of CNT in the matrix due to a decrease in the intensity of van der Waals forces [31], and, therefore, their influence on the sample’s viscosity.

The electrical characterization was achieved via a 2-probe method under both DC and AC. Fig. 8 shows the resistance decrement, in agreement with the literature, characterized by a progressive conductance growth. This agrees with the Halpin-Tsai model [22] as discussed by Zare et al. [16].

Fig. 8 highlights that 0.50 wt% was the critical CNT concentration (φp) required to achieve a stable electrical network within the polymeric matrix. This value was in agreement with equation 4:

\[ \phi_p = \frac{\pi R^2 l}{2\varepsilon R (R+t)} \left[ 1 + \frac{1}{\sqrt{1+2l/R}} \right] \]

where \( \varepsilon \) is the waviness parameter (assumed to be 1.2), \( t \) is the interphase thickness (assumed to be 6 nm), and \( R \) and \( l \) are the filler’s radius and length [23].

The electromechanical testing described in the following paragraphs will involve all the percentages rather than being limited to the abovementioned critical concentration. This will define the strain-sensing capability and suitability of each coating type.

### 3.2 Microscopical observation

The mechanical dispersion of CNT in the film and its microscopical structure were qualitatively evaluated using an optical microscope. Fig. 9 shows a micrograph of the composite porous matrix.
temperatures varying CNT concentration solutions up to CNT0.50. Shows that the viscosity grew proportionally to the CNT fluidity of the composite was assessed at 45°C. Additionally, percentages by weight of polymer were tested concentrations in the solvent evaporation, which solvent concentration led to ~1 M. After progressively modified w/v% was chosen as the optimal ratio between the other concentrations of 1 GΩ. Further, electrical application frequency 1% (assumed to be 12.5 Ω). The electrical characterization was achieved via detection 3.2, a lower solute that showed resistance values in AC, electrical connection achieved throughout the matrix is dependent on the system's structure. This agrees with the Halpin-Tsai model [30], which highlights that the temperature change affected exclusively the system's electrical performance. All samples provided a good electrical response to applied flexural stress, especially at low strain intervals where CNT0.10 resulted in the most sensitive system - below ~17 με, which is still in the preload area. The overall optimal sensing response was achieved by coatings with 0.50 CNT additions in terms of gauge factor and strain interval (i.e., 309 and 0 - 165 με, respectively). Table 3 summarizes the gauge factors and the stress intervals for each type of conductive coating.

The different slopes of the curves were attributed to the influence of varying CNT concentrations on the mechanical properties of the PVDF matrix (e.g., ductility) [9]. Indeed, given their porous layout, the electrical behavior of the composites did not follow the traditional percolation threshold theory (as schematically depicted in Fig. 5 for continuous media). Instead, the conductive mechanism was affected by numerous factors, such as the degree of polymer crystallization – by influencing the distribution and orientation of the CNT in the matrix [30], the system’s viscosity, and the physical and geometrical properties of the conductive filler [21]. This resulted in different physical/electrical interactions between the pore, the CNT, and the polymeric matrix. Thus each electrical connection achieved throughout the matrix is dependent on the filler concentration. Moreover, it was found that the stress intervals tended to increase proportionally to the filler’s percentage (Table 3) because of their microscopical effects on the composite’s response to external load. Regardless of their different performance, however, all curves in Fig. 10 showed a low electrical response at high strains (i.e., low angular coefficient for

3.3 Electromechanical testing

Five different percentages of CNT were tested to assess the coating’s sensing capabilities (i.e., gauge factor) in bending.

Fig. 10 summarizes the relationship between the actual strain that the bottom layer of the beam is experiencing and the electrical value obtained from the PVDF-based coating for different CNT concentrations.

All samples provided a good electrical response to applied flexural stress, especially at low strain intervals where CNT0.10 resulted in the most sensitive system - below ~17 με, which is still in the preload area. The overall optimal sensing response was achieved by coatings with 0.50 CNT additions in terms of gauge factor and strain interval (i.e., 309 and 0 - 165 με, respectively). Table 3 summarizes the gauge factors and the stress intervals for each type of conductive coating.

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![Fig. 9. Optical micrographs of PVDF-based resins with varying CNT concentrations: (a) 0.10 wt%; (b) 0.25 wt%; (c) 0.75 wt%. Images obtained with a Leica optical stereomicroscope.](image)

![Fig. 10. Fractional Change of Resistance from the PVDF coating plotted against the tensile strain experienced by the bottom layer of the mortar beam. The obtained curves are related to different CNT concentrations, i.e., 0.05, 0.10, 0.25, 0.50, and 0.75% by weight of PVDF.](image)
all five lines above 250 με). This agreed with the theory when beyond a characteristic strain value for cementitious substrates, the conductive system presents a non-linear/void response to any further elongation [4].

The FCR response jump of CNT0.75 was related to the microcrack development between 0.57 and 0.75 MPa. Indeed, the microscopical variation of the conductive network resulted in a pore/matrix interaction that reached the highest sensitivity. Above such interval, however, the system was characterized by the lowest sensing capability due to excessive crack propagation. This behavior was only witnessed for polymeric coatings with 0.75% of added CNT because such a concentration modified the ductility of the composite, thus producing a more brittle matrix for the studied strain interval [9]. Moreover, as the pore size and distribution were fixed by the polymer/solvent ratio (discussed in section 3.1), the encountered changes occurred in the CNT connections of the 3D-like structure.

All films experienced higher gauge factors when compared to traditional strain gauges, e.g., 2-5 for metallic foil gauges [26] and 0.25 for crystalline silicon in elastomeric substrates [27]. For strain intervals above 200 με, the sensitivity of the produced films was analogous to the gauge factor of crystalline silicon in polyimide substrates (~43) [28,29].

Table 3. Gauge factors and relative stress intervals for PVDF-based coatings with varying CNT concentrations under bending.

<table>
<thead>
<tr>
<th></th>
<th>GF1</th>
<th>σ1,2 [MPa]</th>
<th>GF2</th>
<th>σ2,3 [MPa]</th>
<th>GF3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT 0.05</td>
<td>47</td>
<td>0.40</td>
<td>140</td>
<td>0.50</td>
<td>28</td>
</tr>
<tr>
<td>CNT 0.10</td>
<td>657</td>
<td>0.20</td>
<td>87</td>
<td>0.64</td>
<td>35</td>
</tr>
<tr>
<td>CNT 0.25</td>
<td>148</td>
<td>0.58</td>
<td>343</td>
<td>0.88</td>
<td>51</td>
</tr>
<tr>
<td>CNT 0.50</td>
<td>309</td>
<td>0.52</td>
<td>164</td>
<td>0.68</td>
<td>31</td>
</tr>
<tr>
<td>CNT 0.75</td>
<td>243</td>
<td>0.57</td>
<td>1785</td>
<td>0.75</td>
<td>13</td>
</tr>
</tbody>
</table>

In conclusion, while the technical literature has moved from the most conductive mix design to the most responsive one (i.e., percolation threshold), this study has proved that adding carbon nanotubes around the percolation interval to PVDF matrices provided a good sensing system with respect to specific stress/strain intervals. So, PVDF-based smart coatings with CNT additions can be applied to cementitious substrates for structural health monitoring purposes. This sensing system has shown great workability, excellent adhesion property, and good electrical response to external load. Furthermore, for future applications, different filler percentages can be employed to tailor the sensitivity of the coating within the required working conditions (e.g., in accordance with Serviceability Limit States or Ultimate Limit States).

4 Conclusions

The strain sensing of mortar beams in bending was assessed in this work. By using CNT-based polymeric coatings, the objective was to characterize the electrically conductive coatings in relation to their sensitivity to the external load.

Based on the findings and discussions in this study, the following conclusions were made:

- Ten minutes of sonicator probe (750 Watt @20%, 20 kHz) provided a homogeneous CNT dispersion in PVDF/DMSO solutions.
- The adhesion between the polymeric coating and cementitious substrate was inversely proportional to its viscosity and, thus, to the PVDF concentration in the solution.
- By keeping a fixed CNT content, the most conductive polymer-to-solvent ratio resulted in 10 w/v%.
- The shear viscosity, when brushing (shear rate ≈10⁵/s), increased almost linearly with the added CNT.
- As the temperature increased, the viscosity decreased – between 17 to 65 mPa.s – for systems with CNT additions.
- The critical CNT concentration required to achieve the maximum resistivity variation in PVDF/DMSO solution was around 0.50% by weight of polymer.
- The microstructure of PVDF/CNT films was not a uniform bulk system but rather a heterogeneous 3D structure with cavities distributed within the matrix. Such a 3D microstructure might justify the variation of the electrical properties, although further simulation studies are needed to better represent and explain the conduction mechanism.
- When the system was subjected to bending – within the elastic domain – the PVDF/CNT coating experienced an increment in the resistance, in response to the CNT concentrations within certain strain intervals.
- Systems with the highest sensitivity up to 200 με were obtained by adding 0.50 w/v% of CNT, followed by a lower but adequate gauge factor. A lower sensing performance was observed within the same strain limits for PVDF-based coatings with CNT additions of 0.25 and 0.75 w/v%, which then quickly increased before stabilizing at a lower gauge factor. On the other hand, both coatings with 0.05 and 0.10 w/v% CNT additions were characterized by a lower monitoring potential.

To summarize, this work has proved the strain-sensing potentiality of PVDF-based coatings. Moreover, by applying a specific CNT concentration, the investigation of specific strain ranges can be achieved for the specific setting of cementitious beams in bending.

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References

The strain sensing of mortar beams in bending was the coating within percentages can be employed to tailor the sensitivity of Furthermore property, and additions can be applied to cementitious substrates for sensing system responsive one (i.e., percolation threshold), t polyimide substrates metallic foil gauges compared to tradi distribution thus producing a more brittle matrix. This behavior was only witnessed for polymeric however, the system was characterized by the lowest 0.75 the microcrack development between 0.57 a microcrack, resulting in 10\(\approx\)43 excessive crack propagation.

Conclusions

The FCR response jump of CNT0.75 was related to \(\mu\) MPa. Indeed, the microcrack development between 0.57 a characteristic strain value for 0.57\(\approx\)20 kHz) provided a homogeneous CNT dispersion in the following conclusions were made:

• The sensitivity to electrically conductive coatings in relation to their

Technical

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