Solvent-free process for the synthesis of highly stretchable piezoresistive sensors based on polydimethylsiloxane filled with graphene nanoplatelets and carbon nanotubes.

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Abstract. This work reports on the design, the development, and a preliminary characterization of highly stretchable polydimethylsiloxane (PDMS) elastomers as matrices for piezoresistive composites with graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) applicable to aircrafts with morphing shape changes. The strategy adopted for the formulation of the polymeric matrices was to use precursors at low molecular weights, in order to avoid the use of solvents, and functionalized with lateral phenyl groups, to improve the filler dispersion and the filler-polymer interactions. The nanocomposites show high deformability (90%), high conductivity (0.85-0.9 S/m), and piezoresistive behavior (Gauge Factor equal to 0.75). Additionally, CNT and GNP show a synergistic effect in the electrical conductivity, since the percolative threshold of hybrid nanocomposites is lower than those observed with CNT or GNP separately.

1. Introduction

Morphing aircraft are multi-role aircraft that change their external shape to adapt to a changing mission environment during flight. The main focus in the designing of morphing aircraft is to develop high performance wings able to change shape and performance substantially during flight to create multiple-regime, aerodynamically-efficient, shape-changing aircraft [1]. In this context, conventional strain sensors (foil strain gauge, Fiber Bragg Grating and semiconductor strain sensor) show weak deformation ability, small measurement range (<2%), and low tailoring capability to irregular non-planar surfaces [2], therefore they cannot be employed in the designing and production of morphing aircraft parts. Hence, the development of highly stretchable sensors, resistant to harsh environmental conditions, highly sensitive, applicable also to the aeronautical morphing becomes essential for this challenging application.

In general, highly stretchable and sensitive piezoresistive sensors can be realized by exploiting the concept of composite materials by using both elastomeric matrix and conductive carbonaceous fillers, i.e., 1D as carbon nanotubes (CNT) and 2D materials as graphene and its derivatives. The dispersion of the conductive fillers into the polymeric matrix alongside with the fine control of the filler-polymer interfaces have been widely considered as an effective strategy to reduce the percolation threshold and realize high performance and economically sustainable composite. Uniform dispersions of fillers, throughout the bulk volume, can be achieved, e.g., using mechanical methods, including ultrasonication, shear mixing, calendaring, ball milling, stirring and extrusion [3]. On the other hand, to improve the
compatibility between carbon-based fillers, e.g., CNT and graphene nanoplatelets (GNP), and polymeric matrices, chemical and physical functionalization are usually adopted, such as the wrapping of MWCNTs with poly(3-hexylthiophene) (P3HT) [4], or the use of alkyl-functionalized graphene in Polydimethylsiloxane (PDMS)-Graphene sensors [5]. In a different approach, the piezoresistive composites are designed and realized by exploiting the potential of the filler segregation to form preferential paths, for instance by means of porous structures, self-assembling latex or 3D printing of raw powder previously wrapped with carbonaceous fillers [6],[7]. These are all valuable routes to obtain highly stretchable and sensitive piezoresistive sensors. Examples are the manufacturing of 3D CNT/reduced graphene oxide (rGO) network with a porous PDMS elastomer with enhanced electrical conductivity under large strains using 2wt% of CNTs/graphene [8]; or 3D porous polymer filled with graphene oxide (GO) and acid-treated MWCNTs using a 3D printing technique [9]; or the addition of cured PDMS particles to the uncured PDMS/MWCNTs mixture to enhance the formation of self-segregated structures without sacrificing the interfacial interaction [10]; or alternatively the segregation can be obtained with the incorporation of silicon dioxide micro-particles [11]. In this context the use of PDMS as polymeric matrix for the realization of the piezoresistive composites is widely investigated because of it is flexible with an excellent thermal stability, fast response speed, high elasticity, easy production, and low cost [12].

The present contribution deals with the design, preparation and preliminarily characterization of highly stretchable elastomers starting from PDMS precursors with low molecular weights, in order to guarantee a homogeneous dispersion of the conductive fillers, i.e., CNTs and GNPs, and avoid the use of solvents. Thus, the research focus is to realize high performance piezoresistive composite through an ease production and sustainable approach, consisting of the crosslinking of PDMS network directly in presence of well-dispersed carbonaceous fillers. Additionally, with the aim to improve the interfacial adhesion between the filler and the polymeric matrix, selected PDMS precursors characterized by lateral phenyl groups were employed. Finally, an ease preparation method consisting of magnetic stirring and casting were employed for the manufacturing of both polymeric matrices and nanocomposites. The present work represents the evolution of a previous work [13], having as additional goal the use of semi-industrial chemicals to further reduce costs.

2. Experimental

2.1. Materials/chemical details
Siloxane precursors, i.e., vinyl-terminated polydimethylsiloxanes DMS-V00 (D) with Mw = 186 g/mol, vinyl-terminated diphenylsiloxane 15-17mol% dimethylsiloxane copolymer PVS-1625 (P) with Mw = 9500 g/mol, methylhydroxiloxane-dimethylsiloxane copolymers HMS-301 (H) with Mw = 2000 g/mol, and the catalyst platinum-divinyltetramethylsiloxane complex in xylene 2.1-2.4% Pt, SIP6831.2LC (C), were purchased by Gelest Inc. All chemicals have solvent content less than 2wt%. Multiwall carbon nanotubes (CNT) NC3100™, with diameter D = 9.5 nm and length L = 1.5 µm, were provided by Nanocyl S.A.. Graphene-nanoplatelets (GNP) N002-PDR with a lateral x-y dimension ≤10µm, a z dimension of 1.0÷1.2 nm, and a surface area of 400-800 m²/g, were supplied by Angstrom Materials Inc..

2.2. Synthesis
The PDMS precursors (P and/or D) were magnetic stirred with the Pt-catalyst (C) for 1h at room temperature, then the cross-linker (H) was added and mixed for 20 minutes. The reaction which takes place between the vinyl-terminated PDMS precursor and the silanol H, is the hydrosilylation reaction. Several matrices, having the molar compositions reported as full and empty circles in Figure 1-a, were prepared. The strategy adopted to formulate the nanocomposite matrices was to keep high the ratio between P and D, in order to maximize the content of lateral phenyl groups and enhance the π−π interactions between the polymeric matrices and the fillers. On the other hand, the addition of D is
essential to increase the pot life of the reaction mixture. It was found that P and D precursors are not always miscible, but an immiscibility curve can be detected (open circles in Figure 1-a). Moreover, most of the prepared formulations were not able to cure, or had poor mechanical properties, probably due to their low molecular weights. Accordingly, to the results from preliminary investigations, three compositions were selected as matrices (M₁, M₂ and M₃) of nanocomposites, indicated as three grey stars in Figure 1-a. The corresponding nanocomposites were prepared by mixing the filler, i.e., CNT or GNP, into the PDMS and catalyst mixture, i.e., P+D+C in Figure 1-b, and then magnetically stirred for one night. For hybrid nanocomposites containing both CNT and GNP, the latter were added to the CNT-PDMS mixture, and mixed for 30 minutes. Then the hardener H was added and mixed for 20 minutes. After casting, the nanocomposites were cured for 15 minutes at 80°C. The procedures are schematically reported in Figure 1-b.

![Figure 1](image-url)

**Figure 1.** (a) Molar composition of all prepared polymeric matrices (●, ○, ▲); (○) are formulations that fall in an immiscibility region and were not considered in subsequent analyses; (▲) are the stoichiometric ratios D/H and P/H; (★) are the selected matrices, M₁, M₂, and M₃. (b) Schematic draw of the nanocomposites synthesis.

### 2.3. Methods and characterizations

The mechanical characterization was performed by using a TA Instrument ARES rotational rheometer equipped with a SER unit (Sentmanat Extensional Rheometer), which consists of two parallel counter rotating wind-up drums (distance between axes L₀ = 12.72 mm) of equal radius R = 5.155 mm, where rectangular samples with length L=40 mm, width W=10 mm, and thickness δ= 0.8 ±1 mm were clamped (see the inset in Figure 2). The test provides torque (T) vs time (t) plots, from which the engineering stress σ vs strain ε curves were obtained, assuming the materials to be incompressible and by applying the equations (1), where F is the applied tensile force evaluated from the resultant torque T measured by the ARES transducer, and A₀ is the initial cross-sectional area of the specimen. The Young modulus E was assessed in the first 5% of elongations. For each investigated sample a minimum of three specimens were tested. All the tests were performed setting the Hencky strain rate at \( \dot{\varepsilon}_H = 0.1 \text{ s}^{-1} \).

\[
\sigma = \frac{F}{A_0} = \frac{T R}{W \delta} \quad \varepsilon = \exp(\dot{\varepsilon}_H t) - 1 \quad (1)
\]

The percolation threshold of nanocomposites was assessed by selecting the optimal amount of filler for which the electrical resistance starts to be lower than 9 \( 10^9 \) Ω.

The electrical conductivity measurements were carried out using a Keithley 6221 current source and a digital voltmeter. The specimens were strips having dimensions of 10x40x1mm coated at the ends with conductive silver paste, in which copper wires were partially embedded to create the electric contacts.
Coupled electrical–mechanical testing was performed to evaluate the sensing characteristics and piezoresistive behaviour of nanocomposites. The experimental setup consists of a mechanical tester (Instron 5564 Tensile & Compression Materials Testing Electromechanical Em Tester) and a multimeter (Agilent 34401A 6½ Digit Multimeter) controlled by a homemade LabVIEW program. The electrical resistance was monitored continuously at room temperature (25 °C) for 120 load-unloading cycles. The samples were pre-strained and submitted out to a tensile deformation with a control of the strain between 0 and 20%, with a rate of 10 mm/min. The measurements were performed by a 2-probe method. Scanning Electron Microscopy (SEM) analyses was carried out by using an Inspect F model FEI apparatus at an accelerating voltage of 10 kV.

3. Results and discussion

3.1. Mechanical characterization

Figure 2 shows the stress-strain curves of the selected polymeric matrices, labelled as M₁, M₂ and M₃ whose formulations are detailed in Table 1. It was found that small differences in the matrices’ composition, i.e., P/H ratio, cause significant variations in the final mechanical properties, in terms of breaking stress (σᵇ), breaking strain (εᵇ) and Young modulus (E) (see Figure 2 and Table 1). In this regard, the higher the ratio P/H, the higher the elongation at break and the lower the Young modulus E. Based on mechanical results, the ratio P/H own of the polymeric matrix M₁ showing the highest modulus was selected to formulate the nanocomposite N₁, whose stress-strain curve and composition are reported in Figure 2 and Table 1, respectively. It should be noticed that in spite of the addition of fillers, εᵇ of N₁ is only 12% minor than that of the corresponding matrix.

![Figure 2. Stress-strain curves of three PDMS matrices (M₁, M₂ and M₃) and the nanocomposite N₁. In the inset, a sample’s strip clamped on the SER is shown.](image)

| ID | P [wt%] | D [wt%] | H [wt%] | C [wt%] | CNT | GNP | σᵇ [kPA] | εᵇ [%] | E [kPa] |
|----|---------|---------|---------|---------|-----|-----|-----------|--------|--------|
| M₁ | 96.07   | 0.2     | 3.71    | 0.02    | -   | -   | 75±9      | 91±5   | 99±16  |
| M₂ | 96.8    | 0.2     | 2.98    | 0.02    | -   | -   | 49±10     | 113±18 | 50±5   |
| M₃ | 97.05   | 0.2     | 2.73    | 0.02    | -   | -   | 38±2      | 112±11 | 37±2   |
| N₁ | 94.36   | 0.35    | 3.64    | 0.15    | 0.05| 1.45| 96±20     | 80±11  | 108±10 |
3.2. Electrical characterization

The percolation thresholds ($\phi_c$) of nanocomposites with CNT and GNP, listed in Table 2, show that the value assessed for the CNT, i.e., 0.05\%, is much lower than those observable in literature [2],[12],[14]-[17], mainly in the range 0.3÷2.5wt\%. Additionally, it was found that CNT and GNP exhibit a synergistic effect in the electrical conductivity, which acts by reducing the percolation threshold due to the single filler, through 1D(CNT)–2D(GNP) interconnections [17],[18]. In fact, the value of $\phi_c$ for the hybrid CNT:GNP (1:9) (Table 2) is 0.25wt\%, distributed as 0.025wt\% in CNT and 0.225wt\% in GNP, both values lower than those observed in nanocomposites with single filler, i.e., 0.05 and 0.25\% respectively.

The measured values of conductivities were compared in Figure 3 to some relevant works found in literature on analogous systems. It is worth noting that the nanocomposites prepared in the present work display conductivity higher than most of systems containing comparable or higher content of filler. Furthermore, the systems reported in literature with lower percolation thresholds take advantage from the use of solvents to favour the filler dispersion; on the contrary, the effort of the present work was to avoid the use of solvent in order to be environmentally safe.

| Filler          | Percolation threshold* (% wt) |
|-----------------|------------------------------|
| CNT             | 0.03 < $\phi_c$ ≤ 0.05      |
| GNP             | 2% < $\phi_c$ ≤ 3           |
| CNT:GNP (1:9)   | 0.1 < $\phi_c$ ≤ 0.25       |

*Filler amount range for which the electrical resistance becomes lower than 10$^9$Ohm.

Figure 3. Electrical conductivity of nanocomposites discussed in the present work compared to the state of the art (x:y refers to CNT:GNP ratio). Green diamond represents the N$_1$ nanocomposite.
3.3. Morphological characterization

SEM images of \( N_1 \) sample (Figure 4 a-d) highlight a uniform morphology with a reduced porosity ascribed to air bubbles embedded during the mixing and casting processes. In the magnifications of Figure 4 a-d the irregular bright protrusions could be attributed to bundles and agglomerates of CNT (Figure 4-c), whereas the flat areas detectable in Figure 4-d could be ascribed to GNPs platelets. Since all morphological variations associated with the fillers appear to be covered with the organic matrix, it can be concluded that pull-out and de-bonding phenomena are absent. This speaks in favour of an excellent affinity between filler and matrix, which is ascribed to the phenyl lateral groups of the polymeric precursor.

![Figure 4. SEM images of \( N_1 \) sample at magnifications of 180x (a), 800x (b), 3000x (c) and 12000x (d).](image)

3.4. Electromechanical characterization

Preliminary result of the electromechanical characterization performed on the \( N_1 \) nanocomposite shows that this sample exhibits a piezoresistive response with a drift during the load-unloading cycles in a wide range of operational conditions (Figure 5-a). It also emerges that there is a good correspondence between the imposed strain and the measured changes in the electrical resistance, despite the slope of the resistance variation is not linear presenting an increment in the loading phase and a reduction during the unloading phase (Figure 5-b). This behaviour can be attributed to a conductive network which changes during the loading/unloading cycles, with a significant increment of percolative paths and the formation of effective contact point between the CNTs, after each load/unloading cycle. In fact, as consequence, the R values decrease during the test (Figure 5-b) both at maximum tensile strength and when it returns to zero.

The sensitivity of the \( N_1 \) sample as piezoresistive strain sensor can be quantitatively expressed as the gauge factor (GF):

\[
GF = \frac{\Delta R/R}{\varepsilon} \quad (2)
\]
where $\Delta R/R$ is the normalized resistance and $\varepsilon$ is the mechanical strain. The GF, assessed as 0.75 for $N_1$, reveals a poor sensitivity of this nanocomposite as piezoresistivity sensor, if compared to homologous systems found in literature, e.g., $4.3 \div 6.5$ [14],[18].

Figure 5. Resistance (R) and strain ($\varepsilon$) of $N_1$ nanocomposite vs time (a); in (b) an enlargement is shown.

4. Conclusions
The goal of this work was to design and formulate highly stretchable polydimethylsiloxane (PDMS) elastomers to be used as matrices for piezoresistive sensors for aeronautical applications. In order to assure a good dispersion of the conductive fillers, i.e., carbon nanotubes (CNT) and graphene nanoplatelets (GNP), avoiding the use of solvents, polymeric precursors at low molecular weights were employed for the matrices’ formulations. One of the selected precursors was functionalized with lateral phenyl groups, in order to improve the interfacial adhesion between filler and matrix during the operational conditions. The nanocomposites prepared starting from the designed formulations show high deformability (90%), high conductivity (0.85-0.9S/m), piezoresistive behavior with a GF=0.75, and high affinity between filler and polymeric matrix. Both CNT and GNP were added as conductive fillers, since together they showed a synergistic effect in the conductivity, by lowering the respective percolative threshold to values comparable with (or even lower than) those reported in literature for systems prepared though processes involving solvents.

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