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CNT-POLYDIMETHYLSILOXANE NANOCOMPOSITES FOR PROSTHESIS INTERFACES

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Summary: *Amputation causes profound changes in individual's health. The prosthesis must fulfil a series of conditions; its proper application is directly dependent on the correct selection of materials, according to their structure, properties and behaviour. The prosthesis interface, or liner, has particular importance, due to its function in establishing a direct connection between the stump and the prosthesis, being responsible for the transmission of ground reaction forces, damping gait loads and tissue protection. Its inadequacy may result in serious problems. Carbon nanotubes (CNTs) have generated great interest for several biomedical applications, mainly due to their mechanical, electrical and thermal properties, as well as chemical stability. However, to the best of our knowledge, they have never been used in prosthesis liners. Thus, the aim of this work was to develop a new alternative material to prosthesis interfaces, based on CNT-polydimethylsiloxane (CNT-PDMS) nanocomposites. Physical, mechanical and thermal properties of the composite and competitor materials were evaluated. The results show a good dispersion of CNTs in the PDMS matrix and good composite stability. An increase of the thermal conductivity was observed when compared to other interface materials. In addition, an interesting relationship between the stiffness and the dissipation of energy was found. From the overall characteristics of the CNT-PDMS nanocomposite, it was concluded that this material presents promising properties to be used as prosthesis interface.*

1 INTRODUCTION

Amputation causes profound changes in individual's health [1]. The rehabilitation plan of a lower limb amputee goes through a set of performed cares, but the correct prosthetization is one of the most important factors, which depends on the choice of the best components for each patient's prosthesis [2]. The proper application of the prosthesis components is directly dependent on the correct selection of materials, according to their structure, properties and behaviour [3]. In the absence of joints and tissues for cushioning the impact on the amputated limb, the stump becomes vulnerable to the transmission of loads [2,4]. The repetitive impact load that exists between the heel and the ground when walking, coupled to the referred absence of anatomical structures, can lead to pain on the stump [2]. These mechanical loads associated with the loss of heat transfer mechanisms of the skin, poor permeability and low thermal conductivity of interfaces generate an environment of high temperatures, closed and humid (due to sweating). These conditions cause discomfort and skin lesions [5] as ulcers, contact dermatitis, eczema, epidermoid cysts and fungal infections or bacterial infections [6] and can also seriously compromise walking and carrying out daily life activities [2].

Thus, the interface has a special importance, due to its function in establishing a direct connection between the stump (*i.e.* the individual) and the prosthesis. Materials like silicone, silicone gel and urethane elastomers have been used in its confection. Several liners manufacturers have tried to develop composite materials to improve their performance, specifically the inclusion of skin care ingredients in silicone matrices, as Vaseline or Aloe Vera.

Carbon Nanotubes (CNTs) are considered ideal materials for several applications, as ranging from ultra-strong fibres to field emission displays [7], due to their physical and chemical properties such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behaviour, high surface area and excellent chemical and thermal stability [8,9]. Ever since the discovery of CNTs, researchers have been exploring their potential in biological and biomedical applications [10]. CNTs are currently being studied to be a suitable substrate for the growth of cells for tissue regeneration, as delivery systems for a variety of diagnostic or therapeutic agents or as vectors for gene transfection [11], bioactive peptides to the immune system [12], potential novel vaccine delivery tools [13], oligonucleotide transport inside living cells [14], as a culture substrate for neural cells [15], and to stimulate the neurophysiological activity of cells [16]. Considering the applications described in the literature, carbon nanotubes have strong potential in the general biomedical field and specifically for orthopaedics. Since, carbon fibre composite materials are widely used across a wide range of applications in modern orthopaedic medicine and prosthetic devices, particularly in dentistry and in the design of lower-limb prostheses for sports [17]. The main advantages in using these kinds of composites are associated with their exceptional specific strength characteristics and biocompatibility [17]. However, to best of our knowledge, they have never been used in prosthesis liners.

Thus, the aim of this work was to develop a new alternative material to prosthesis liners, based on CNT-polydimethylsiloxane nanocomposites, which should be biocompatible and lead to an improved thermal and mechanical behaviour of the interface, in order to better accommodate the tissues, distribute the load, reduce the impact on the stump and increase the comfort and quality of life of the amputees.

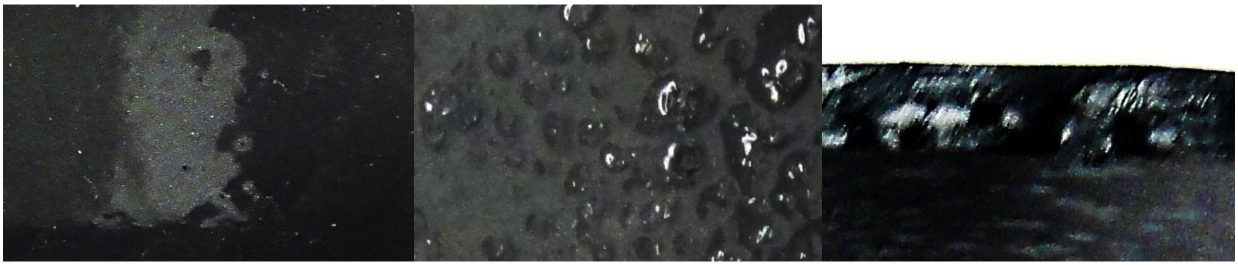
2 METHODS

2.1 CNT-PDMS composite synthesis

Commercial multi walled CNTs (MWCNTs) were functionalized with carboxyl groups by a chemical treatment with HNO_3 (15.7 M), in an ultrasonic bath at 70°C for 30 minutes.

Then, the solution was washed in double distilled water and dried at 40°C during two days. After CNTs functionalization, the composite was prepared with the following procedure. First, a suspension of CNTs in toluene was prepared and stirred with sonication for 15 minutes. Next, a PDMS (SYLGARD 184 Silicon Elastomer) and toluene (99.8% purity, Sigma-Aldrich) solution was made and placed in the ultrasonic bath for 5 minutes. Then, the CNTs suspension was mixed with the PDMS solution with sonication for 10 minutes. The curing agent was then added, followed by stirring again in the ultrasonic bath for 5 minutes. The mixture was poured into a petri dish and allowed to evaporate the solvent overnight. The composite was cured at 100°C for 60 minutes, after previous vacuum (10^{-3} bar) during 30 minutes at 25°C.

Various composite formulations were prepared with different mass percentages of CNTs (1.5%, 3% and 4.5%) and different solvents (toluene and ethyl acetate), but only the formulation with 1.5% of CNTs that used toluene could be successfully reticulated and had homogeneous appearance (Figure 1).



(a) (b) (c)

Figure 1: Selected composite: a) top side; b) bottom side; c) cross-section.

2.2 Composite characterization

The selected composite was characterized regarding its physical and mechanical properties and thermal conductivity. To better understand the contribution of CNTs to the measured properties, a sample of the PDMS matrix (without CNTs) was also characterized. Moreover, to evaluate the composite application feasibility for interfaces, some results were also compared to results of mechanical, structural and thermal characterization of three types of commercial interface materials [18]. The selected materials are representative of the most used materials in interfaces for tibial prosthesis – a block copolymer, a silicone gel and a silicone elastomer.

The morphology of the composite was observed, on fractured surfaces, by a *Philips XL30 TMP* scanning electron microscope (SEM). The sample was coated with gold by physical vapour deposition, during 20 s, in order to allow a better observation. The images were obtained either with secondary or backscattered electrons to improve the contrast. The bulk density was evaluated, based on the volume and weight of the samples. The thermal conductivity was calculated from the data collected with a *Hot Disk Thermal Constants Analyser*, model *TPS2500*, at 20ºC. The used equipment has reproducibility better than 1% and accuracy better than 5%.

The mechanical experiments under static loading were conducted in a *Shimadzu AG-X plus* universal testing machine, adjusted to a compression test. This machine has a load cell of 5 kN and tests were done with a loading rate of 5 mm/min and a data acquisition rate of 10

Hz. During tests, there was no radial constriction of specimens. The samples were compressed with a 16 mm diameter punch until reaching a strain of 0.4. The active area of compression was the area of the circular punch. For each sample, 5 replicas were done.

An *Instron ElectroPuls™* fatigue machine was used to perform the dynamic compression tests. In these tests, all the samples were tested applying a cyclic sinusoidal compression with a frequency of 10 Hz and the displacement amplitude was adjusted as a function of the specimen thickness to avoid the effect of the bearing surfaces.

3 RESULTS AND DISCUSSION

From SEM observation (Figure 2), it is possible to conclude that the surface morphology of the composite (Figure 1a) is similar to that of the commercial silicone elastomer (Figure 1b). It is also possible to observe small vertical ribs in the composite, which are not present in silicon elastomer. These ribs indicate that the CNTs are well dispersed and aligned in the PDMS matrix.

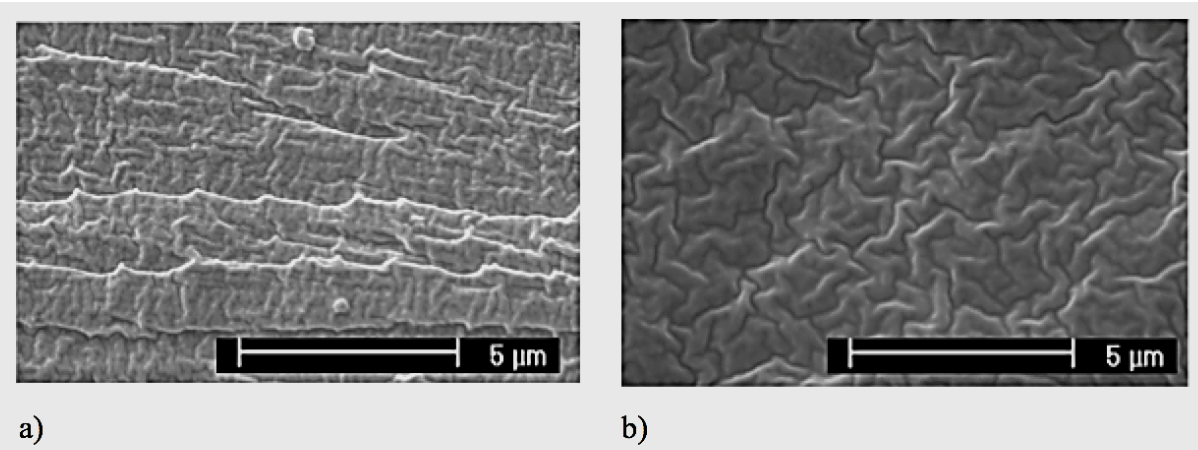


Figure 2: Surface morphology: a) CNT-PDMS composite; b) silicone elastomer [18].

Bulk density values for CNT-PDMS composite, PDMS matrix and commercial liners are presented in Table 1. The composite shows a small density increase when compared to the matrix. In fact, the CNTs show very low density, which can ensure a strong and stable composite with low increase of weight. The commercial materials show density values in the same order of magnitude, but the silicone interfaces, which are chemically more close to the PDMS matrix here studied, have higher densities. This indicates that the prepared composite has appropriate density for the intended application and it represents an important advantage in weight that is relevant for the amputee's gait [19], when compared to commercial similar materials.

Thermal conductivity values are also presented in Table 1. Although the very high thermal conductivity of the CNTs, the composite only shows a modest increase of this property when compared to the PDMS matrix. This suggests that the CNTs are not forming an interconnected network in the PDMS matrix and a higher amount would be necessary to increase more significantly the thermal conductivity. As higher amounts of CNT are causing problems in terms of the matrix reticulation, more work should be done to solve this issue.

Anyway, the obtained thermal conductivity value is in similar range of the commercial materials, even slightly higher, indicating that the current composite presents appropriate thermal conductivity for the intended application. Future studies with amputees will be required to determine if the increase in thermal conductivity has some relevance in terms of reduction of skin injuries and increase of comfort on amputee's day life.

Table 1: Bulk density and thermal conductivity of the liners.

Samples	Bulk density (Kg/m^3)	Thermal conductivity (W/(mK))
CNT-PDMS composite	876.94	0.2057
PDMS matrix	860.93	0.1808
Block copolymer	826.66	0.1543
Silicone gel	938.05	0.1970
Silicone elastomer	907.88	0.1974
CNTs	0.0026[20]	3000 [22]

These results also confirm that the silicone interfaces are better for heat transfer from the stump than block copolymer interfaces, as already mentioned by Klute *et al.* [21] and Huang *et al.* [19]. In Huang *et al.* study [19], the skin temperature on the stump during the gait was evaluated, on subjects in the same conditions, using silicone and thermoplastic elastomer interfaces. It was found that, after the end of the walking period, the subject with the silicone interface experienced a much smaller increase in the stump's temperature (1.5°C) than the subject with the thermoplastic elastomer interface (3.1°C). To confirm this, the thermal conductivity of the interfaces was also measured and it was shown that the silicone interface had a conductivity of approximately 0.176 W/(mK) against 0.040 W/(mK) of the thermoplastic elastomer.

The stress-strain (σ-ε) curves obtained for PDMS matrix and CNT-PDMS composite, under static loading, are depicted in Figure 3. The composite material shows a very similar mechanical behaviour when compared to the commercial materials [18], the static results showing a first linear phase, with constant stiffness followed by a continuous increasing of the stiffness. This behaviour was represented, in an earlier work [18], by the model shown in Equation (1), which presents a double branch law with a linear part up to $\varepsilon_{\text{elas}}$ (strain at the elastic limit) and a more complex equation corresponding to the nonlinear portion.

$$\sigma = \begin{cases} A\varepsilon, & \varepsilon < \varepsilon_{\text{elas}} \\ A\varepsilon + B(\varepsilon - \varepsilon_{\text{elas}})^n, & \varepsilon \geq \varepsilon_{\text{elas}} \end{cases} \tag{1}$$

Table 2 presents the results of the parameters of this model for the composite and matrix, resulting from the behaviour observed under static compression (Figure 3). This table also shows the same parameters obtained in the same test conditions, in a previous study, for the commercial materials [18].

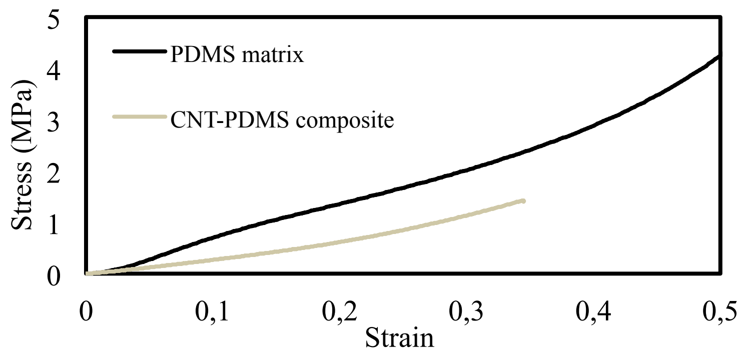


Figure 3: Comparison of the stress-strain curves of the PDMS matrix and CNT-PDMS composite.

Table 2: Constants of the characteristic stress-strain curves of materials.

Samples	*A* (MPa)	ε_{elast}	*B* (MPa)	*n*
CNT-PDMS composite	2.85	0.14	9.64	1.94
PDMS matrix	6.97	0.38	25.19	1.58
Block copolymer	0.13	0.11	0.07	1.36 [18]
Silicone gel	0.75	-	-	- [18]
Silicone elastomer	0.17	0.09	0.21	1.46 [18]

The PDMS matrix and the CNT-PDMS composite have higher values (one order of magnitude above) of elastic modulus (constant *A*), when compared to the commercial interfaces. However, the linear strain (ε_{elas}) of the composite has a similar value. As the CNTs have an incredible high elastic modulus, 1.2 TPa [20], and the matrix exhibited a high elastic modulus too, we consider that the composite elasticity results from the appropriate dispersion of CNTs in the polymeric network of the matrix, as SEM analysis already showed, and interference of CNTs in the reticulation, making the composite less stiff then the matrix.

The block copolymer displays the lowest stiffness (Table 2) when compared to the other materials, exhibiting a higher strain in the elastic limit than the other commercial materials, but not so high as the composite.

Table 3 presents the results of the mechanical parameters obtained for the CNT-PDMS composite, PDMS matrix and the commercial materials under dynamic loading. Figure 4 shows the stress-strain curves of the composite and matrix under dynamic loading, which exhibit a hysteresis loop.

Table 3: Bulk modulus, E', lost modulus, E", and tangent of the phase angle, tan δ.

Samples	*E*' (MPa)	*E*'' (MPa)	tan δ
CNT-PDMS composite	5.63	2.43	0.42
PDMS matrix	21.54	6.46	0.30
Block copolymer	1.62	0.43	0.27 [18]
Silicone gel	11.9	3.31	0.28 [18]
Silicone elastomer	1.64	0.94	0.57 [18]

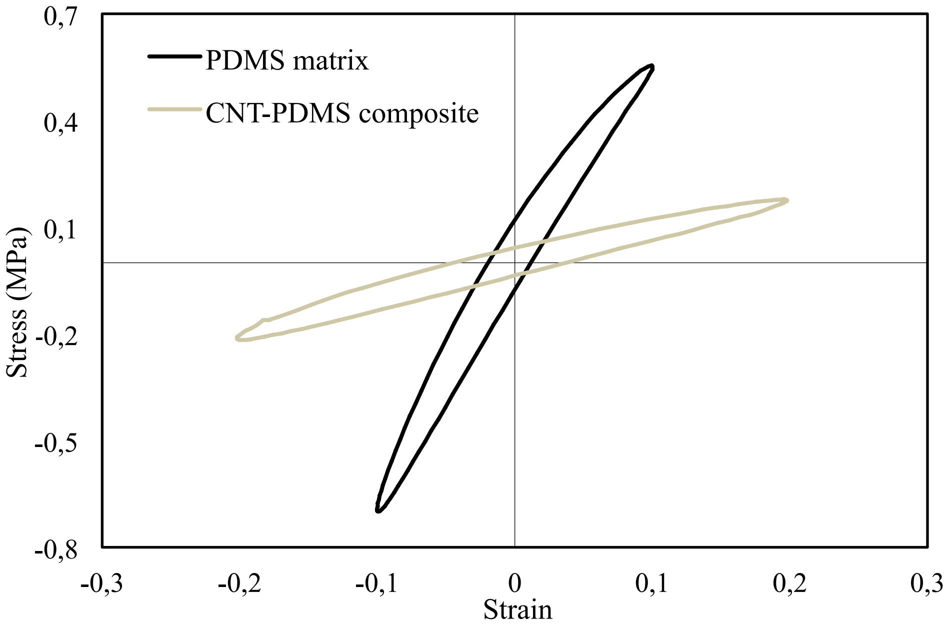


Figure 4: Comparison of the stress-strain dynamic loops of the PDMS matrix and CNT-PDMS composite.

The obtained results are in agreement with the static results. The PDMS matrix has the highest bulk modulus, which is reduced by the inclusion of CNTs in the composite. The bulk modulus of the composite is much lower than for the silicone gel and the dissipation of energy (tan δ) is higher, what confirms again the potential application of this material in prosthetic interfaces. This ability that CNT-PDMS composite revealed to dissipate more energy agrees with the higher n value of the model fitted to the results of the static tests (Table 2). In fact, the highest nonlinearity of the composite is correlated to his higher energy dissipation.

The relation between stiffness and softness is very important in prosthetics interfaces. The higher the percentage of energy absorbed, more work the amputee must do while using the prosthesis. Lower impact force experienced by the amputee will result in a greater comfort [23,24]. So, more dissipative materials provide protection for bony prominences and stiffer materials support better the soft tissues [24].

4 CONCLUSION

The most important factors identified by lower limb amputees for worse quality of life are the use of prosthesis, comorbidities, phantom-limb pain and residual stump pain [25]. The unnatural mechanical conditions that result from the interaction between the soft tissues of the residual limb and the prosthetic socket often lead to pain, edema or pressure ulcers [26]. The elasticity of an interface should be appropriate to the type of stump. The ideal prosthetic interface material should provide a good response (high stiffness), protection from impact, and have a minimal change in thickness during use. It may also be desirable to possess mechanical properties similar to the replaced biotissues [24].

Thus, it can be concluded from this study that the composite material here developed can be used as prosthesis interface, since it demonstrated good dispensation, stability and a thermal and mechanical behaviour very similar with the commercial materials. This material shows a slight increase in thermal conductivity and an interesting relation between the stiffness and the dissipation of energy. More samples need to be tested, but the CNTs inclusion on an elastomeric matrix may represent a prothetization improvement, in biomechanics terms and durability of the interface component.

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