3D printing-directed flexible strain sensors of accordion-like architecture to achieve ultrastretchability with the assist of ultrasonic cavitation treatment

Y F Qu1, J H Ma1, Y Q He1, L Zhang1, F C Ren2, B Li1

1 School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai 200237, PR China
2 Shanghai Institute of Special Equipment Inspection and Technical Research, Shanghai 200062, PR China
libo@ecust.edu.cn (Corresponding author: Bo Li)

Abstract. A new class of accordion-like cellular architecture with sinusoidal struts is designed to enhance the planar stretchability of cellular solids, aiming to fabricate flexible strain sensors with ultrastretchability. The combination manufacturing process of fused deposition modeling (FDM) 3D printing technique and ultrasonic cavitation-enabled treatment was introduced into the fabrication of flexible strain sensors made of thermoplastic polyurethane (TPU) substrate and carbon nanotubes (CNTs). A negative Poisson's ratio (NPR) architecture made of TPU was firstly 3D-printed by FDM. The ultrasonic cavitation treatment was then conducted on the soft auxetic structure immersing in CNTs liquid, aiming to embed the CNTs into the surface layer of the flexible TPU substrate with NPR configurations. Instead of 3D printing the TPU matrix composite after hybridization inside the matrix material, the hybrid manufacturing procedure can ensure that the intrinsic excellent mechanical properties of TPU are not embrittled. Besides, the sinusoidal struts in accordion-like cellular architectures offer a design route to extend the material property chart to achieve ultrahigh stretchability in lightweight 3D printable flexible polymers for the applications that require combined stretchability, lightweight, and energy absorption such as soft robotics, stretchable electronics, and wearable protection shields.

1. Introduction
In recent years, flexible electronic sensors have attracted great interest in the fields of human health monitoring, environmental monitoring for crops, and service condition monitoring of complex elastic structures or soft machinery [1-3]. The flexible strain sensors can play an important role in the above respect owing to the simple conversion principle. With the externally applied tensile and pressure, the distribution density and contact state of the conductive material are changed and makes the resistance of the sensor change periodically [1].

The optimization of conductive material and sensor structure are commonly considered in detail by researchers to improve the performance of flexible electronic sensors. Chen et al. employed a carbon nanotube-polyurethane (CNT-PU) sponge to develop a lightweight, low-cost, and retractable sensor [4]. A flexible and highly sensitive pressure sensor was fabricated by Rinaldi et al. using soft foam coated with graphene nanosheets. Their sensors were loaded with 0.96 wt.% of multilayer graphene nanosheets. It was characterized by the highly repeatable pressure-dependent conductance after several stable cycles [5]. In addition, there are some researches on improving the sensor architectures. For
instance, Wang et al. fabricated flexible strain sensors based on the network cracks formed in the multilayer carbon nanotubes (CNTs) films/polydimethylsiloxane (PDMS) composites. Adjusted by the number of CNTs layers, the obtained flexible stretchable strain sensor showed an excellent sensing range (up to 100%) [6]. Wang et al. manufactured highly stretchable and sensitive multidirectional strain sensors with tunable strain gauge factors by employing a digitally controlled printer to incorporate carbon nanotube (CNT) layers into polydimethylsiloxane (PDMS) substrates [7].

According to the previous studies, most of the flexible electronic sensors need to be packaged or other customized processes, which makes the sensor less reproducible and difficult to mass production and application. Considering this, herein a method combined fused deposition modeling (FDM) and ultrasonic post-processing is created. Firstly, the FDM-assisted thermoplastic polyurethane (TPU) based flexible substrate which has an accordion-like architecture is well fabricated. Secondly, the flexible substrate is dropped into the CNTs suspension. The CNTs are bombarded to the surface of the sensor by ultrasonic processes. The sensors fabricated by this method have good sensing performance and the original mechanical properties and elasticity are also greatly maintained. Owing to the stability of the manufacturing process, such as FDM printing parameters and ultrasonic processing parameters, the sensors have good reproducibility. In addition, the sinusoidal struts in accordion-like architectures offer a design route to extend the material property chart to achieve ultrahigh stretchability in some lightweight 3D printable flexible polymers for the applications that require combined stretchability, lightweight, and energy absorption such as soft robotics and stretchable electronics [8, 9].

2. Experimental details

2.1. FDM printing of TPU flexible substrate with an accordion-like architecture

Herein, an accordion-like architecture was selected as the flexible substrate, as sketched in Fig.1a. Fig.1b exhibits the accordion-like structure composed of a sine function curve, which can avoid large stress concentration at sharp Angle connection. The Sine curve formula is given by

\[ F_n(x) = \frac{L}{2} \cos \left( \frac{2\pi n x}{H-2t} \right) \]

where \( H \) is 11.5mm, \( L \) is 5.75mm, \( t \) is 1, and \( n \) is 3. The geometric meaning of parameters in the above formula corresponds to Fig.1b. After modeling with Solidworks software, the accordion-like structure model was saved in STL format and imported into Simplify3D software for slice processing. After setting printing parameters, the printing device was started to complete the printing process. The 3D printing process was conducted by a desktop FDM printer, which was customized for printing TPU-based parts. The FDM printer has a nozzle diameter of 0.35 mm and a layer depositing resolution of 0.1 mm. The fabrication procedure of the TPU-based flexible substrate was stated as follows.

![Figure 1](image-url)
drawn using computer-aided design software, was saved as STL format and then imported into 3D slicing software for slicing. The sliced file was imported into the printer. The nozzle temperature was set as 200 ℃. The printing line-interval parameter was set as 0.4 mm. The printing speed was set as 3600 mm/min. The depositing layer thickness was set as 0.2 mm. Here, what should be illustrated is that the FDM process parameters were the results of adequate experiments for process optimization. Then, the FDM printer was able to print the designed parts.

2.2. Ultrasonic assisted post-treatment of the flexible substrate

The TPU flexible substrate with an accordion-like structure was unable to sense without conductive filler. In this study, CNTs were selected as conductive fillers to be fixed to the surface of the flexible substrate by ultrasonic energy. The process of post-treatment was as shown in Fig.2. 100 mg CNTs was added into 80 ml deionized water and put into an ice water bath. The ultrasonic treatment was carried out in the ultrasonic cell crusher for sixty minutes, with a power of 180 W. After that, uniform CNTs dispersion was obtained. The FDM printed flexible substrate with an accordion-like structure was put into the CNTs dispersion. The CNTs were combined with TPU flexible substrate by ultrasonic energy under 450 W power for sixty minutes. After the sample was taken out, it was repeatedly cleaned with the deionized water in the ultrasonic cleaning machine until the water became transparent. The unstable CNTs not embedded in the surface of the TPU flexible substrate were removed. After the first two times ultrasonic cleaning, the deionized water was discolored, indicating that the unstable CNTs on the surface of TPU were removed. But in the third to fifth cleaning, the deionized water became transparent. It could be understood that the unstable CNTs on the surface of TPU were almost removed, leaving stable CNTs combined with TPU flexible substrate which were difficult to peel off without packaging. Then the sample was placed in the fume hood for 24 hours to become dry.

2.3. Testing of strain sensing behavior

The testing experiments on the fabricated flexible strain sensors were implemented for inspection and evaluation of dynamic response. A resistance tester was connected to the sensor to gain the real-time resistance values. Two couples of insulated clamp ends were attached to the edges of the sensor, aiming to be held by the fixture ends of a mechanical tension instrument. When the cyclic tensile load was added to insulated clamp ends, the sensor resistance changed dynamically. For the calculation, the above-mentioned performance parameters for inspection and evaluation were gained by the computer software equipped with the resistance tester. $R$ is defined as the sensor resistance value under a certain
strain variable. $\Delta R$ is defined as the variable in resistance under this strain variable. Then, the $\Delta R/R_0$ is the resistance change rate of the strain sensor.

3. Results and discussion

3.1. Evaluation of the FDM printed flex-sensor with the assist of ultrasonic treatment

After obtaining TPU flexible substrate by FDM printing, CNTs were thus embedded into the surface layer of the flexible matrix by ultrasonic energy to form a flexible strain sensor. After FDM printing and removing it from the substrate, the TPU substrate with accordion-like architecture is shown in Fig.3a. Fig.3b exhibits the flexible strain sensor after the ultrasonic cavitation-enabled treatment in the CNTs liquid. Fig.3c shows the morphologies of the TPU flexible matrix with an accordion-like structure under different strain variables, showing its ultrastretchability, which is of great value to the flexible strain sensors. The total size of the samples is designed to be large enough such that all of the geometrical features of the designed architecture can be 3D printed by the adopted FDM 3D printer in the current study. As evident in Fig.3c, the sinusoidal architecture made of a brittle polymer stretches significantly before ultimate fracture, which indicates a 3D printing strategy for elastomeric structural materials. In addition, the sharp corners in constitutive struts of the conventional cellular architectures cause stress concentration and structural failure, before allowing the other parts of constitutive building blocks to experience the applied stress. To enhance the stretching capability of cellular architectures, sharp corners in constitutive struts should be avoided. As shown in Fig.4, the sharp corner was not serious due to the compensation policy during the printing or relying on the FDM 3D printing software settings. Moreover, some additional padding also enhances the corner structures.

It should be noticed that the CNTs were well embedded into the surface layer of the TPU substrate, as shown in Fig.4c. It indicates that the exposed CNTs are intertwined on the surface to form a tight conducting network. The process of CNTs embedded in the flexible substrate is explained as follows. Firstly, the energy of ultrasonic generates cavitation bubbles in deionized water. Then the cavitation bubbles break when contact with the CNTs and generate huge energy which makes the CNTs and TPU collide with each other and bond closely.

![Figure 3. FDM printed accordion-like flexible substrate without CNTs (a) and with CNTs embedded into the surface layer (b), and deformation morphology of the accordion-like TPU structure (c).](image-url)
Figure 4. SEM of FDM printed local multi-layer sharp corner configuration of the accordion-like structure substrate (a, b), and the SEM of CNTs embedded into the surface layer of TPU substrate (c).

The performance of the flexible strain sensor with an accordion-like structure is tested. It is found that the relationship between the resistance change rate and strain variable does not show a regular curve. As shown in Fig.5, the resistance change rate presents a complex curve in the stretching cycle, so this kind of accordion structure is not suitable for the flexible strain sensor prepared by this method. The reason for this phenomenon may be that the accordion-like structure is complex, and in the case of \( n=3 \) (\( n \) is the period of sinusoidal function), the relative density of accordion-like structure is large, the distance between different sinusoids is small, and random contact occurs in the deformation process, affecting the output resistance value. The special structure gives it a large amount of extensibility, which means that it will produce complex deformation in the stretching cycle, resulting in irregular output resistance. The combined action of many factors makes the output signal of the accordion-like structure complex.

Figure 5. The dynamic response curve of flexible strain sensor with accordion-like structure.

3.2. Micro-mechanism of strain sensing behaviors

For the flexible strain sensor, the mechanism of the conductive property can be explained by the conductive network formed by CNTs on the surface TPU flexible substrate. With ultrasonic, some of the CNTs were embedded in the TPU substrate and some of them were exposed to the TPU substrate surface. The internal and external conductive networks of TPU were in parallel, which worked together to affect the sensing performance of the flexible strain sensor. The CNTs embedded in the TPU flexible substrate were interconnected to form a conductive network, which can be explained by the percolation theory. When the CNT content in TPU flexible substrate is small, the conductive network can not be formed in TPU; When the content of CNT in TPU flexible substrate exceeds the percolation threshold, CNTs contact and entangle with each other to form a conductive network. With the deformation of the TPU flexible substrate under tension, the CNT network inside will deform and be destroyed. With the increase of the deformation of TPU flexible substrate, the destruction of the CNT network will increase and more CNTs will come out of contact, increasing the resistance. In addition, there is also a tunneling effect between CNTs in TPU flexible substrate. When the distance
between CNTs is less than a certain value, electrons can pass through the ‘barrier’ to realize the electron transmission between two CNTs and form the conductive network.

4. Conclusion
FDM 3D-printed TPU flexible substrate with accordion-like structure and CNTs embedded into the surface layer of the flexible substrate with ultrasonic assistance was prove to be an effective and fast method for flexible strain sensor fabrication, which improved sensing performance and maintained the flexibility of the sensor at the same time. The flexible strain sensor was proved effective in the sensing performance. The strain sensing micro-mechanisms of the flexible sensors benefited from the conductive network disconnection mechanism and the tunneling effect. The CNTs, both in the TPU substrate and exposed to the surface, built the conductive paths and network to sensitively change the resistance of the negative Poisson’s structure during the stretching and restoring of sensors. In addition, the flexible sensor with an accordion-like structure was feasible in human health monitoring.

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