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BIO-INSPIRED 3D-PRINTED MICROSTRUCTURES FOR TOUGHENING BIO-BASED EPOXY MATRIX

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Abstract

Aiming to aid the sustainable transition to fossil fuel-free epoxy materials and enhance the toughness of bio-based epoxies, here we integrate an overlapping curl microstructure consisting of coiling fiber with sacrificial bonds and hidden lengths into a bio-based epoxy matrix. Inspired by natural material, where exceptional properties are achieved at low environmental cost, the microstructure mimics the molecular structures of spider silk, known for its exceptional fracture resistance. The 3D-printed overlapping curl shows a saw-tooth mechanical response with continuous load-carrying ability thanks to the break of sacrificial bonds and unfolding of the hidden lengths. By embedding the overlapping curl into the compact-tension configuration of the bio-based epoxy, an extrinsic toughening mechanism is triggered as the hidden length unfolds. Experimental results show that a single-sided overlapping curl structure is able to improve the toughness of bio-based epoxy by 19%.

1. Introduction

The demand for a sustainable transition in load-bearing structures in the mobility and energy sector, with low carbon emissions and high safety requirements, drives the need for the replacement of fossil fuel-based materials with bio-based materials. Despite being more sustainable, bio-based epoxies, for example, face strong limitations in engineering applications due to their low mechanical properties such as fracture resistance [1] when compared to their fossil fuel-based counterparts. Through evolution over millions of years, natural materials provide a wealth of sophisticated and hierarchical structures with high fracture resistance at low environmental costs, including spider silk, bone, and nacre [2,3,4]. One of the key features that contribute to the high fracture resistance of these biological materials is the presence of sacrificial bonds and hidden length (SBHL) in their organic structures. Upon stretching, the sacrificial bonds will first break and then the hidden length unfolds, providing a residual load and avoiding the sudden fracture.

Drawing inspiration from these biological structures, this work presents a bio-inspired microstructure named overlapping curl (OC) containing coiling fiber with sacrificial bonds and hidden lengths to mimic SBHL features to delay crack propagation in a bio-based epoxy matrix and improve its intrinsic fracture resistance. Fused filament fabrication 3D-printing was adopted to fabricate OC with polylactide (PLA) material and its mechanical behavior was first characterized through tensile tests. Subsequently, the OC structure was embedded into a bio-based epoxy and tested under Compact tension (CT) tests.

2. Experiments

2.1 3D-printing fabrication of overlapping curl

As shown in Figure 1, the overlapping curl structure containing coiling fibers with sacrificial bonds and hidden lengths was produced using a polylactic acid filament (PLA, ReFormTM – rPLA, Formfutura BV, Nijmegen, Netherlands) with a commercial Prusa i3++ 3D printer. The molten PLA material was firstly extruded from the printer nozzle at the temperature T . With the nozzle moving horizontally with the speed F , the extruded PLA filament coiled under the buckling effect [5] and then intersected itself. By controlling the printing parameters (nozzle height Z and filament extrusion E) to a specific ratio region, the coiling fibers with different curl sizes and orientations (single-sided and double-sided) can be fabricated and are listed in Table 1.

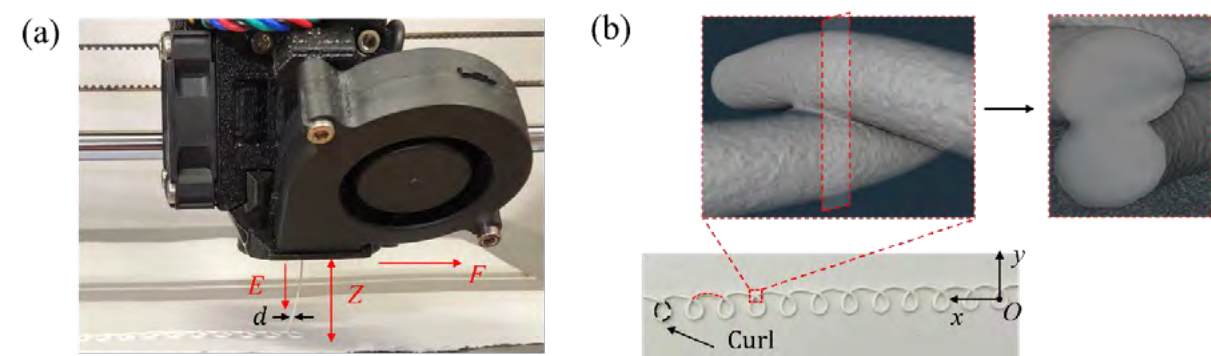


Figure 1. (a) The 3D-printing process and (b) the OC structure contains coiling fiber with sacrificial bonds and hidden lengths.

Table 1. 3D-printing parameters and structures of overlapping curl. T : temperature of the printer nozzle, F : nozzle horizontal speed, Z : nozzle height, and E : filament extrusion.

OC type	T (°C)	Z (mm)	F (mm/min)	E (mm/min)	Structures
Single_Z10	275	10	750	75	
Single_Z5	275	5	750	75	
Double_Z10	275	10	1000	60	
Double_Z5	275	5	1000	60	

2.2 Compact-tension sample manufacturing

A silicon mold was designed for manufacturing compact-tension (CT) samples with consistent geometry shapes, as shown in Figure 2. A two-component bio-based epoxy (SR GreenCast 160) was mixed at a mixing ratio of 1:0.42, before being placed into a vacuum chamber for degassing for around 1 hour. After that, the bio-based epoxy was poured into the mold with the overlapping curl (represented as the blue dashed line in Figure 2) embedded in the vertical direction regarding the crack path and cured for 7 days at room temperature. The thickness of the CT sample was controlled around 8 mm. The CT samples are designated as CT-pure and CT-OC without and with overlapping curl, respectively.

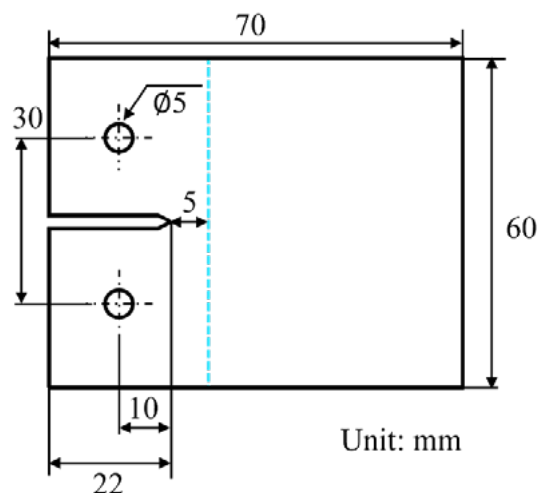


Figure 2. The geometry and dimensions of the CT specimen (thickness of 8 mm). The blue dashed line represents the position of the embedded overlapping curl structure.

2.3 Mechanical testing and characterization

The tensile test and compact-tension test using a universal Zwick loading frame were performed to obtain the corresponding mechanical response of the OC and CT samples. A 100 N load cell was used for loading OC under tensile at a speed of 5 mm/min. During the test, a high-resolution camera is used to capture the deformation process of the OC. Also, a mechanical extensometer is attached to measure the actual separation displacement. For CT tests, a 10 kN load cell is adopted and the tensile loading is applied at a rate of 2 mm/min. Besides, a high-resolution camera and a traveling microscope are set from both sides of CT samples to record the crack advance in the CT testing. The energy release rate (toughness) of the CT samples is obtained from the following equation (Eq. 1) [6],

$$G_I = \frac{P^2}{2t} \frac{dC}{da} \quad (1)$$

Where P is the load, t is the thickness of the sample, C is the fitted compliance of the load-displacement curve, and a is the crack length.

3 Results and discussions

3.1 Overlapping curl mechanical response

Figure 3 shows the representative mechanical response and deformation process of OC under the uniaxial tensile test. With the displacement extension, the load increases until the first sacrificial bond breaks (i) and a load drop happens accordingly. As the curl unfolds (ii), the load rises again reaching the

force limit of the next sacrificial bond (iii). This process continues after all the sacrificial bonds break and a subsequent final failure of the straightened OC (v). This feature leads to the typical saw-tooth curve of the OC structure.

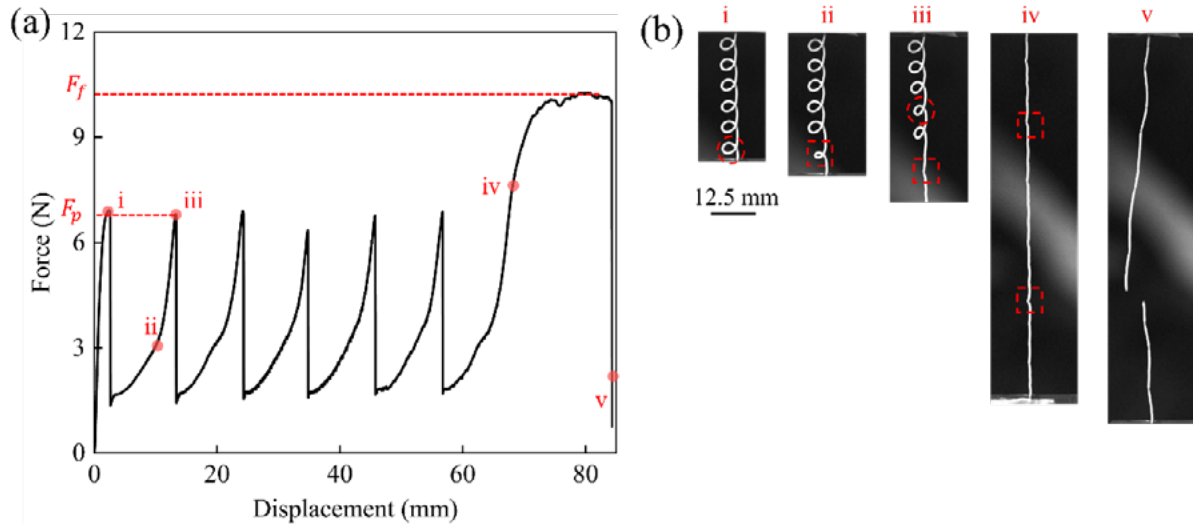


Figure 3. (a) The representative saw-tooth mechanical response curve of Single_Z10 OC and (b) the corresponding deformation process. The red dashed ellipse indicates the broken sacrificial bond and the red dashed rectangle outlines the remaining hidden lengths.

From the load-displacement curves of OC in Figure 4(a), the single-sided overlapping curl structures (Single_Z10 and Single_Z5) show full extension, i.e., all the sacrificial bonds break and hidden lengths unfold. There is also some necking of the filament before the final failure as seen in the final plateau in the load-displacement curve. For the double-sided overlapping curls (Double_Z10 and Double_Z5), they break early, the hidden length is not fully unfolded, and the extension is truncated. To better characterize the mechanical parameters, the sacrificial bonds peak force F_p and failure force F_f of OC, as defined in Figure 3(a), are compared.

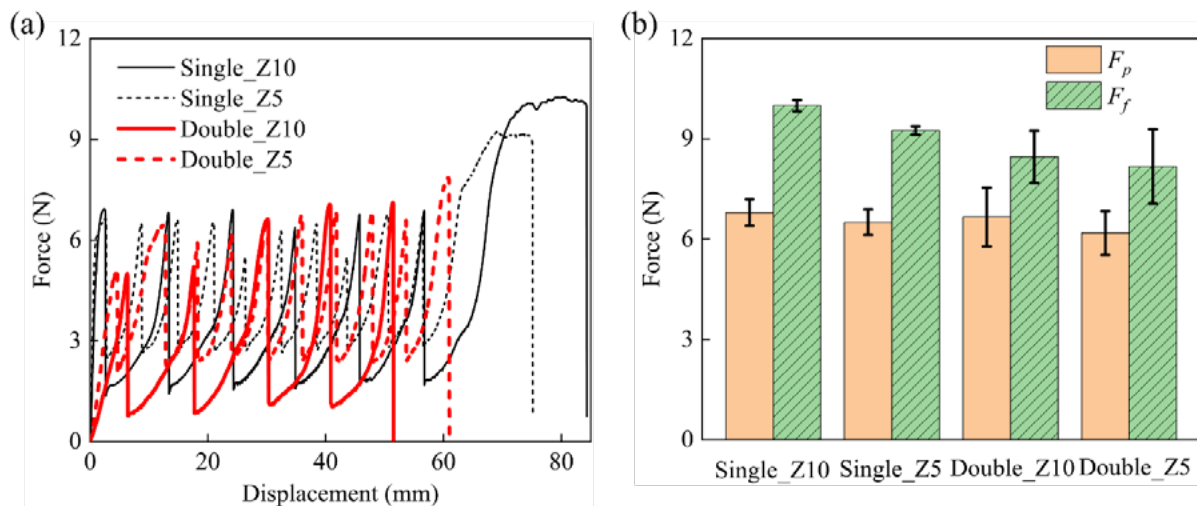


Figure 4. (a) The representative load-displacement curves of the four coiling fiber patterns. (b) The averaged sacrificial bonds peak force F_p and failure force F_f of the coiling fibers.

The average values and standard deviations of F_p and F_f values are shown in Figure 4(b). It can be observed that the F_p values are similar across the four types of structure, while the F_f varies. Both single and double Z5 structures show smaller F_f than their Z10 counterparts. This may be due to the smaller curl size of the Z5 overlapping curl, possibly resulting in more stress concentration while unfolding, causing an early failure and hence lower F_f when compared to Z10. Furthermore, the double-sided structures show lower F_f than the single-sided structures, which may also relate to the higher stress concentration in the double structure since during the manufacturing process, the extruded filament shifts the orientation direction [7].

3.2 Compact-tension test results

To study the effect of the integrated structure on the toughness of bio-based epoxy, CT samples with and without overlapping curl were tested. Figure 5(a) shows the representative load-displacement curves (the load is normalized by the sample thickness). Six typical points in the curve are picked to analyze the OC/epoxy interaction during fracture. Immediately after reaching the peak load, the load decreases faster in the sample with the OC (CT-OC) than without the OC (CT-pure). At point 2 of the CT-OC, the slope in the load-displacement curve changes as the OC starts to affect the crack advance. In Figure 5(b), the delay in crack advance is unnoticeable around point 2 but becomes evident starting from point 3. Figure 5(c) shows the toughness values vs crack length, from point 3 until point 6. An average of 19% toughness improvement is observed. In Figure 6 the fracture process is captured to help illustrate the extrinsic toughening mechanism. Based on Figure 6 - point 2, it can be observed that there is already a gap between the coiling fiber and the epoxy (indicated by the red arrow) indicating that at this point the sacrificial bond has already broken and the hidden length started to unfold. From this point onwards, the OC is believed to start affecting the crack propagation. When the crack tip reaches the position of the overlapping curl (point 3), the hidden length unfolds further, posing a residual load behind the crack tip which delays the crack propagation. The curl completely unfolds at point 4 and breaks at the crack advance of 23mm (point 6). It is also observed an epoxy ligament (highlighted by the red ellipse in Figure 6 - point 6) is also triggered, possibly delaying the crack propagation, and enhancing further the toughness values.

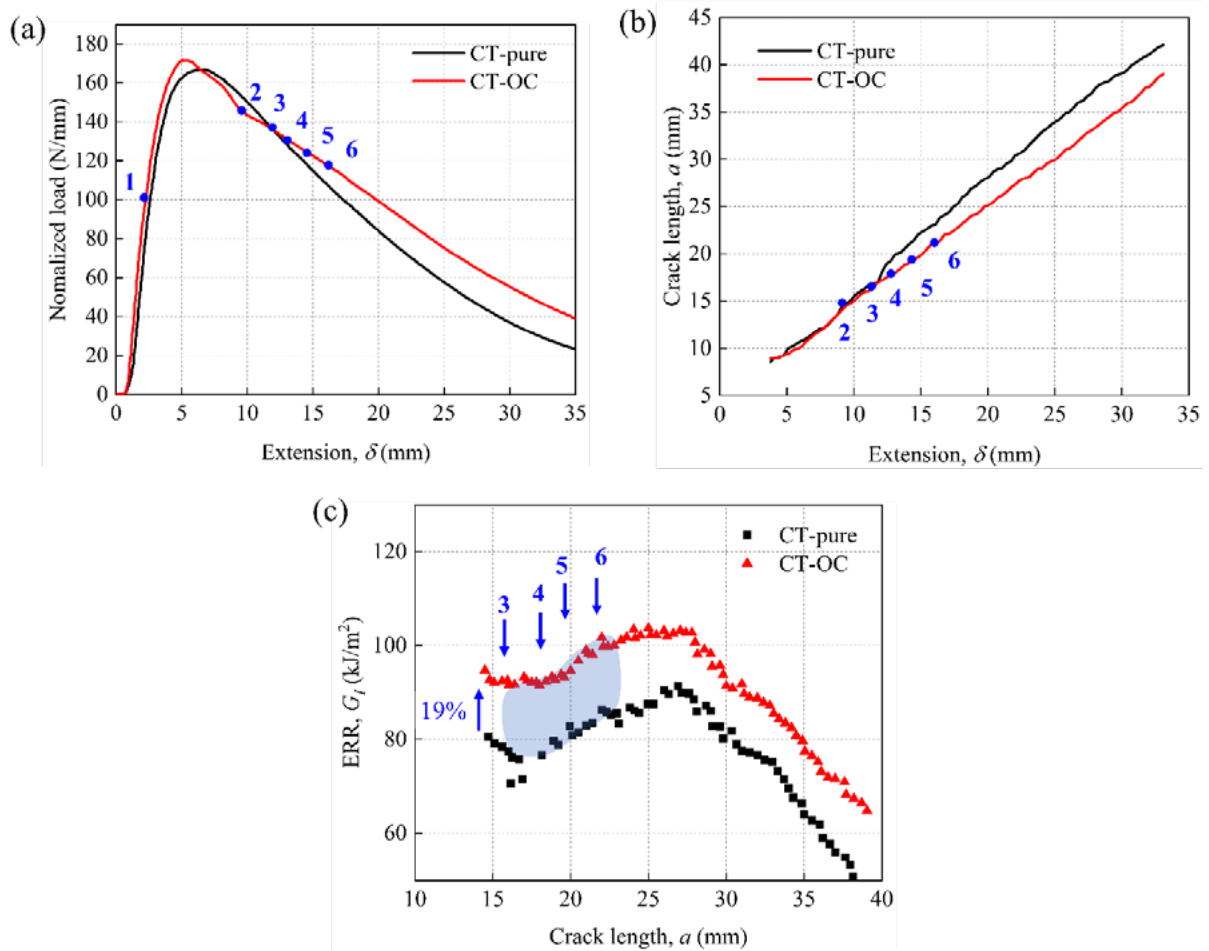


Figure 5. (a) Typical load-displacement curves of CT-pure and CT-OC samples. The load is normalized by the sample thickness. (b) Crack length vs extension curve, and (c) toughness R curve.

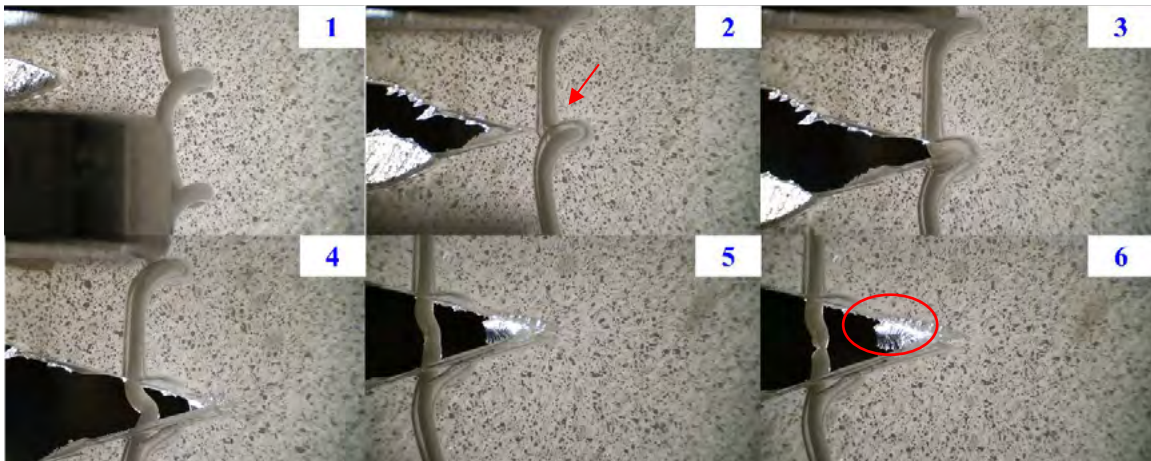


Figure 6. Snapshots during crack propagation of CT-OC sample. The red arrow indicates the gap between the coiling fiber and epoxy. The red ellipse highlights the epoxy ligament.

4. Conclusions

A bio-based epoxy reinforced with a spider silk-inspired overlapping curl consisting of coiling fiber with sacrificial bonds and hidden lengths was designed and tested. The 3D-printed overlapping curl alone shows the typical saw-tooth curve attributed to the break of the sacrificial bonds and unfolding of the hidden lengths. The single-sided overlapping curl structure shows longer extensions than the double-sided ones. Compact tension test of the single-sided overlapping curl structures embedded in the bio-based epoxy shows an average 19% toughness increase when compared to pure bio-based epoxy. As the crack crosses the coiling fibers, and the hidden length unfolds, it is expected that a reinforced load is applied to the crack path delaying crack propagation and contributing to the mechanical performance increase.

Acknowledgments

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