Rapid Communication

Chiral graded structures in biological plywoods and in the beetle cuticle

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ABSTRACT

Biological chiral fibrous composites, known as biological plywoods, found throughout nature including the exoskeletons of insects and plant cell walls have optimized structural and functional properties, such as the iridescent colors observed in beetle cuticles. In many cases the micron-range chirality of the fibrous ordering is usually spatially graded, multi-periodic or layered as opposed to uniform. The challenge to discover structure–property relations in biological plywoods relies on the accuracy of determining the usually space-dependent chiral pitch of the plywoods. Here we use a recently developed geometric model and computational visualization tool to determine the complex spatial gradients present in beetle cuticle which is a canonical example of graded biological plywoods, extensively studied using optical methods. The proposed computational structural characterization procedure offers a complementary tool to optical and other experimental measurements. The new procedure has wide application in biological material characterization and in biomimetic engineering of structural and functional materials.

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Biological materials are distinguished by hierarchical structures, multi-functionality and self-assembly, which are attributes of liquid crystals and unsurprisingly mesophase organization is then found throughout nature with building blocks like collagen, and chitin [1–4]. Biological plywoods (BPs) are recognized as solid liquid crystal analogues formed through an efficient entropy-driven self-assembly process [1,4–6]. Bouligand was the first who successfully described these materials with the twisted plywood architecture model (TPA) [7] in which fibrils are arranged as in a chiral nematic liquid crystal, presenting an average orientation of fibrils that change orthogonally to the fibril orientation; the micron-range distance required for a full (2π) rotation is known as the pitch p_o, whose sign (+ or -) represents the handedness of the helical axis (**h**); see Fig. 1. TPAs include: i) ideal plywoods with constant pitch ($p_0 = const$) and helix axis, and ii) non-ideal TPAs with pitch gradients ($p_0(z)$). Non-idealities are due to specific cellular processes [7] and a response to external stimuli such as the pH dependence of the self-assembly process observed in collagen [8,9] with structures that range from ideal TPA to orthogonal plywoods, with abrupt changes of 90° in the fibril orientation on adjacent planes [10]. Other ubiquitous non-idealities such as defects and gradients in both **h** and p_o arise during the plywood self-assembly in the presence of secondary phases [11] which result in poly-domain helicoids [12,13].

In this paper we focus on non-idealities arising from spatial pitch variations ($dp_0(z)/dz \neq 0$) in beetle cuticles ('aurigans scarab') [14],

where the chiral arrangement results in color iridescence [15] and possible thermal regulation [16]; color iridescence due to surface wrinkling is discussed elsewhere [17,18]. This cuticle can be classified as a graded plywood with pitch gradients in **h** direction. For ideal BPs, oblique incisions lead to the ubiquitous arced patterns with identical arcs throughout the incision plane as a result of the homogeneity in both **h** and p_o observed by Bouligand in crab cuticles [7], whereas for non-ideal plywood arcs with varying periodicity can be observed in the incision plane due to the pitch variation. The reconstruction of the 3D structure out of 2D observations is a classical inverse problem, and the well-known challenges are due to unavoidable ill-conditioning (small changes in input lead to large changes in output) and solution multiplicity in structure reconstruction.

A method for characterizing ideal plywoods that essentially overcomes these challenges has been reported recently [19] for ideal plywoods using geometric modeling and computational tools, which is extended here to a representative graded plywood of the 'aurigans scarab' cuticle. These new tools do not rely on optics as the Cano–Grandjean defect disclination line method or the Bragg reflection, methods that are known to be limited by its range of applicability and/or its accuracy [20,21], hence the geometric modeling and computational procedure can complement experimental techniques, leading to a more robust characterization of the ubiquitous chiral structure.

The objective of this communication is to describe a methodology capable of reconstructing the 3D structure of a graded plywood ($p_o(z)$) of 'aurigans scarab' as a canonical example of a complex biological plywood. In this paper the experimentally determined non-monotonic spatial pitch variations in the beetle cuticle [14] are used to

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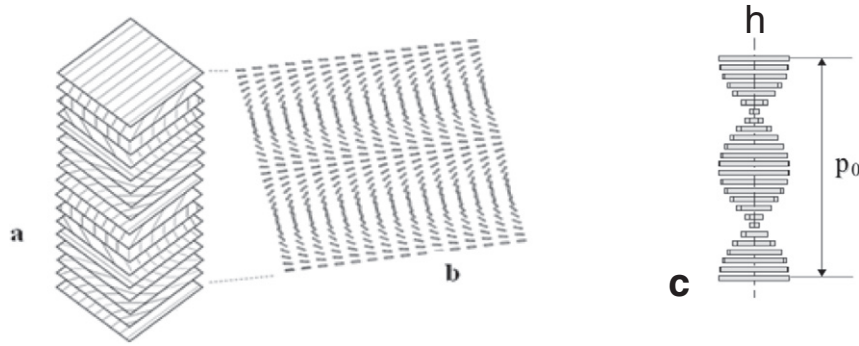
Fig. 1. (a–b) Schematics of the ideal biological plywoods. Oblique sections (b) give rise to the characteristic arced patterns. (c) Normal view schematic of the helical axis, defined by the helix orientation **h** and the pitch p_o.

construct arbitrary in silico arced patterns, since no experimental arced patterns are accessible, and then each of these sections are used to perform 3D chiral reconstructions. When slicing a plywood at an arbitrary incision angle (α), we obtain a 2D layered arced patterns of period L, and each arc is characterized by a maximum curvature κ_{max}. We introduce a novel geometry–chirality phase diagram and demonstrate that in this diagram a set of (L, κ_{max}) values found experimentally leads to one and only one value of the pitch regardless the incision angle α. The key aspect of our method is that when the 2D patterns are space dependent ($L(z)$, $\kappa_{max}(z)$), the predicted chirality from our model is also space dependent, $p_o(z)$. Finally we prove that the accuracy of the 3D reconstruction methodology decreases with α.

The analytical description of biological plywoods are obtained through the geometric modeling previously published [19] is summarized as follows: the trajectories of the arced patterns are a function of α and p_o (implicitly a function of the periodicity of the arcs "L"), leading to a system with one degree of freedom with multiple solutions. To eliminate this degree of freedom, the curvature κ of the arcs, which is a function of α and L, is introduced. By measuring the curvature of the experimentally observed arcs and fitting the analytical expression one can obtain the incision angle α and finally the pitch p_o with a straightforward calculation. The equations for the arced patterns and the curvature within each layer are [19]:

$$\frac{dx}{ds} = \frac{\cot\left[\frac{2\pi(\sin\alpha)s}{p_0}\right]}{\cos\alpha} \tag{1}$$

$$\kappa(s,\alpha,L) = \frac{-\csc^2\left(\frac{\pi s}{L}\right)}{\cos\alpha\left\{1 + \left(\cot\left(\frac{\pi s}{L}\right)/\cos\alpha\right)^2\right\}^{3/2}}, \quad L = \frac{p_0}{2\sin\alpha}. \tag{2a, b}$$

For graded plywoods as the beetle's plywood, the maximum curvature on a given layer is:

$$\kappa_{max} = \frac{\pi}{L\cos\alpha}. \tag{3}$$

Combining the maximum curvature κ_{max} and the 2D periodicity of the arcs L, leads to the following equation that represents the phase diagram in terms of L and κ_{max}:

$$\left(\frac{2}{p_0}\right)^2 L^2 - \left(\frac{2\pi}{p_0}\right)^2 \frac{1}{\kappa_{max}^2} = 1. \tag{4}$$

Eq. (4) is a family of hyperbolas for different values of p_o, shown in Fig. 2. The negative values for curvature indicate a shift in the

handedness of the helical axis. Considering one of the hyperbolas for constant pitch, there are an infinite number of combinations of periodicity and inverse of curvature leading to that precise value of pitch. However, there is one and only one value of the pitch that intercepts both axis of the phase plane for a particular value of α as established in Eqs. (3) and (4). The phase diagram (Fig. 2) shows several hyperbolas for different values of p_o, and the straight lines from Eq. (3) show that for a given α there is only one combination of curvature κ_{max} and 2D periodicity L intercepting these lines. The two limiting lines correspond to $\alpha = 0°$ and $\alpha = 90°$, corresponding to cuts normal and parallel to the helix. We note that as the helix vector **h** is usually unknown a priori, finding α through Eq. (3) is a crucial step. Small α angles lead to ill-conditioning as the hyperbolas essentially asymptotes the lines. The practical implementation to determine $p_o(z)$ using the phase diagram (Fig. 2) is as follows: (1) perform the experimental sectioning of the BP, (2) determine (L, κ_{max}) in a given layer of the 2D arc patterns, (3) use (L, κ_{max}) to determine from the phase diagram (Fig. 2) $p_o(z)$ and α for the given layer, (4) repeat procedure for all layers, and (5) finally obtain $p_o(z)$ spatial profile. This procedure is schematically depicted in Fig. 3. The stars shown in such figure indicate only one interception of L, κ_{max} per each α leading to only one value of p_o.

As mentioned, the arced patterns for the beetle cuticle were created using the 3D visualization tool Mayavi, by first introducing the cholesteric director field and then creating an incision plane with the VectorCutPlane module, and using the experimental information of Libby et al. [14] for aurigans scarab, showing the spatial variation of
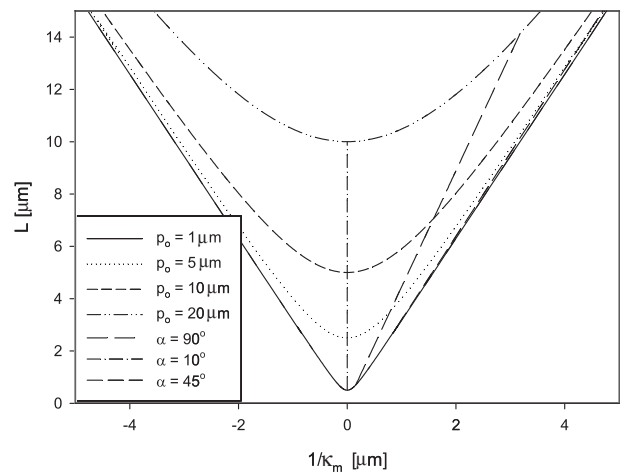
Fig. 2. Chirality phase diagram in terms of L and arc's reciprocal maximum curvature κ_{max} for several values of pitch. The hyperbolas are from Eq. (4) and the lines from Eq. (3). Performing a section of a real plywoods yield L, κ_{max} and the plot gives p_o, and α.