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LETTER

Fracture of *Ensis siliqua* mollusk shell reveals multiple delaminations as a potential defence and toughening mechanism

David J. Scurr · Stephen J. Eichhorn

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Shells display remarkable mechanical properties, particularly their ability to direct crack-growth along boundaries between the calcium carbonate crystals they comprise. This crack deflection acts as a defence mechanism against attack from predators. Some shells, such as *Ensis siliqua*, are dominated by prismatic layers, a particular microstructural arrangement of calcium carbonate. These layers give the shell a laminated structure, allowing it to resist bending, but also to act as regions that promote delamination. This short communication shows that judicious placement of many prismatic layers close to the innerside of the shell, where the mollusk resides, gives rise to multiple delaminations of shell material. Sections of *Ensis siliqua* shell are bent in an electron microscope, mimicking the action of an attack by a crab or other predator. It is shown that many cracks form close to the innerside of the shell. Images of these cracks are taken during the deformation process within the electron microscope and later processed to determine work of fracture. Delaminations are shown to significantly increase fracture resistance compared to values obtained for non-biogenic aragonite. These mechanisms are discussed with reference to predation, but also in relation to designing materials that could exploit this property.

S. J. Eichhorn (✉)
School of Materials and the Northwest Composites Centre
Sackville Street, University of Manchester,
Manchester M1 7HS, UK
e-mail: s.j.eichhorn@manchester.ac.uk

Present Address:
D. J. Scurr
School of Pharmacy, The University of Nottingham,
University Park, Nottingham NG7 2RD, UK

There are a number of microstructural forms that shells can take, the most common of which are the nacreous, prismatic and crossed lamellar types [1]. Considerable work has been conducted on the fracture properties of the nacreous form of shells [2–6], and on crossed lamellar shell structures [2, 7–10]. The crossed lamellar structure has been termed a 'plywood-like' ceramic [11, 12] due to its complex structure comprising a series of sub-layers within each ply. Calcium carbonate, which is the main component of the shell, is ordered hierarchically at many different levels or lamellae (Fig. 1a). This makes it hard for cracks to propagate through the structure, being deviated in a tortuous path along many interfaces. Multiple microcracking has been identified in such structures as a form of toughening mechanism [8], but extensive delamination has never been previously reported for shell material.

Some shell structures, such as *Ensis siliqua* (more commonly known as razor shells) contain prismatic layers, which intersperse the main cross lamellar region forming a laminated structure. It has been shown that these prismatic layers contain residual compressive strain [13, 14] using an X-ray diffraction method developed by Zolotoyabko and Quintana [15–18]. These residual compressive strains have been shown to be capable of redirecting crack growth along the boundaries between the laminations in razor shells [13, 14]. Damage to the shell can be caused from the repeated retrieval and escape from commercial dredging activities, or from attacks from predatory crabs such as *Carcinus maenas*, as reported by Robinson and Richardson [19]. In this study the authors show how cracks propagate in a cross-section of a razor shell during an in situ three-point bending test performed in an electron microscope. It is shown that delaminations of the structure occur, and that these occur most frequently close to where the mollusk resides inside the shell. The geometric placement of many

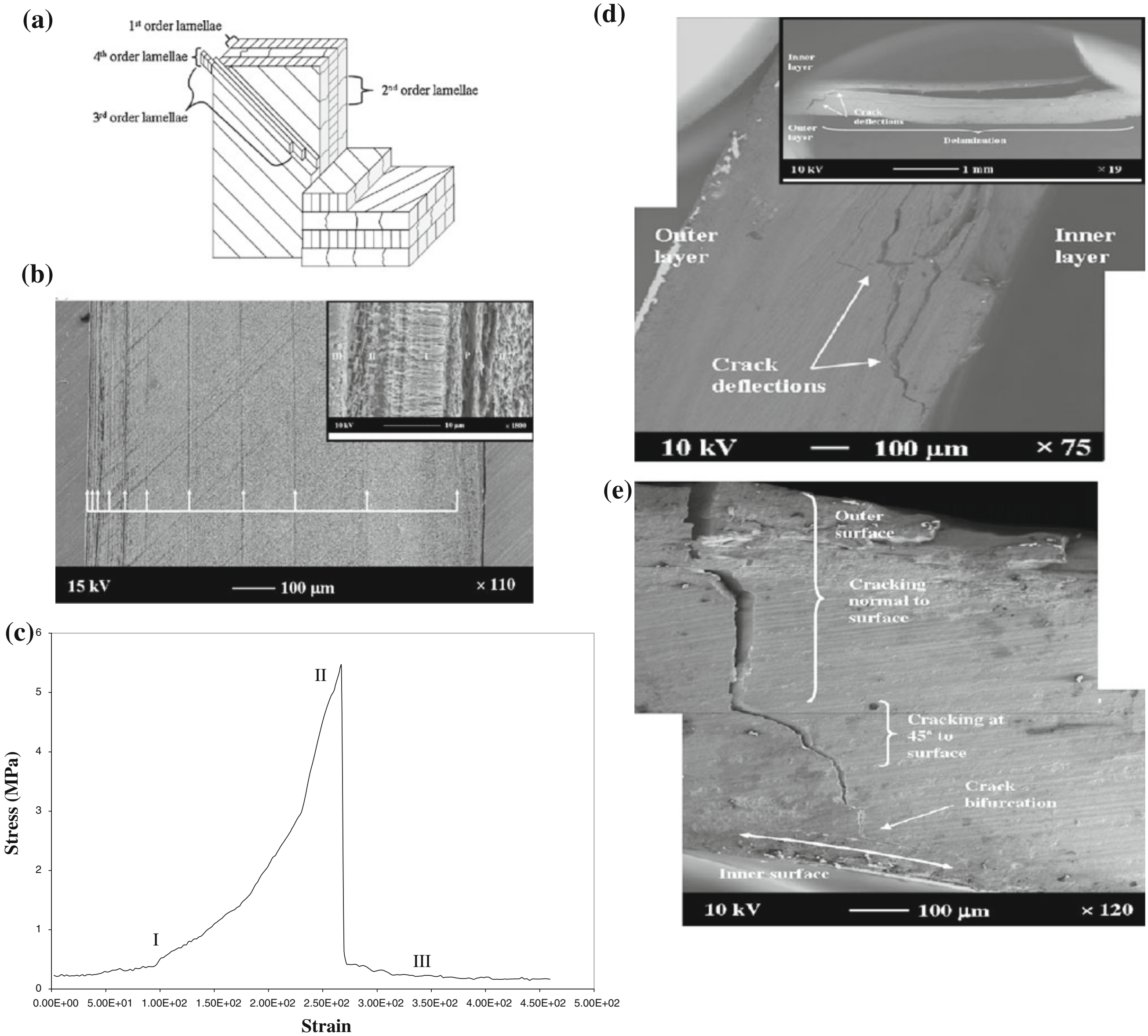

Fig. 1 **a** Schematic showing a crossed lamellar structure with several orders of lamellae. **b** An SEM image of the cross-section of *Ensis siliqua* shell indicating the presence of prismatic layers (*white arrows*) and the *inset* showing a magnified image of a prismatic layer (I), surrounding crossed lammelar material (II), epoxy resin used to mount sample (III) and pitting (P) caused by chemical etching. **c** A typical stress–strain curve for a shell specimen tested in three-point bending where (I) is the initial part of the trace where cracks are initiated close to the innerside of the shell (II) is the point of maximum load where the sample fails and (III) is the form of the trace after the specimen has failed. **d** An in situ SEM image of a typical fracture in *Ensis siliqua* shell specimen subjected to three-point bending showing the presence of crack deflections close to the inner surface of the shell, and in the inset a lower magnification image of the formation of a large delaminated fragment of shell material is shown. The crack was initiated from the inner surface of the shell. **e** An in situ SEM image of a typical fracture in *Ensis siliqua* shell specimen subjected to three-point bending, propagating a crack from the outer surface of the shell towards the inner surface

prismatic layers close to the innerside of the shell is discussed in terms of the shells resistance to crack growth and therefore protection against predators.

Samples of razor shells (*Ensis siliqua* shell) were collected from a beach located at Lytham St Annes, UK in September 2003. Sections were cut from regions close to the anterior dorsal corner (near the hinge of the shell) of the shells using a hand-held diamond cutting wheel. This region of the shell was chosen as it does not have pronounced growth rings, and is also thicker than other regions, which allows samples to be more easily machined without introducing defects. Samples were cut across the shell thickness into sections with dimensions $15 \times 5 \times 0.75$ mm^3. The span to depth ratio was therefore 20, which

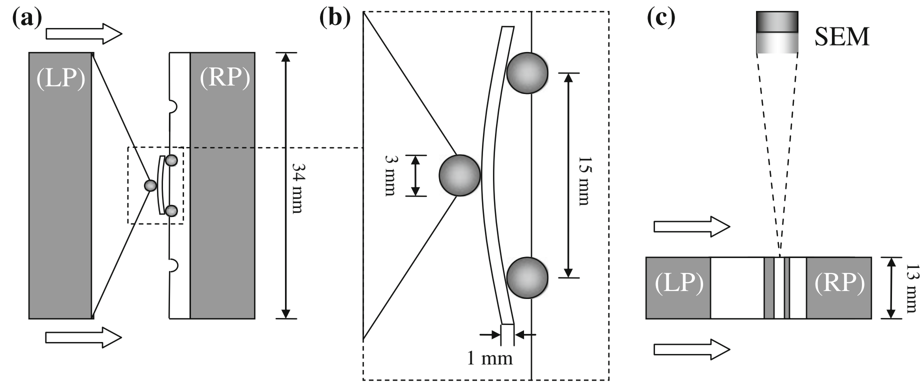

Fig. 2 **a** The *left* (LP) and *right* (RP) platens of the mechanical testing device used to apply three-point bending to the shell specimens, **b** a close up of the geometry of the three-point bending tests and **c** a schematic of the in situ SEM performed on the shell. *Arrows* indicate the loading direction

is above the limit of 15 recommended by Jackson et al. [4] for nacreous shells.

The shell specimens were tested in three-point bending using a DEBEN microtest bending stage with a 2 kN load cell, as shown in Fig. 2a and b. The specimens were loaded continuously in the direction indicated in Fig. 2a and c. All samples were imaged during deformation in a JEOL 6300 Scanning electron microscope (SEM) with an aperture size of 50 μm (Fig. 2c). All electron micrographs were taken using a scan time of 60 s. At the onset of obvious cracking events the load was held, and an image was acquired. For imaging purposes all samples were gold coated. It is acknowledged that this process could change the fracture properties of the shell, and cracking of the gold can be confused with a mechanical event. The cracks that appeared in the shell specimens were, however, sufficiently large, and exposed inner-shell material, as distinct from a crack forming in the gold coating. The mechanical data obtained for the gold-coated samples was also found to be consistent with values obtained for samples tested outside the SEM chamber.

A typical SEM image of a cross-section of a razor shell is shown in Fig. 1b. It is clear that laminations occur periodically through the structure, concurrent with the presence of a prismatic layer. These laminations are most concentrated close to the shell's inner surface, and the prismatic layers that define their boundaries are approximately 5 μm in thickness (see SEM image in the inset of Fig. 1b). Further away from the inner surface the location of prismatic layers becomes more spread out which generates a core laminate-like structure which can resist bending. A typical stress–strain curve for a three-point bending test performed on a section of shell material within the electron microscope is shown in Fig. 1c. It can be seen that the stress increases monotonically up to failure at approximately 5.5 MPa. The initial part of the stress-strain curve (labeled (I) in Fig. 1c) is typified by a gradual increase in load, interrupted by small drops. A typical image of the shell material, taken from a cross-section under in situ loading is shown in Fig. 1d. It can be seen from this image that a crack has propagated from one side of the sample to the other via a convoluted pathway. The crack is initiated on the innerside of the shell in order to mimic the action of a crushing attack by a predator. The crack initially propagates for a short distance perpendicular to the inner plane of the shell, but is then soon deflected parallel to this plane, possibly by prismatic layers. This deflection, parallel to the inner plane of the shell occurs many times proximal to this plane and is thought to be the cause of the form of the data in the initial part of the stress-strain curve. The crack then continues into the central region of the shell at a 45° angle to the inner plane of the shell. During this point the load increases up to the failure point of the shell material (label (II) in Fig. 1c). These initial crack deflections are thought to dissipate energy. The presence of many prismatic layers close to the innerside of the shell (see Fig. 1b) prevents catastrophic failure of the material. Large delaminations of shell material often occurred during bending tests (see inset of Fig. 1d). The integrity of the shell was always maintained, even when sections of about 4 mm in length were delaminated from the shell. Tests were also performed using the opposite geometry, where cracks were propagated from the outer surface of the shell, towards the inner surface, where the high density of prismatic layers occurs. An image of the path of a typical crack obtained using this set-up is shown in Fig. 1e. The crack is noted to pass through the bulk of the material, with little crack deviation (some 45° deviation is noted), and is only arrested close to the inner face at the prismatic layers. This is clear evidence of the role of prismatic layers in deviating cracks in the structure, leading to delamination.

Little information is available on the predation of the *Ensis siliqua* mollusk, with only one report showing the effects of crab attacks on population [19]. Suction dredging of sands by machinery is the main process by which *Ensis* mollusks are reported to become vulnerable to attack by crabs [19]. This form of dredging is the main technique used for harvesting bivalves. The forces experienced during a crab attack are likely to be large; about 800 N has been reported by Vermeij [20]. This is clearly much higher than would be required to fracture a shell. It maybe then that the mollusk is designed to resist predation by species other than crabs, although this hypothesis has not been tested. The structure of the shell could also have evolved to resist bending and cracking due to the suction forces imposed on the shell during heavy dredging. Again, this hypothesis would require further investigation.

The work of fracture of the shell material (W_f) has been determined using the equation $W_f = E_d/S_a$, where E_d is the total energy dissipated, or the area under the load–displacement curve (= load × displacement), and S_a is the fracture surface area. This assumes that all energy is consumed by the generation of cracks. In order to calculate W_f the crack contour length was determined and multiplied by the specimen width. To determine S_a, convoluted crack lengths were measured using calibrated SEM images. The crack pathway was then traced and measured. The crack path lengths were then multiplied by the sample width to determine the surface area parameter (S_a).

For a crack passing straight through the structure, without impediment and deflection, a much lower value of W_f would be obtained. Therefore, more energy is required to drive a crack through a convoluted pathway, and the shell material is in effect toughened by the presence of delaminations. A value of 0.09 ± 0.02 kJ m^{-2} ($n = 5$) was obtained for the work of fracture of the shell samples, which is several orders of magnitude higher than a reported value of 0.6×10^{-3} kJ m^{-2} for non-biogenic aragonite [4, 6] but two orders of magnitude lower than a value of 4 kJ m^{-2} for *Strombus gigas* shell material [2]. The fact that the work of fracture for the razor shells is much higher than non-biogenic aragonite is attributed to the presence of large delaminations arising from deviations of the crack along prismatic layers during deformation. This material has a lower fracture resistance than *Strombus gigas* shell due to the fact that it has a much thinner cross-section and may also comprise a slightly different microstructure. The placement of many laminations close to the inside of the shell serves to dissipate energy during the early stages of fracture, and therefore increases the resistance of the mollusk to attack from a predator. It is known that when mollusks repair their shells, they often lay down prismatic layers [21]. It is proposed then that prismatic layers could be used as a line of defence against predation.

The approach of placing multiple delaminations close to the surface of an engineering material is an interesting approach to enhance fracture resistance at the expense of surface damage. It could be used as a strategy for a number of fracture resistant materials, including body armour and composites.

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