



Multiscale structure and damage tolerance of coconut shells

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ABSTRACT

We investigated the endocarp of the fruit of *Cocos nucifera* (i.e., the inner coconut shell), examining the structure across multiple length scales through advanced characterization techniques and *in situ* testing of mechanical properties. Like many biological materials, the coconut shell possesses a hierarchical structure with distinct features at different length scales that depend on orientation and age. Aged coconut was found to have a significantly stronger (ultimate tensile strength, UTS = 48.5 MPa), stiffer (Young's modulus, $E = 1.92$ GPa), and tougher (fracture resistance (R -curve) peak of $K_{IC} = 3.2$ MPa m^{1/2}) endocarp than the younger fruit for loading in the latitudinal orientation. While the mechanical properties of coconut shell were observed to improve with age, they also become more anisotropic: the young coconut shell had the same strength (17 MPa) and modulus (0.64 GPa) values and similar R -curves for both longitudinal and latitudinal loading configurations, whereas the old coconut had 82% higher strength for loading in the latitudinal orientation, and > 50% higher crack growth toughness for cracking on the latitudinal plane. Structural aspects affecting the mechanical properties across multiple length scales with aging were identified as improved load transfer to the cellulose crystalline nanostructure (identified by synchrotron x-ray diffraction) and sclerification of the endocarp, the latter of which included closing of the cell lumens and lignification of the cell walls. The structural changes gave a denser and mechanically superior micro and nanostructure to the old coconut shell. Additionally, the development of anisotropy was attributed to the formation of an anisotropic open channel structure throughout the shell of the old coconut that affected both crack initiation during uniaxial tensile tests and the toughening mechanisms of crack trapping and deflection during crack propagation.

1. Introduction

The image of a coconut fruit falling from a tree onto the cranium of an unsuspecting individual below represents a classic trope, but not a baseless one, as the lethality of such incidents is well documented (Barss, 1984; Mulford et al., 2001). The fruit's capability to inflict fatal blows is particularly remarkable considering the well-known toughness of human bone, one of the most damage tolerant biological materials (Koester et al., 2008). While the structure and mechanical properties of human cranial bone (Coats and Margulies, 2006; McElhaney et al., 1970; Motherway et al., 2009) and the biomechanics of human skull fracture (Delye et al., 2007; Yoganandan et al., 1995) have been extensively studied, much less is known of its similarly spherical adversary. Bone and many other biological materials have been found to possess multiscale hierarchical architectures that not only provide toughness and protection for the host species (Imbeni et al., 2005;

Kruzic et al., 2003; Meyers et al., 2008; Naleway et al., 2016; Nalla et al., 2003; Nalla et al., 2005; Yang et al., 2015; Zimmermann et al., 2013; Zimmermann et al., 2011), but also inspire the design of next generation materials (Meyers et al., 2011; Meyers et al., 2013; Munch et al., 2008; Naleway et al., 2015; Wegst et al., 2015). In contrast, very few secrets of the coconut structure and mechanical properties have been similarly revealed.

The coconut is the fruit of the coconut tree, a drupe containing prized flesh and water (endosperm) protected by three distinct sections: the skin-like outermost exocarp, the thick fibrous mesocarp, and the hard inner endocarp. While the former two sections comprise a thick but soft husk of fibers (coir) encased in the thin and relatively weak skin of the exocarp, in the present work we are interested in the globular endocarp, which is the hard, woody shell that provides the core structure and protection of the seed, and which is known to consist of cellulose, hemi-cellulose, and lignen with small amounts of pectin and

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proteins (Dardick and Callahan, 2014).

The biomechanical function of the coconut is to resist impact upon falling from the tree, to retain the coconut milk for the seedling, and to impede opening by humans or animals without modern tools. These joint purposes require a combination of strength and toughness that, as in many natural materials limited to biologically available constituents (such as fish scales, bones, etc.), is accomplished through aforementioned multiscale hierarchical architectures providing both intrinsic and extrinsic fracture resistance mechanisms (Ritchie, 2011; Zimmermann et al., 2015). Strength typically originates from small length scales (sub-micrometer) in the hierarchical structure, where organic polymers or proteins (e.g., collagen, cellulose, keratin) assemble into fibrils. These small length-scale structures generate strength and resist plasticity through intrinsic mechanisms, such as stretching and sliding (Zimmermann et al., 2011; Zimmermann et al., 2013). Toughness is largely derived from larger length scales (e.g., osteons in bones, graded interfaces in fish scales) that resist propagation of a crack through extrinsic toughening mechanisms, such as crack bridging and crack deflection (Koester et al., 2008; Nalla et al., 2003; Nalla et al., 2005).

In industry, the mechanical potential of coconut has been recognized in the context of structural composites, particularly for application of its fibers as a cheap, environmentally friendly matrix reinforcement for polymers (Harish et al., 2009; Justiz-Smith et al., 2008; Monteiro et al., 2008), and even concrete (Ali et al., 2012; Gunasekaran et al., 2011; Ramli et al., 2013). However, the fibers examined in these cases constitute only the weaker, outer layer of the fruit's protection. Similar to the work on coconut coir reinforced composites, some researchers have examined using ground up particulates of the shell as a natural filler to reinforce polymer matrices (Bledzki et al., 2010; Chun et al., 2013; Pradhan et al., 2004; Sarki et al., 2011). However, it is expected that by grinding the shell into a fine powder any potential benefits of multiscale toughening mechanisms from complex and hierarchical microstructures seen in most biological materials would be lost. Furthermore, studies of the coconut shell microstructure are highly limited and have been motivated by understanding the potential of the shell as a precursor for activated carbon for water filtration rather than its mechanical potential (Achaw and Afrane, 2008).

Coconuts are known to change dramatically with age (Fig. 1), exhibiting reductions in exocarp, deposition of endosperm, and possible changes within the shell. Hardening of the endocarp is a common feature of all drupes and it is thought to be associated with secondary cell wall formation and lignification; however, the details of this process have not been studied in detail (Dardick and Callahan, 2014). Overall, both age and orientation are seen as important parameters affecting the mechanical properties of biological materials. *In vivo* biological structures tend to exhibit anisotropic properties that are well adapted to the surrounding mechanical environment (Currey, 1999, 2003), and various properties can evolve differently over the lifetime of the organism. For instance, while human bone strength and toughness are both highly anisotropic properties (Nalla et al., 2003; Reilly and Burstein, 1975), they do not trend the same with age. Indeed, human bone strength increases during skeletal growth and maturation up to approximately the age of 30 years, after which bone strength degrades over the rest of the owner's lifetime (Currey and Butler, 1975; Martin and Atkinson, 1977). In contrast, human bone toughness appears to degrade continuously with aging. (Currey, 1979; Currey and Butler, 1975; Nalla et al., 2006; Nalla et al., 2004; Zioupos and Currey, 1998).

Coconut shells have interesting biomechanical functions and potential industrial applications. However, to the authors' knowledge, there have been no studies to date to understand the relationship between the shell's multiscale structure and its underlying mechanical properties, and how those properties are influenced by orientation and age. Accordingly, the present work examines the effects of age and orientation on the tensile strength and fracture toughness of coconut shell. The aim of examining the coconut shell's microstructure-mechanical prop-

erty relationships is to inform its future use in composite applications and better understand its potential as a structural material. More generally, exploring the failure mechanisms of biological materials helps us to better understand the complex property of toughness while providing necessary insight for the developing field of biologically inspired structural design.

2. Methods

2.1. Materials

Commercially available young and old coconuts, the fruits of the coconut tree (*Cocos nucifera*), were purchased from a local market (Mi Pueblito Market) in the Mission District of San Francisco, California, USA. All fruits were initially center-drilled to allow removal of coconut water via a conventional plastic straw. Subsequently, fruits were equatorially bisected, as per Fig. 1a, with a hacksaw. To isolate the shell hemispheres, the soft meat of the young coconut was scraped using a spoon while the solid meat of the old coconut was carefully excised using a small knife while assuring no damage to the shell.

2.2. Structural characterization using micro x-ray computed tomography (μ XCT)

Three-dimensional imaging using helical cone-beam micro x-ray computed tomography (μ XCT) was conducted using 16×13 mm pieces cut from both the young and old coconut shells. The young and old samples were dried and scanned together at $6.75 \mu\text{m}$ resolution using a 30 kV x-ray source. Preliminary scans were conducted at 30, 60, and 80 kV and it was determined that 30 kV gave the best contrast. Each projection was collected using a 3040×3040 pixel detector, and 3600 projections were collected over ~ 12 h of acquisition time. Finally, the 3D reconstruction was performed using resources at the Australian National Computational Infrastructure. Additional information on helical cone-beam μ XCT scanning and reconstruction methods may be found in (Varslot et al., 2011).

2.3. Characterization of the sub-structure using focused ion-beam (FIB microscopy)

Imaging of the finer microstructure was performed using an FEI Helios NanoLab 650 SEM (FEI, Hillsboro, OR, USA) equipped with a focused ion-beam. Dried samples of roughly $6 \times 6 \times 2$ mm were sputter coated with 40 nm of carbon using a Gatan 682 PECS (Gatan, Pleasanton, CA, USA) to reduce charging during milling and imaging. Ion milling was performed at a beam energy of 8 kV and an ion current of 2 nA. After milling, the revealed cross-sections were imaged at an acceleration voltage of 2 kV.

2.4. Strength and fracture toughness tests

To assess the material's mechanical properties and anisotropy, strength and fracture toughness tests were performed on rectangular sections of the shell cut with a low speed saw both parallel and perpendicular to the stem axis of the coconut, in directions analogous to lines of longitude and latitude on a globe (in the "equatorial" region), henceforth labeled "longitudinal" and "latitudinal" samples (Fig. 1). Eight samples per orientation were prepared for both young and old coconuts, divided equally between strength and fracture toughness ($n=4/\text{group}$). Since not all subsequent tests could be conducted immediately after sectioning, to prevent molding shell samples were stored dry at ambient temperature and rehydrated in water for ~ 12 h prior to testing.

Segments designated for uniaxial tensile testing were nominally 30 mm long and 4 mm wide. Each sample was ground and polished with SiC paper to a uniformly rectangular ~ 2 mm thickness, the maximum

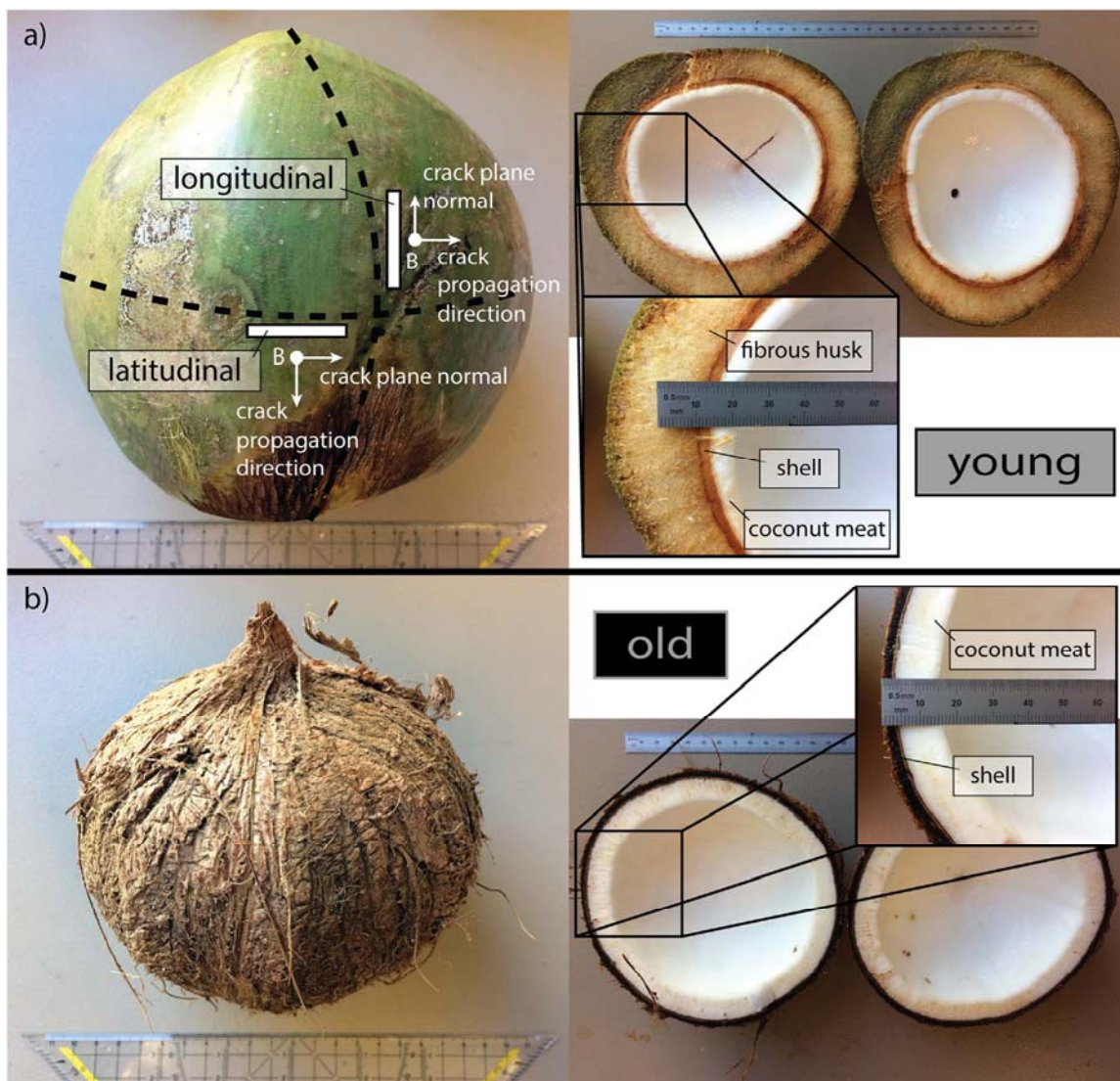


Fig. 1. Overview and cross-sections of young and old fruits of the coconut tree (*Cocos nucifera*). Commercially available coconuts were used to investigate structure and mechanical performance of young (a) and old (b) coconuts. Fruits were equatorially bisected revealing the thick, soft fiber husk that comprises the outermost exocarp and the mesocarp, and the hard, inner endocarp, i.e., the hard, woody shell of the coconuts. The shell provides protection of the seed and is known to consist of cellulose, hemicellulose, and lignin with small amounts of pectin and proteins (Dardick and Callahan, 2014).

that could be prepared from the thin endocarp. Old coconut samples were much stronger than the young, so depending on maximum force required, i.e., the coconut age, samples were loaded in tension using either an Instron 5944 2kN capacity testing system (Instron Corporation, Norwood, MA, USA) or a Gatan MicroTest 150 N capacity stage (Gatan, Abingdon, UK). In both cases, ~10 mm gauge section was used between the tensile grips and a constant displacement rate of 0.1 mm/min was applied while the load and displacement data were recorded simultaneously. In a few cases, prior damage or slipping invalidated a test and hence 3 to 4 stress-strain curves are displayed for each sample type. To analyze the influence of both age and orientation on strength, strain to failure and modulus results, a two-way analysis of variances (ANOVA) was performed. Furthermore, to assess the pairwise statistical significance between mean values, Tukey's post hoc test was used. In all cases, Statgraphics Centurion XVII software (Statpoint Technologies, Inc. Warrenton, VA, USA) was used with $p < 0.05$ considered statistically significant.

Samples for fracture toughness testing were similarly obtained, with a width, $W \approx 4$ mm, thickness, $B \approx 2$ mm, and length, $L \approx 20$ mm. The crack propagation direction and crack plane normal are clearly defined in Fig. 1, and the sample thickness B was always oriented parallel the

radial direction of the shell. Thus, the crack propagation direction in longitudinal samples was latitudinal, and vice versa. One surface area of each sample ($W \times L$) was prepared by polishing with SiC paper to a 1200 grit finish. Each sample was then notched with a low speed saw across the center of L to ~0.4 W depth and razor micronotched to a root radius of ~10 μ m. To remove any damage from the notching procedure, the previously polished surface was subsequently gently re-polished with the 1200 grit SiC paper, which simultaneously induced a small crack to $a_0 \sim 0.6 W$. Samples were then loaded into the same Gatan MicroTest stage now configured for three-point bending with a 16 mm loading span while within a Hitachi S-4300SE/N variable-pressure scanning electron microscope, VP-SEM (Hitachi America, Pleasanton, CA, USA) operating at 35 Pa in variable pressure mode. From these load-displacement data, fracture toughness (using K_J to account for plasticity) was determined in general accordance with ASTM standard E1820 (ASTM, 2007). In this methodology, the stress intensity, K_{el} is first calculated in the conventional linear elastic manner as

$$K_{el} = \frac{PS}{BW^{3/2}} f(a/W), \quad (1)$$

where P is the applied load, S is the major (three-point) loading span,

and $f(a/W)$ is a geometry dependent function of the crack length to width ratio provided in ASTM Standard E1820 (ASTM, 2007). The crack length was determined from VP-SEM images taken throughout the failure process. This easily provides, J_{el} , the elastic component of the J -integral, from the standard $J - K$ equivalence (mode I) relationship $K_{el} = (E' J_{el})^{1/2}$, where $E' = E$, Young's modulus in plane stress and $E = E / (1 - \nu^2)$ in plane strain; for E we used the values from Table 1, for ν , the Poisson's ratio, we used 0.33. J_{el} is then added to the plastic component, J_{pl} , of the J -integral which is determined from the plastic area under the load displacement curve as

$$J_{pl} = \frac{\eta A_{pl}}{Bb}, \quad (2)$$

where $\eta = 1.9$, A_{pl} is the plastic area underneath the load-displacement curve, and b is the uncracked ligament width (i.e., $b = W - a$). Finally, K_J is back-calculated from the total J ($= J_{el} + J_{pl}$) using again the standard $J - K$ equivalence (mode I) relationship, all assuming plane-strain conditions. This value can then be plotted against the crack extension measured in the VP-SEM to produce a K_J -R ("resistance") curve, showing total toughness and how it changes over the course of failure.

2.5. Tensile tests during wide-angle x-ray diffraction (WAXD)

Separately, nanoscale deformation of the coconut shell was measured through synchrotron wide-angle x-ray diffraction (WAXD) performed during tensile tests (Zimmermann et al., 2013; Zimmermann et al., 2011). At numerous time points during the mechanical tensile tests, measurements of the macro-level stress-strain behavior (i.e., coconut stress, coconut strain) were acquired as well as the 2D WAXD patterns, which were analyzed to derive nanoscale deformation.

Young and old coconut shell samples for WAXD were acquired immediately after bisecting the coconuts near their midsection either parallel (i.e., latitudinal) or perpendicular (i.e., longitudinal) to the equatorial cleavage point ($n = 3$ –4/group). Samples were cut with a low speed saw and ground to a final dimension of $15 \times 2.5 \times 1$ mm for the young coconut and $15 \times 1.5 \times 0.3$ mm for the old. The samples were air dried for 1 h and then silicon carbide paper was glued to the ends of the samples with cyanoacrylate glue to provide a surface to grip during mechanical tensile testing. The gauge length of the samples was 10 mm. The samples were then rehydrated for 30 min in water before testing.¹

The young and old samples were loaded in tension at a strain rate of $5 \mu\text{m/s}$ and $1 \mu\text{m/s}$, respectively. Different strain rates were implemented to maximize the number of data points acquired and to minimize the radiation exposure. The samples were loaded in tension in a Linkam TST350 tensile testing stage (Linkam Scientific, Tadworth, Surrey, UK) positioned in beamline 7.3.3 at the Advanced Light Source (ALS) synchrotron radiation facility (Lawrence Berkeley National Laboratory, Berkeley, CA), such that WAXD data collection could be recorded simultaneously with mechanical loading (Hexemer et al., 2010). At beamline 7.3.3., a Pilatus 300K-W detector (Dectris, Baden-Dättwil, Switzerland) was positioned at ~ 200 mm from the sample at an angle of 18° to collect WAXD data using an x-ray energy of 10 keV. During the tests, the young samples were exposed to x-rays for 0.5 s at 5 s intervals. The old coconut samples were exposed to x-rays for 0.5 s at 10 s intervals.

The analysis software IGOR Pro (Wavemetrics) was used in conjunction with the custom macro NIKA (Jan Ilavsky, Argonne National Laboratory, Chicago, IL, USA) to convert the 2D data to 1D. First, the sample-to-detector distance and beam center were calibrated using a hydroxyapatite standard. The 2D WAXD data were converted to 1D by

Table 1

The mean values $\pm$ standard deviation for ultimate tensile strength, failure strain, and elastic modulus.

Age	Orientation	UTS (MPa) ^a	ϵ_f (%) ^a	E (GPa) ^a
Old	Long.	26.6 ± 4^a	2.47 ± 0.1^d	1.74 ± 0.09^f
Old	Lat.	48.5 ± 11^b	$4.3 \pm 1^{d,e}$	1.92 ± 0.25^f
Young	Long.	17.6 ± 1^c	6.3 ± 1.2^e	0.56 ± 0.16^g
Young	Lat.	16.4 ± 3^c	$4.7 \pm 1^{d,e}$	0.71 ± 0.04^g

^a Matching superscripts indicate no statistically significant difference was found between the values using Tukey's post-hoc test.

radially integrating over a 4° sector oriented parallel to the direction of loading. The location of the peak at approximately $q = 1.57$ ($1/\text{\AA}$) was found by fitting the 1D datasets with a Gaussian and linear function. The strain in the cellulose was measured as the change in position of the corresponding peak's center divided by its location at zero load.

The tissue strain was measured by imaging the change in spacing of horizontal lines marked on the sample's surface, which were later analyzed using a custom image analysis algorithm utilizing the software package Vision Assistant 8.5 (National Instruments, Austin, TX, USA). The displacement of the lines was divided by the separation at zero load to determine the bulk tissue strain.

3. Results

3.1. Microstructure

As with most biological materials, the microstructure of coconut displays structural features at different length scales that evolve with age (Fig. 2). At the coarsest level, the characteristic features are hollow channels (Fig. 2d inset and Fig. 2i) running through the densest center part of the shell, roughly elliptical with cross-sectional major and minor axes of $340 \pm 40 \mu\text{m}$ and $140 \pm 40 \mu\text{m}$, respectively, spaced one half to one millimeter apart. While these channels appear in both the young and old shells, they become more distinct in the older shell and can be seen in Fig. 2g segmented from the μXCT image of the surrounding old shell. In both types of shells, the channels are lined by hollow fibers with approximately elliptical axes of $20 \pm 7 \mu\text{m}$ and $13 \pm 5 \mu\text{m}$, as shown in Fig. 2d,i-j. SEM images showed that these consist of concentric rings connected in a ladder structure along the length of the fibers (Fig. 2i-k). μXCT revealed that the channel network is highly connected in all directions; however, the larger main channels appear to run more latitudinal, with smaller connecting channels running longitudinally (Fig. 2g).

At the next finer length scale, SEM revealed that the densest part of the young coconut shell has a hollow cellular structure with thick cell walls (Fig. 2e). The hollow cells, again roughly ellipses, are axially $37 \pm 11 \mu\text{m}$ by $17 \pm 4 \mu\text{m}$ with walls of $7 \pm 2 \mu\text{m}$ in thickness. There is inter-cell porosity between the cell walls where the cells do not perfectly fill the volume, as well as fine channels of porosity $\sim 1 \mu\text{m}$ in diameter running through the cell walls and connecting the cells, leading to about 1% total porosity. In the old coconut, these cells have mostly been filled during the fruit's maturation leaving a much denser overall structure (Fig. 2h). However, hints of the younger coconut cell structure can be seen in terms of porosity, revealing where the former cell walls and interiors were located. Finally, FIB microscopy revealed the structure of the cell walls, as shown in Fig. 2f. Sectioned views of the young coconut reveal a complex structure that includes nano scale porosity (with a diameter of $69 \pm 19 \text{ nm}$) and a layered structure (with lamellar thicknesses of $527 \pm 105 \text{ nm}$). In contrast, similar sections of the old coconut revealed no features on this length scale.

3.2. Strength and fracture toughness

Taken as a whole, our mechanical data demonstrate the relative

¹ As these samples were prepared and tested immediately after bisecting the fruits, they have never been fully dehydrated and stored and were hence only rehydrated for 30 min compared to the 12 h of the strength and fracture toughness samples.

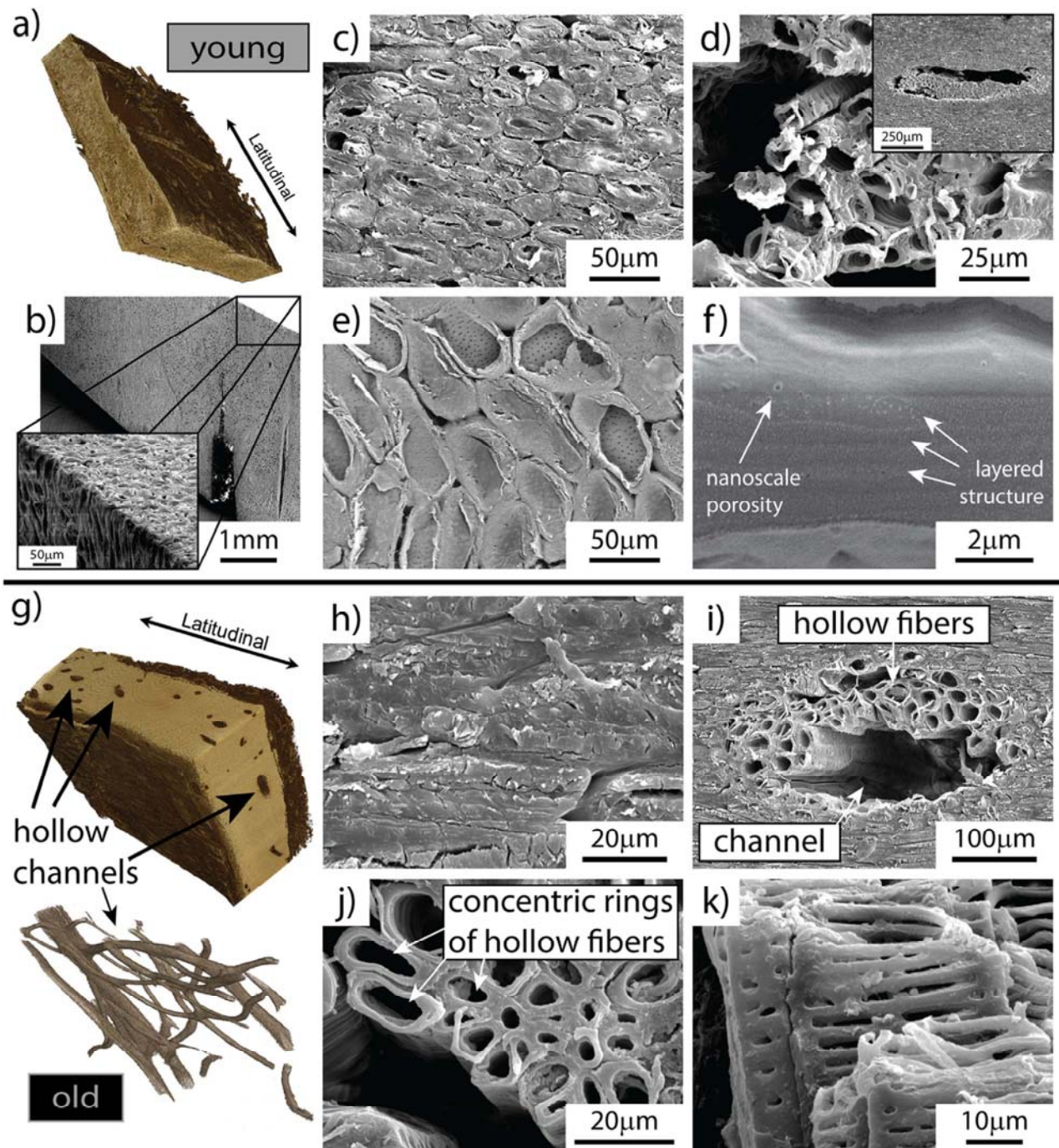


Fig. 2. Multiscale structure of young and old coconut shells. μ XCT scans of young (a) and old (g) coconut shells reveal hollow channels which become more distinct in the older shell and appear to run more latitudinal, with smaller connecting channels running longitudinally (g). These channels run continuously through the entire cross section of the shell (b,d,i-j) representing the coarsest structural feature of the material. Higher resolution micrographs show that the channels are roughly elliptical with cross-sectional major and minor axes of $340 \pm 40 \mu\text{m}$ and $140 \pm 40 \mu\text{m}$, respectively. Channels are lined by hollow fibers with approximately elliptical axes of $20 \pm 7 \mu\text{m}$ and $13 \pm 5 \mu\text{m}$ (d,i,j) which consist of concentric rings connected in a ladder structure along the length of the fibers (i-k). At a finer length scale, the young coconut shell has an elliptical, hollow cellular structure (b,c) roughly $37 \pm 11 \mu\text{m}$ by $17 \pm 4 \mu\text{m}$ with cell walls of $7 \pm 2 \mu\text{m}$ in thickness (e) that largely disappears in the older sample (h). FIB microscopy revealed the nanoscale structure of the cell walls with pores of about $69 \pm 19 \text{ nm}$ diameter and a layered structure with lamellar thicknesses of $527 \pm 105 \text{ nm}$ (f).

mechanical superiority for old and latitudinal samples in terms of strength, stiffness, and toughness. As shown in Fig. 3a-b, the resultant stress-strain curves lacked a clearly defined linear region and the elastic modulus was calculated from linear regression of the initial portion of the curves, between roughly 5 and 15% of the (ultimate) tensile stress. The two-way ANOVA statistical test revealed that both age and orientation influenced the strength; however, only age influenced the modulus. Mean strength, strain to failure, and modulus values are shown in Table 1 along with the results of the statistical tests. From

Table 1 it can also be seen that there was no anisotropy in the strength, strain to failure or modulus for the young coconut shell and that the anisotropy in tensile properties only evolves with age.

Similarly, Fig. 3c-d show that the fracture toughness is both higher and more anisotropic for the old coconut shell relative to the young one. Fig. 4 illustrates how the crack interacted with the microstructure in each case to give rise to the fracture toughness differences. It can be seen that the crack path is fairly straight for both young orientations, while with age crack path tortuosity increases significantly in both

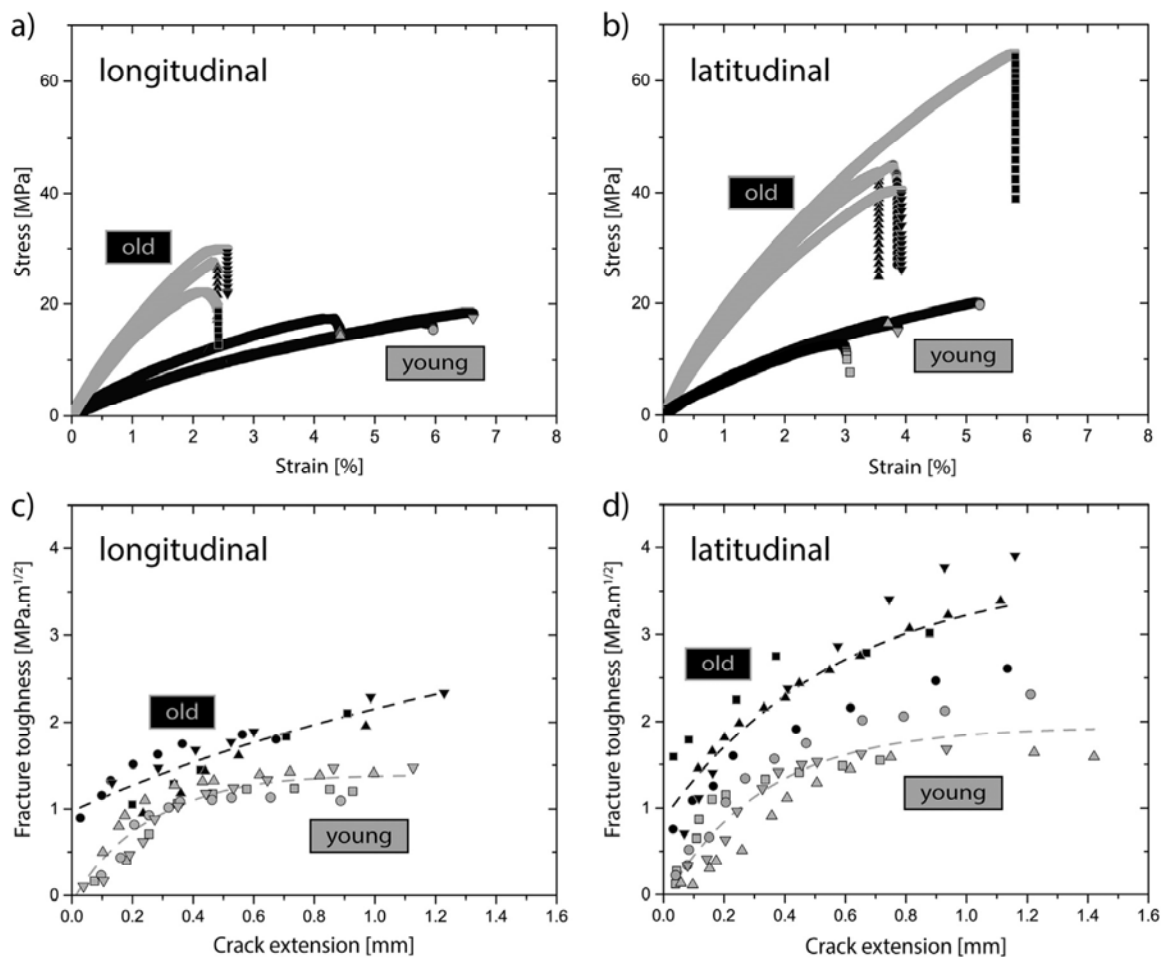


Fig. 3. Strength and toughness of young and old coconut shells. Tensile tests of bulk coconut, both young and aged, were performed on samples with a) longitudinal and b) latitudinal orientations, with each curve shaded according to age, allowing determination of elastic modulus, tensile strength, and strain to failure. Beams were also subjected to *in situ* three-point bending in the VP-SEM to measure the fracture toughness, shown in the same orientations for c) and d), from which K_{I} (resistance) R -curves were constructed based on visually measured crack extensions, showing notable improvements in both initiation and growth toughness in the old coconut.

orientations. Crack deflections out of the mode I plane become more pronounced particularly in the latitudinally orientated samples.

3.3. Deformation on the substructure level

Tensile test results were additionally collected for the coconut samples during the synchrotron experiments. The stress–strain curves for the young and old coconut samples are shown for the longitudinal and latitudinal orientations, respectively (Fig. 5a–b). As was also seen in Fig. 3, the young coconut has a lower strength than the old one in both orientations. While the strains to failure of the young coconut in both orientations are comparable and roughly consistent with the data shown in Fig. 3, the strains to failure of the old coconut in the longitudinal orientation are slightly lower than in the other orientation. Although values are lower than the results of the larger sized strength tests, the trend is again identical.

2D wide-angle x-ray diffraction spectra were acquired at fixed time points during the tensile tests. Representative 1D x-ray diffraction spectra from young and old coconut shells are shown in the inset of Fig. 5c; the spectra were similar in both orientations. The major peak that is present represents the (002) plane in the cellulose nanostructure at $q = 1.57 \text{ 1/\AA}$ (Johar et al., 2012; Thomas et al., 2015; Xu et al., 2015).

If the location of the diffraction peak shifts during the tensile tests, then the nano structure is deforming in response to the applied deformation. In Fig. 5c–d the nanoscale strain is shown for the young and old coconuts in the longitudinal and latitudinal orientations. In the

old coconuts, the (002) plane in the cellulose crystal structure is deforming during the tensile tests; however, no deformation was measurable in the young samples. Interestingly, in the young samples, appreciable background scattering is present in the diffraction pattern (inset Fig. 5c) in contrast to the old samples, which implies less crystallinity in the young samples. Furthermore, the location of the peak had considerable variation in the young cases that contributed to the noise in the nanoscale strain measurement (Fig. 5c–d), which reflects variations in the (002) plane's spacing and thus lower crystallinity.

4. Discussion

Nature often produces structures with impressive mechanical properties despite working with limited available constituent materials. In comparison to other plant materials, the coconut shell is found to be similar in mechanical properties to wood and in terms of strength and the elastic modulus is comparable to the low end of the palm's own timber (Wegst and Ashby, 2004). Furthermore, coconut shell provides an excellent case study in multiscale hierarchical structures controlling the mechanical properties. Indeed, as will be discussed below, changes in both the micro and nanoscale structure appear to be responsible for aging effects on the mechanical properties.

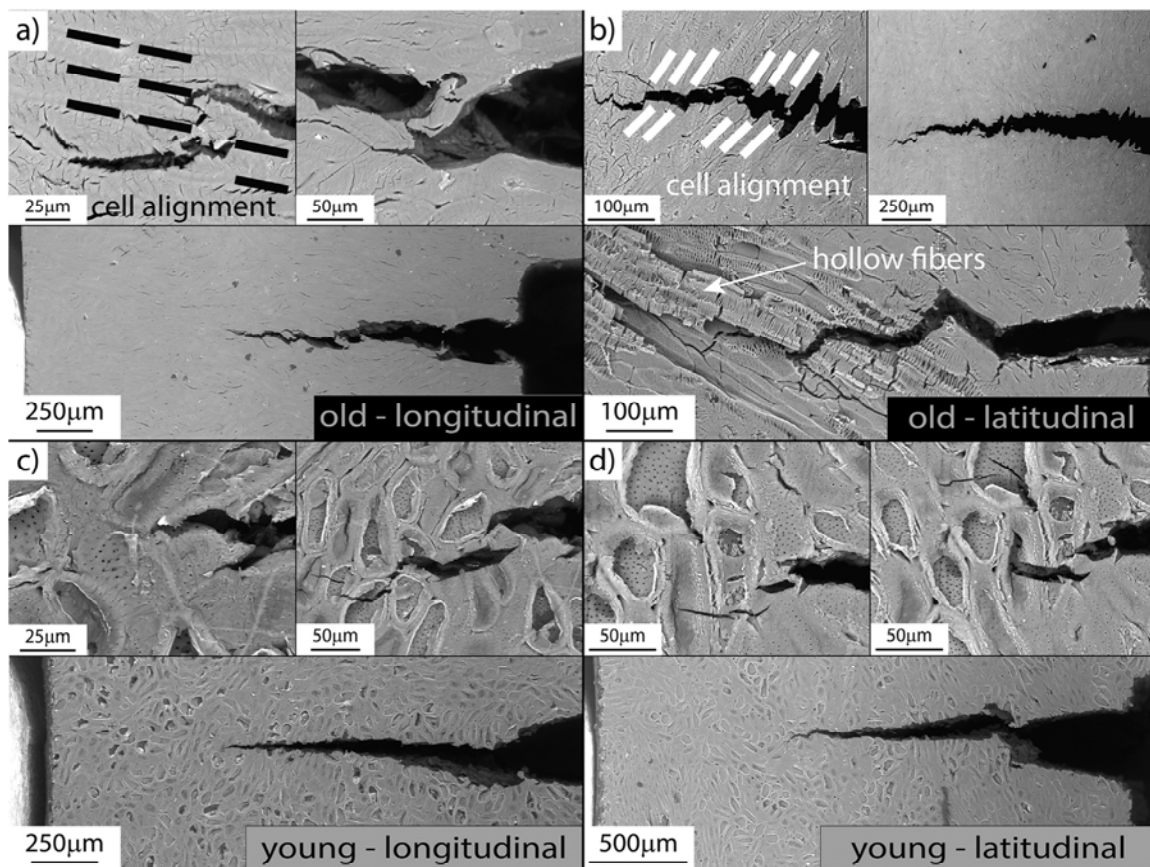


Fig. 4. Crack paths recorded during VP-SEM in situ fracture toughness tests in young and old coconut. The orientation label (longitudinal in a) and c), for b) and d) latitudinal) refers to beam length direction, i.e., normal of crack plane. In a) and b), the top row exemplifies crack tortuosity driven by intercellular crack propagation in combination with a crack path parallel (longitudinal) and across (latitudinal) the main channels of the hollow tube structure of the aged coconut. In both c) and d), the top row shows equivalent cell cleavage as mechanism for crack growth, corroborating to indistinguishable mechanical properties. Bottom rows illustrate a complete post-failure crack path, similarly straight in c) and d), resulting from the weakly developed tube structure, and most notably tortuous in b).

4.1. Aging effects on structure and properties

The densification, or sclerification, of the endocarp with age is a phenomenon common to drupe fruits involving the thickening and lignification of the cell walls (Seymour et al. 2008; Hammami et al., 2013; Dardick and Callahan, 2014). In the case of the old coconut, Fig. 2 indicates the cell walls have thickened to completely obliterate the cell lumens. The mechanical superiority of the denser structure of the old coconut shell is reflected in the higher strength (Table 1), higher modulus (Table 1), and markedly higher initiation toughness on the *R*-curves (Fig. 3). The denser structure of old coconut provides a more uniform load distribution, giving higher stiffness and strength. The lower density of the young coconut is also seen at nanoscale where it exhibits a nanoporous lamellar cell wall structure when compared with the old coconut. The lignification of the cell walls results in the loss of nanoscale porosity. Lignin is thought to be a reinforcing agent for the cell walls, polymerizing in the cell walls to stiffen them and prevent cell buckling under mechanical stress (Burgert and Dunlop, 2011). Accordingly, both the cell microstructure and the cell wall nanostructure appear to evolve with age for the coconut endocarp, giving rise to the observed improvements in macroscopic mechanical properties.

Further nanostructure effects were revealed by the tensile tests during WAXD to investigate the nanoscale deformation. Here, deformation of the nanoscale cellulose crystal structure was observed in the aged coconut but not in the young coconut (Fig. 5). Nanoscale deformation in terms of stretching and sliding of organic polymers and proteins is a well-known intrinsic toughening mechanism in biological materials that contributes to their strength (Fantner et al., 2005; Ritchie, 2011; Zimmermann et al., 2011; Zimmermann et al.,

2013). Therefore, additional aging-related nanoscale structural changes occurring within the coconut, such as changes in the bonding between cellulose fibers or crystals, are likely contributing to the increased load transfer and strength with aging. In terms of the nanoscale cellulose crystal structure, our x-ray diffraction spectra (Fig. 5c inset) suggest that the crystallinity of the coconut shell may be increasing with age. Increased crystallinity has long been associated with higher strength for cellulose fibers (Rong et al., 2001; Ward, 1950), and thus may also contribute to the increased strength observed for the old coconut shell. Therefore, aging-related changes in the microscale cell structure and the nanoscale cell wall porosity and cellulose crystal structure are all likely contributors to the observed differences in intrinsic mechanical behavior (i.e., strength and crack-initiation toughness) between the young vs. old coconut shells.

The higher rising *R*-curves, and thus higher crack-growth toughness, observed for the old coconut can be attributed to the more tortuous crack paths seen in Fig. 4. In the younger coconut, cracks propagate by successively cleaving porous and hollow cells despite the presence of often significant intercellular voids that could provide a path of less resistance, as shown in Fig. 4c-d. In contrast, Fig. 4a-b indicate that cracks in older coconut tend to bypass the denser, filled cells and travel circuitously along boundaries. In addition, the well-developed open channel structure of the old coconut shell (Fig. 2) also provides many sites for crack trapping (by blunting) and deflection, while the more homogeneous structure of the young coconut endocarp provides few barriers to crack propagation (Fig. 4) and lower toughness (Fig. 3c-d).

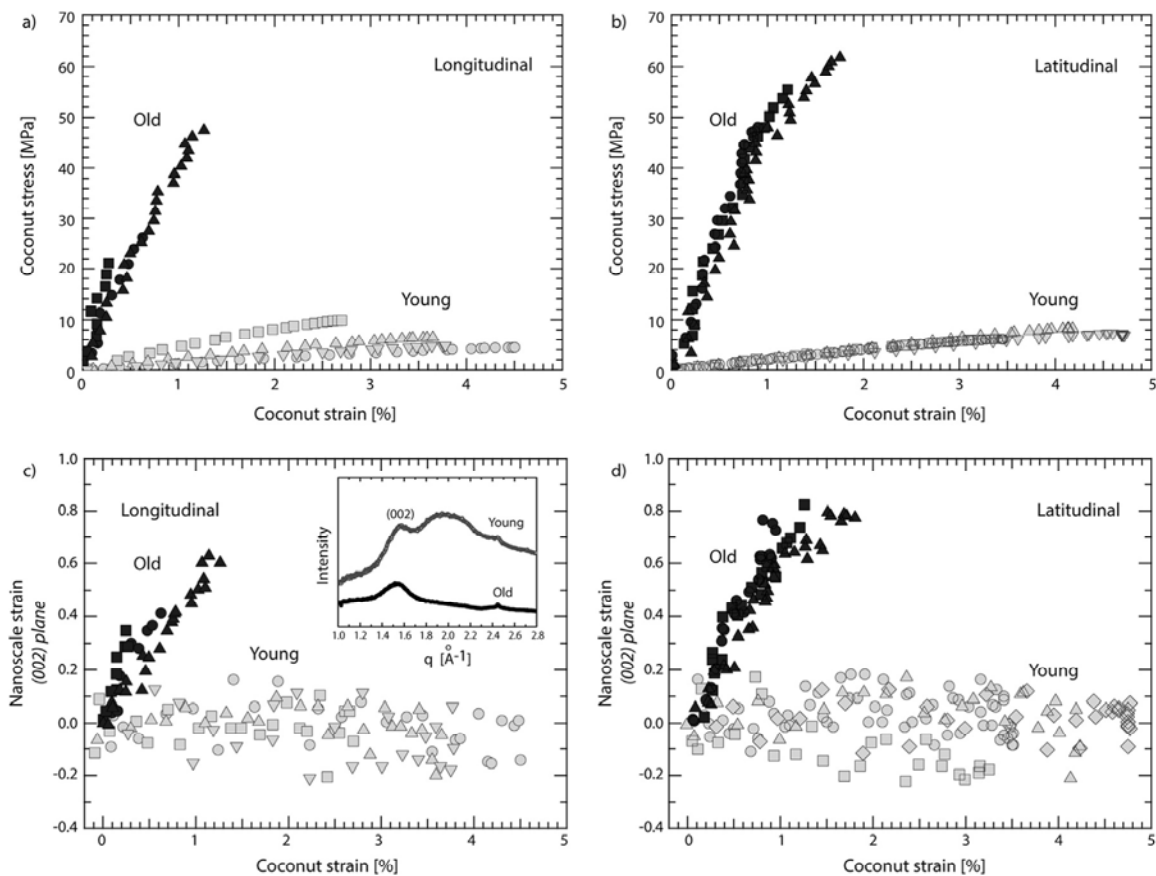


Fig. 5. Mechanical deformation at small and large length scales. Nanoscale deformation was measured by performing a uniaxial tension test on a rectangular sample of the coconut shell to measure the macro-level deformation and simultaneously exposing the sample to synchrotron x-rays to measure nanoscale deformation. The macro-level stress-strain behavior of the young and old coconuts is shown for the a) longitudinal and b) latitudinal orientations. c) The inset shows the wide-angle x-ray diffraction patterns of the young and old samples. Here, the (002) plane of the cellulose nanostructure diffracts x-rays. The location of the (002) peak in the diffraction pattern was followed during the tensile test to determine if load was being transmitted to the nanostructure. In both the c) longitudinal and d) latitudinal orientations, the (002) plane deforms in the old coconut but not in the young coconut.

4.2. Orientation effects on structure and properties

The young coconut shell is not only relatively more homogeneous, but also more isotropic in the mechanical properties than the old coconut shell. Indeed, for the young coconut there is no statistically significant orientation effect on the strength, strain to failure and modulus (Table 1), and the *R*-curves largely overlap over the first 0.4 mm of crack extension (Fig. 3c–d). In contrast, the old coconut shell shows significant anisotropy in both strength and fracture toughness, and also in the tensile elongation to failure.

The observation of cell cleavage vs. intercellular crack growth, discussed above, also provides a possible explanation for the anisotropy of mechanical properties in old coconut when considered in conjunction with ovoid cell geometries. As is visible in Fig. 4, the longer axes of cells are generally oriented in the latitudinal direction in an almost brick-like structure. Thus, a crack propagating transverse to this orientation would have to travel further perpendicularly to follow intercellular voids, whereas the longer cell boundaries provide a favorable path to cracks traveling latitudinally, i.e. in longitudinal samples. Therefore, latitudinal samples, with cracks growing further and perpendicular to cell alignment, exhibit greater resistance to fracture, and hence toughness, than longitudinal samples in which cracks grow parallel to the cell's orientation. As some intercellular growth is also observed in the young coconut, this mechanism might also explain the slightly higher growth toughness of the young latitudinal samples visible in Fig. 3d.

Mechanical property differences are also attributed, at least in part, to the observed anisotropy in the channel structure of the old coconut (Fig. 2). While the channel structure is highly interconnected, the large

main channels are observed to run latitudinally, with smaller connecting channels running longitudinally. As such, for tensile tests in the longitudinal orientation the larger channels act as larger stress concentrations that can promote earlier failure. In contrast, for fracture toughness tests with a latitudinal crack plane, the crack runs in the longitudinal direction and interacts with the large latitudinal channels, thereby generating more crack trapping by blunting at the channels, and more crack tortuosity.

5. Conclusions

In the present study, the mechanical properties of coconut shell were observed to significantly improve with age, but also to become more anisotropic. While the young coconut shell had essentially identical tensile properties and toughness for the two orientations tested, the old coconut showed an 82% higher strength for loading in the latitudinal orientation, and > 50% higher crack growth toughness for cracking on the latitudinal plane. Structural aspects affecting the mechanical properties across multiple length scales with aging were identified as improved load transfer to the cellulose crystalline nanostructure and sclerification of the endocarp, the latter of which included closing of the cell lumens and lignification of the cell walls. This structural evolution with aging gave a denser and mechanically superior micro and nanostructure to the old coconut shell. Additionally, the development of anisotropy in strength and toughness was attributed to the development of an anisotropic open channel structure through the shell of the old coconut. The anisotropy of this channel structure is thought to affect both crack initiation during tensile tests and the toughening mechanisms of crack trapping and deflection during crack

propagation.

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