Research paper

Branching toughens fibrous networks

C.T. Koh\textsuperscript{a,b}, M.L. Oyen\textsuperscript{a,*}

\textsuperscript{a} Cambridge University Engineering Department, Trumpington Street, Cambridge CB2 1PZ, UK
\textsuperscript{b} University of Tun Hussein Onn Malaysia, 81310 Parit Raja, Johor, Malaysia

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form
5 March 2012
Accepted 14 March 2012
Published online 28 March 2012

Keywords:
Fibrous networks
Branching
Cross-links
Collagen
Kinks
Fracture
Toughness
Hyperelastic

ABSTRACT

Fibrous collagenous networks are not only stiff but also tough, due to their complex microstructures. This stiff yet tough behavior is desirable for both medical and military applications but it is difficult to reproduce in engineering materials. While the nonlinear hyperelastic behavior of fibrous networks has been extensively studied, the understanding of toughness is still incomplete. Here, we identify a microstructure mimicking the branched bundles of a natural type I collagen network, in which partially cross-linked long fibers give rise to novel combinations of stiffness and toughness. Finite element analysis shows that the stiffness of fully cross-linked fibrous networks is amplified by increasing the fibril length and cross-link density. However, a trade-off of such stiff networks is reduced toughness. By having partially cross-linked networks with long fibrils, the networks have comparable stiffness and improved toughness as compared to the fully cross-linked networks. Further, the partially cross-linked networks avoid the formation of kinks, which cause fibril rupture during deformation. As a result, the branching allows the networks to have stiff yet tough behavior.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Stiff yet tough materials are desirable in many applications such as protective clothing (Sundarrajan and Ramakrishna, 2007) in military applications, and in intravascular balloon catheters (Pruitt and Furmanski, 2009) and stents (Robertson and Ritchie, 2007) in medical applications. However, stiff yet tough materials are difficult to produce because stiffness and toughness are normally mutually exclusive in engineered materials. For example, brittle materials such as ceramics, which have large stiffnesses, have small toughnesses as the applied energy is released in fracture rather than deformation (Fratzl, 2008; Launey and Ritchie, 2009). Natural collagenous fibrous materials such as the amniotic membrane (Calvin and Oyen, 2007) and cartilage (Chin-Purcell and Lewis, 1996), however, exhibit an excellent compromise in stiffness and toughness. Further, they have nonlinear strain stiffening behavior which allows them to be compliant at small strains and to become stiffer at large strains (Oyen-Tiesma and Cook, 2001).

The strain stiffening behavior of fibrous materials can be explained by the detailed studies of their microstructures, which are in the form of networks (Kendra et al., 2010). Fibrous protein networks also exist in many major structural constituents of the human body such as actin in cells (Chaudhuri et al., 2007) and fibrin in blood clots (Brown,...

\* Corresponding author. Tel.: +44 1223 332 680; fax: +44 1223 332 662.
E-mail address: mlo29@cam.ac.uk (M.L. Oyen).

1751-6161/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jmbbm.2012.03.011
et al., 2009). The detailed studies of these microstructural architectures indicate that the mechanical behavior of fibrous networks depends not only on the properties of the individual fibril, e.g. fibril length, diameter and mechanical properties, but also on the quality of the networks, e.g. cross-link density, cross-linkers length-and fibril orientation (Wagner et al., 2006; Lin et al., 2010; Chen and Shenoy, 2011; Hatami-Marbini and Picu, 2009).

While the deformation of fibrous networks has been extensively studied, the understanding of toughness is still incomplete. Various studies on rubbery materials indicate that hyperelastic, viscoelastic and nonlocal behaviors govern fracture of materials (Krishnan et al., 2008; Wang and Chen, 2005; Buehler et al., 2003). The precise measurements of near-tip structure reveal that there is a hierarchy of linear and nonlinear zone in the vicinity of the crack-tip in brittle neo-Hookean materials (Livne et al., 2010). These studies suggest microstructural architectures of fibrous networks are crucial in the study of fracture toughness, in order to capture hyperelastic network behavior and several aspects of fracture behavior.

The objective of the work presented here is to examine how a specific microstructural architecture i.e. branching in a natural type I collagen network, provides both stiff and tough mechanical responses. Finite element (FE) analysis was used to examine nonlinear hyperelastic behavior of fibrous networks, as governed by fibril length and cross-link density. Further, detailed modeling of microstructures at a notch root addresses crack-tip blunting, which improves network toughness. The understanding of the mechanics the branched bundles offers guidelines to the production of fibrous materials with enhanced toughness, such as novel electrospun scaffolds (Stachewicz et al., 2011).

2. Finite element modeling

2.1. Modeling of fibrous networks

Two-dimensional fibrous networks were generated in MATLAB (The MatWorks, Natick, MA) by constructing lines from random points with random angles. The fibrils were then modeled by beam elements, with length equal or smaller than 1 μm, in finite element software ABAQUS (Version 6.7, SIMULIA, Providence, RI). The beams were defined by stretching stiffness μ (i.e. axial force needed to stretch a unit axial strain) and bending stiffness κ (i.e. bending moment needed to bend a unit radius of curvature). A noodle-like behavior resembling collagen fibrils was defined: the fibrils were very easy to bend (κ = 1 × 10^{−15} Nm^{2}) but difficult to stretch (μ = 5 N), resulting in a large value of stretch to bend ratio μ/κ = 5 × 10^{15}. Both of the stretching and bending stiffness depend on not only the Young’s modulus but also the cross-sectional area of fibrils (Dillen et al., 2008). The network properties including fibril modulus E = 100 MPa and fibril diameter d_{f} = 50 nm (Oyen et al., 2004) are representative of the collagenous network in amnion (Calvin and Oyen, 2007). All simulations were performed using nonlinear finite element analysis, which considers large strain and rotation. Moreover, convergence studies were performed to ensure that the cell size does not affect the results.

The main focus of this study is on the branched fibrous networks which resemble a natural type I collagen network i.e. amnion (Fig. 1(a)). The SEM image was taken from the human amnion by the same sample preparation procedure used in the previous study (Oyen et al., 2005). A cross-link density ρ_{b} = 17 μm^{−2} was determined by counting the overlapping points in a unit square box in the SEM image. As there is no evidence that all overlapping points are bonded to each other (i.e. that the network is fully cross-linked), three random networks with the same fibril number (N = 390) were generated, with partial cross-linking, and are named “branched” networks in this study. The partially cross-linked fibrous networks are defined by prescribing three branch angles, i.e. 20°, 30° and 45°: only when the intersection angle is less than the prescribed branch angle were cross-links introduced. For all other intersection points, the fibrils are allowed to slide friction-free along each other. These branched fibrous networks have smaller cross-link density than the fully cross-linked network at 17 μm^{−2}: the 20° branched network has 1 μm^{−2} cross-link density; the 30° branched network has 2.4 μm^{−2} cross-link density; the 45° branched network has 5 μm^{−2} cross-link density.

Two microstructural features are explicitly compared here: short fibrils (SF) versus long fibrils (LF), and partially cross-linked (PC) networks versus fully cross-linked (FC) networks. Fig. 1(b) schematically illustrates three types of fibrous networks studied in this paper, which are the fully cross-linked short fibrils (FC + SF) networks, the fully cross-linked long fibrils (FC + LF) networks and the partially cross-linked long fibrils (PC + LF) networks. The FC + LF networks are identical to the branched fibrous networks except for the cross-link density. Both the FC + SF and the FC + LF networks have rigid bonding at all intersection points. The FC + SF networks consist of fibrils with 10 μm length; the FC + LF networks consist of fibrils with infinite length (i.e. fibril length much longer than unit cell size). These long fibrils were modeled by extending fibrils to cut across the unit cell edges at both ends. These two types of fibrous networks were studied with two cross-link densities, namely sparse networks (2.4 μm^{−2} cross-link density) and dense networks (17 μm^{−2} cross-link density). The dense networks have the approximate bonding density as the overlapping point density obtained from the SEM image of a natural type I collagen network. The sparse networks have the same bonding density as the 30° branched network.

2.2. Pure shear analysis

The fibrous networks were constructed in 50 × 50 μm^{2} unit cell models. The unit cell was loaded in pure shear: the fibrils were bonded at rigid plates at all edges, the bottom plate was pinned, and the top plate was sheared horizontally. The left and right plates rotated freely with a pin fixed at the bottom. The “actin-like” fibrous network studied by Onck et al. (2005) was also recreated. Similar to the FC + SF network, this repeated model consists of 10 μm length fibrils which are rigidly bonded at all intersection points. The fibrous network with fibril density (i.e. the sum of fibril length per unit area) of 2516 mm^{−1} and cross-link density of 2.2 μm^{−2} was
considered. For Onck’s model, the unit cell size is 40 \times 40 \mu m^2.

The beams were also defined by different material properties to represent microfilaments of an actin network instead of a collagen network, with \( \kappa = 16 \) N and \( \mu = 8.53 \times 10^{-17} \) Nm². The deformation of fibrous networks was evaluated by examining their stress–strain responses. The shear stress \( \tau \) was calculated from the total horizontal reaction force at the top edge of the unit cell, divided by the cell size and the beam width. The shear strain \( \gamma \) was calculated from the horizontal displacement of top edge, divided by the unit model width. The slopes of the stress–strain curves describe the stiffness \( G \) of the fibrous networks.

### 2.3. Fracture analysis

The fibrous network was constructed in a circular unit cell model with 25 \mu m radius and with a 25 \mu m length notch. The outer boundary was subjected to the displacement field associated with the macroscopic crack tip field for a homogeneous and isotropic solid: by defining the origin at the notch root, the displacement components \( (u_1, u_2) \) can be expressed in terms of the polar co-ordinates \( (r, \theta) \) as (Kanninen and Popelar, 1985).

\[
\begin{align*}
u_1 &= \frac{1}{2} \sqrt{\frac{K_1}{2\pi G}} \left( \kappa + 1 + 2 \cos \frac{\theta}{2} \right) \sin \frac{\theta}{2} \\
u_2 &= \frac{1}{2} \sqrt{\frac{K_1}{2\pi G}} \left( -\kappa + 1 + 2 \sin^2 \frac{\theta}{2} \right) \cos \frac{\theta}{2}
\end{align*}
\]

where \( K_1 \) is the mode I stress intensity factor and \( G \) is shear modulus. The fibrous networks are assumed to be in plane stress by having \( \kappa = (3 - \nu)/(1 + \nu) \) with Poisson’s ratio \( \nu = 0.3 \). The shear modulus \( G \) was defined as 4 MPa which is approximately the same modulus of the dense FC + LF network (see Fig. 2).

### 2.4. Failure criterion

The failure criterion was defined in both the deformation and fracture analysis as following: a fibril ruptures whenever local stress exceeding the tensile fracture strength of fibrils, defined as \( \sigma_f = 30 \pm 3 \) MPa. In the deformation analysis, the network stress corresponding to the first fibril rupture defines the strength of the fibrous networks. In the fracture analysis, the crack was predicted to start propagating when the first fibril ruptures. The corresponding stress intensity factor defines the critical stress intensity factor \( K_{IC} \). Although the fracture strength of fibrils is a rough estimation due to inconsistency of the experimental measurements of fibrils which vary from 20 to 600 MPa (Carlisle et al., 2010; Grant et al., 2008), a similar qualitative behavior is expected for other values of fracture strength.

---

Fig. 1 – (a) SEM image of fibrous network in type I collagen (amnion). An unit box, used to determine the cross-link points (circles), are highlighted in red. (b) Schematic illustration of the finite element models of the FC + SF network (top left); the FC + LF network (top right); the FC + LF networks including the 30° branched network (bottom left); and the 20° branched network (bottom right). All intersection angles that are unlabeled are larger than 30°.

Fig. 2 – Stress–strain responses (upper) and shear modulus (lower) of the FC + SF networks and the FC + LF networks at different bonding densities.
3. Results

3.1. Deformation of fibrous networks

The stress–strain curves obtained from the FE analysis of the short and the long fully cross-linked networks are shown in Fig. 2. These networks are first compared with the stress–strain behavior of the repetition of Onck’s model. Note that our repeated stress–strain responses are well aligned with Onck and coworkers’ results (Onck et al., 2005). The stress–strain curve of Onck’s network is close to the sparse FC + SF network cross-link density at small strain (Fig. 2). However, the Onck network has larger strain-stiffening, thus allowing it to become stiffer than the FC + SF network at large strain. Fig. 2 illustrates that the deformation of fibrous networks is dependent on cross-link density. The dense fibrous networks are approximately four times stiffer than the sparse fibrous networks. All dense networks including the FC + SF network and the FC + LF network have linear behavior, while the sparse networks have nonlinear strain-stiffening behavior. Furthermore, the deformation of fibrous networks also depends on fibril length. The FC + LF networks are significantly stiffer than the FC + SF networks.

Fig. 3 shows the stress–strain curves of the FC + LF networks (i.e. the 20°, the 30° and the 45° branched networks), which are compared to the FC + LF networks. Exhibiting strain-stiffening behavior, the branched networks have a stiffness that crosses that of the dense FC + LF network at 18% strain. Moreover, the branched networks are twice as stiff as the sparse FC + LF network. Note that the 30° branched network also has the same cross-link density as the sparse networks. Interestingly, the 20°, the 30° and the 45° branched networks have similar stress–strain curves. These branched networks have the same number of fibrils but different cross-link density. Therefore, the deformation of branched networks is dependent on fibril density but independent of cross-link density.

3.2. Failure of fibrous networks

The stress–strain curve of the dense FC + LF network failed when the maximum local stress in a fibril exceed the fibrils strength. The corresponding ultimate stress of the network is less than 0.6 MPa (Fig. 2). On the other hand, the FC + LF networks (i.e. the 20°, the 30° and the 45° branched networks) deformed without failure at ultimate stress more than 0.6 MPa, which is in agreement with the experimental measurement in a range of amion strength of 0.5 to 1.5 MPa (Oyen et al., 2004). Network toughness was further quantified by the area under the stress–strain curve, which indicates the energy per unit volume needed to initiate defects. The dense FC + LF network has 0.03917 MJ mm⁻³, the branched networks have 0.10973 MJ mm⁻³; the sparse FC + LF network has 0.03503 MJ mm⁻³. A smaller area under the stress–strain curve indicates a lower toughness of the dense FC + LF network compared to the branched networks.

The initiation of fibril rupture can be investigated by qualitatively observing deformation mechanisms in fibrous networks for pure shear, as shown by the deformed FE models (Fig. 4). Different types of fibrous networks have different deformation mechanisms. The short fully cross-linked fibrous networks allow for more fibril reorientation during deformation, the long fully cross-linked fibrous networks exhibit stretching dominant deformation, and the branched fibrous networks exhibit both stretching and bending dominant deformation.

The deformed fibrous networks with critical crack opening are shown in Fig. 5. The critical crack opening indicates the notch opening profile when the crack starts propagating. Blunting was observed at the crack tip in branched fibrous networks (Fig. 5). Two important deformation mechanisms were observed in the deformed fibrous networks. Firstly, the FC + LF networks allow sliding among fibrils at crack tip. Secondly, fibrils in the branched fibrous networks are flexible at the near-tip region. These unconstrained fibrils caused the branched networks to become compliant near the crack. In contrast, the FC + LF networks were confined along the crack opening due to large bonding connectivity. The blunting allows for a large critical crack opening of the branched fibrous networks compared to the dense FC + LF network (Fig. 6). Moreover, all PC + LF networks (i.e. the 20°, the 30° and the 45° branched networks) have a similar critical crack opening compared to the sparse FC + SF network. This suggests that the branched networks and the sparse FC + SF network have comparable toughness.

In addition to the comparison of critical crack opening, damage tolerance of fibrous networks was identified by studying maximum stress σmax of the most-stressed fibrils which occurred at crack tips (Fig. 7). Confined crack tips in the FC+LF networks always demonstrate greater maximum stress compared with the rest of the networks. This large concentrated stress would cause fibrils to rupture and allow the crack to propagate. All PC+LF networks (i.e. the 20°, the 30° and the 45° branched networks) and the sparse FC + SF network have approximately the same critical stress intensity factor KIC, when the maximum stress reaches the fibril strength σf.
4. Discussion and conclusions

The FE results show that the mechanical responses of fibrous networks are affected by fibril length and cross-link density. Next we discuss how these important factors determine nonlinear hyperelastic behavior, and further determine both the stiffness and the toughness of the networks. Then, two important factors which affect networks toughness will be discussed. First, the formations of kinks (Section 4.2) which can result in fibril ruptures were further studied by buckling analysis. Second, blunting (Section 4.3) founded in the branched networks postponed the crack propagation.

4.1. Hyperelastic behavior of fibrous networks

The strain stiffening behavior originates from either the non-affine collective deformation of the fibrous networks, e.g. fibril reorientation (Onck et al., 2005; Heussinger et al., 2007), or the nonlinear viscoelastic mechanical responses...
Moreover, the existing studies links at every intersection point (Onck et al., 2005; Head et al., 2000). These fibril branches are likely to be formed by either interfibrillar fusion or new tip growths (Starborg et al., 2009) and have two distinct features in comparison to chemically cross-linked fibrils. First, new tip growth at branch points suggest long fibrils. Second, the branching suggests that not every intersection point is bonded. On one hand, fibrils which fuse together or newly grown fibril tips have rigid bonding at branch points. On the other hand, there is less evidence of the bonding of overlapping fibrils at the intersection points. These bonded and unbonded intersection points are observed in natural type I collagen (amnion) fibrous network in our SEM image as shown in Fig. 1(a), which is in line with existing studies on collagen gels (Vader et al., 2009).

In addition, different deformation mechanisms were also found in the dense and the sparse networks. The dense fully cross-linked networks exhibit a linear behavior while the sparse fully cross-linked networks and the branched networks exhibit a nonlinear strain-stiffening behavior. The dense networks have approximately seven times greater cross-link density than the sparse networks. As a result, the dense networks have more constraints per fibril that limit reorientation and bending of fibrils during deformation, and this results in their linear behavior.

Interestingly, although the branched networks have relatively smaller cross-link density than the dense FC + LF networks, they have comparable stiffness with the dense FC + LF networks. This reason for having large stiffness at small cross-link density is due to the fact that the stiffness of branched networks is dependent on the fibril density (i.e. sum of fibrils length per unit area) rather than cross-link density (see Figs. 3 and 4). In contrast, the stiffness of fully cross-linked networks is proportional to the cross-link density, which is in agreement with existing studies on polymers (Treloar, 2009).

4.2. Kink formation in deformed fibrous networks

The different deformation mechanisms result in different defect formation. Kinks (inset, Fig. 8) were observed in the FC + LF networks (Fig. 4). The large stress concentration at the sharp edges of kinks caused the fibrils to rupture. On the other hand, crimps (inset, Fig. 8) were observed in the branched fibrous networks (Fig. 4). Fibrils which have very small bending stiffness have very small stress and thus avoiding fibril rupture. Similar to the deformation analysis, fracture analysis shows kinks at the region near the crack in the FC + LF networks. These kinks can cause extra defects in addition to the crack propagation at crack tip.

To explain the formation of kinks and crimps in fibrous networks, buckling analysis was considered. The 20°, the 30° and the 45° branched fibrils have large slenderness and this makes the fibrils buckle into crimps. The slenderness is proportional to the contour length, \( L_c \) defined as the distance between two bonding points as shown in Fig. 4(b). It was calculated in our two dimensional random networks by:

\[
L_c = \frac{f_b A}{\rho_b A + n}.
\]

(Eq. 1)

The fibril density \( \rho_f \) is defined as the sum of fibrils length per unit area and the cross-link density \( \rho_b \) is defined as the sum of bonding point per unit area. A refers to the area of the
Our detailed study on fibrous networks in the vicinity of crack tip suggests that the branched fibrous networks have different stress–strain behavior in the region near-tip and far-tip. The near-tip region is more compliant due to the unconstrained fibrils, while the far-tip region obeys the stress–strain behavior exhibited in the deformation analysis. This small stiffness at crack tip allows crack to blunt instead of propagating (Hui et al., 2003). Interestingly, this compliant region at near-tip is small and dependent on the branch angles. Although this region is small, it results in critical effects in the crack opening field. In contrast, fibrils in fully bonded networks are confined at the crack tip, resulting in similar stress–strain behavior in near-tip and far-tip regions and thus allowing for a small crack blunting effect. Similar behavior has been observed in fracture tests of electrospun fibrous networks (Stachewicz et al., 2011).

Our analysis of fibrous network architectures suggests that the assumption of linear elasticity fails to capture phenomena in the vicinity of a crack. Similar studies have been performed in isotropic lattices (Fleck and Qiu, 2007) and for paper materials (Isaksson and Hagglund, 2009), in which non-affine deformation was investigated in the near-tip region by assuming affine linear elastic deformation at the periphery of FE model. Future work will examine this assumption and consider nonlinear elasticity in the far-field boundary conditions.

One further possible toughening mechanism in soft tissues, which was not examined here, is viscous dissipation. Natural tissues, which consist of fibrous networks, ground substance and water, exhibit time-dependent mechanical behavior (Boyce et al., 2007). Possible mechanisms that govern such behavior include the viscoelastic behavior of a single fibril (Shen et al., 2011), the rearrangement of networks, the viscosity of ground substance, and the friction between networks and ground substance (Liao et al., 2007). Experimental measurements show a longer relaxation time in collagenous tissues than to a single fibril; this suggests that water and ground substance play a crucial role in governing the time-dependent behavior of collagenous tissues. (Shen et al., 2011). Future studies will aim to incorporate various time-dependent mechanisms into this fibrous network model, to consider their varying contributions to soft tissue toughening.

4.4. Concluding remarks

Various studies suggest that the stiffness of fibrous networks can be amplified by increasing the cross-link density of the networks (Head et al., 2003; Mackintosh et al., 1995; Stylianopoulos and Barocas, 2007). Our study highlights that while cross-link density stiffens the fully cross-linked fibrous networks, fibril density stiffens the partially cross-linked networks with long fibrils. A major problem of increasing stiffness by cross-link density is the formation of defects i.e. kinks in dense fibrous networks. The approach of partial bonding among long fibrils in the branched fibrous networks can avoid kinking failure and at the same time maintain the network stiffness. Further, these branched networks form a compliant region in a near-tip region that can avoid crack propagation. The unbounded condition of overlapping fibrils allows sliding of fibrils, which contributes to toughening the networks. Such results give useful guidelines for materials
researchers to produce stiff yet tough materials by mimicking the branched bundles architecture with partial cross-linking, producing a combination of properties that has been always a challenge to achieve in synthetic materials such as electrospun scaffolds (D’Amore et al., 2010; Blond et al., 2008).

Acknowledgments

The authors acknowledge the support from the Ministry of Higher Education, Malaysia.

REFERENCES


