Philosophical Magazine Letters, 2013
http://dx.doi.org/10.1080/09500839.2013.783241

Elasticity of sparsely cross-linked random fibre networks

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(*Received 10 February 2013; final version received 1 March 2013*)

The elastic modulus of two-dimensional random fibre networks is determined for structures in which, the degree of cross-linking is varied. The relationship between the network parameters – fibre axial and bending stiffness, fibre density and degree of cross-linking – and the overall elastic modulus is discussed and presented in terms of a master curve. It is shown that master curves for sparsely cross-linked networks with various degrees of cross-linking can be collapsed to a unique curve, which is also valid in case of fully cross-linked network.

Keywords: fibre network; elasticity; soft matter

1. Introduction

Materials having a random fibre network as the main structural element are frequently encountered in the biological and engineering world. Almost all types of tissue are composed of random fibre networks of various compositions, while the structural element of eukaryotic cells, the cytoskeleton, is a dense composite fibre network made from F-actin and microtubules. The nucleus and cellular organelle are embedded in this network, which transmits across the cell the stress/strain fields produced by the applied tractions. The cytoskeleton is a highly dynamic network which reorganizes itself in response to the applied mechanical excitations, continuously adjusting its degree of cross-linking [1]. In the engineering realm, rubber and gels, paper, various types of nonwovens, etc., personal care products, baby diapers, are just a few examples of fibre-based materials and structures.

In some of these examples, the fibres are bonded to each other, forming a network with a well-defined elastic behaviour, for example [2]; while in some others, fibres are just entangled for example [3, 4]. In non-bonded entangled networks, the fibres slide and rearrange relative to each other leading to hysteresis, rate sensitivity and unrecoverable strains after monotonic loading [5].

Bonded networks exhibit an elastic response with finite stiffness once the density and the density of cross-links are large enough, that is, beyond the stiffness percolation threshold. Stiffness percolation takes place at higher densities than the geometric

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percolation, and for 2D structures with rigid cross-links at all fibre intersection points, it occurs at a density which scales inversely with the fibre length, L_0, as $\rho_p = 6.7/L_0$ [6].

The response of bonded networks is generally non-linear [7], but can be approximated with a linear constitutive equation at small strains [8–12]. The elastic constants depend on system parameters such as the fibre properties – axial and bending stiffness (as well as torsional stiffness in 3D) – the network density and degree of cross-linking. Fibre curl and crimp are also important parameters. Likewise, the existence of a residual, self-equilibrated stress state in the network before deformation influences the elastic properties. The relationship between the small strains elastic moduli and these system parameters has been discussed extensively in the literature. The older works were mostly concerned with relatively dense networks [8,13], case in which the deformation is approximately affine and the network behaves as a (approximately) homogeneous material. Newer literature [9–12] has emphasized that deformation is highly non-affine in low-density networks, such as those representative of some gels and biological materials. Both the affine limit and the non-affine behavior were described using a constitutive law which was presented in the form of a master curve [9–11].

In realistic networks, cross-linking is rarely occurring at all fibre crossings. In paper, where the fibre number density is high, and fibres are pressed together and form H-bonds, the system may be considered densely cross-linked. In most soft materials having a fibre network structure, this is generally not the case. In [14], it was shown that the degree of cross-linking in F-actin networks (e.g. the cytoskeleton) can be controlled by controlling the concentration of the cross-linking protein scruin, such that filaments are not physically bonded to each other at all points where they come in contact or sufficiently close to each other. A similar situation is expected to exist in other biological fibre networks, such as in most collagenous systems.

In this work we examine the variation of the network Young's modulus, E, with the degree of cross-linking, and we show that the previously developed master curve which was obtained for fully cross-linked networks [9–11], remains valid for the sparsely cross-linked systems, provided the density is normalized with a cross-link density-dependent parameter. Therefore, the number of cross-links per fibre must be considered as an additional parameter of the problem.

2. Model

The network studied here is constructed by depositing fibres of length, L_0 in a 2D domain, with random positions of their centroids and random orientation. Rigid cross-links are introduced at points where the fibres intersect, with probability, $\bar{p}$. A rigid cross-link prevents relative translations and rotations of the two fibres at the contact point. A state characterized by $\bar{p} = 1$, in which every contact point is a cross-link is denoted as 'fully cross-linked'. The works reported in references [9–11], refer to such fully cross-linked systems.

The fibres are considered athermal and linear elastic, and hence are characterized by their axial stiffness, $E_f A$, and bending stiffness, $E_f I$, where E_f is the Young's modulus of the fibre and A and I are the cross-sectional area and moment of inertia. In these models, all fibres in the given system are considered identical.

The fibres are represented using the Timoshenko beam model [15]. The total energy of the system is the sum of the strain energies associated with bending, axial and shear deformation, that is,

$$U = \frac{1}{2}\sum_{\text{fibres}} \int E_f I\left(\frac{d\psi(s)}{ds}\right)^2 + E_f A\left(\frac{du(s)}{ds}\right)^2 + \lambda G_f A\left(\frac{dv(s)}{ds} - \psi(s)\right)^2 ds \tag{1}$$

In this expression, $v(s)$ represents the transverse displacement and $\frac{du(s)}{ds}$ is the axial strain at position s along the fibre. The rotation of the fibre cross-section is $\frac{dv(s)}{ds}$, while $\psi(s)$ represents the rotation of a plane which remains perpendicular to the neutral axis of the beam. Hence, $\frac{dv(s)}{ds} - \psi(s)$ represents the shear deformation of the beam; λ is a constant which is considered 0.88 (for beams with circular cross-section).

Due to the pronounced heterogeneity of the network which is introduced by the random process of network generation, the overall mechanical response is affected by strong size effects. In [16], it was shown that the size effect is stronger in low-density networks or in cases in which fibres are soft in bending. Under such conditions, the model size should be at least 15 times larger than the fibre length in order to eliminate the size effect. If the density is high or the bending stiffness of fibres is larger than the axial stiffness, the system size should only be 2–3 times larger than the fibre length. In this work we consider systems large enough to eliminate the size effects in all cases.

The network is deformed by applying boundary conditions along the perimeter of the model, which is a square of size L. The solution is found by minimizing the potential energy, using a finite element solver.

As mentioned above, the system parameters are: the fibre length, L_0, the fibre density, $\rho = NL_0$, where N is the fibre number density, the degree of cross-linking, $\bar{p}$, and the fibre mechanical properties, $E_f I$ and $E_f A$. It has been discussed in the literature [9–12] that the axial and bending stiffness of fibres enter the constitutive equation only through the parameter, $l_b = (\frac{E_f I}{E_f A})^{1/2}$, which indicates the relative importance of the bending and axial stiffness.

3. Results

The objective of the paper is to present a structure-property relation that predicts the overall elasticity of networks with sparse (stochastic) cross-links. The system geometry is discussed first. When the network is fully cross-linked, the fibre segment lengths are Poisson distributed with the mean, $l_c(1)$, which depends on density through the Corte-Kallmes equation $l_c(1) = \pi/2\rho$ [17]. Here it was made explicit that $l_c(1)$ depends on $\bar{p}$, and for fully cross-linked systems, one has $\bar{p} = 1$. It is possible to evaluate the probability distribution function of segment lengths, $p(l,\bar{p})$, in systems with $\bar{p} < 1$ since the sparsely cross-linked system is constructed from the fully cross-linked one by randomly removing cross-links at fibre intersection points. The probability of existence of a segment of specific length, l, in such network is the summation of the probabilities of existence of segments of length l formed by concatenating k (k=1, 2, 3…) segments of the network with $\bar{p} = 1$. Let us call these 'original segments'. The probability to have a segment of total length l formed by concatenating two original segments of length l_1

and l_2 is, $dp_1dl = p(l_1, l)dl_1p(l_2, 1)dl_2\bar{p}(1-\bar{p}) = p(l_1, 1)dl_1p\ (l-l_1, 1)dl\bar{p}(1-\bar{p})$. Considering that $p(l, 1)$ is a Poisson distribution and after integrating over l_1 (which takes values from 0 to l), one obtains $p_1dl = lp(l, 1)\ dl\bar{p}(1-\bar{p})/l_c(1)$. Following the same line of thought, the probability to have a segment of total length l formed by concatenating three original segments becomes $p_2dl = l^2p(l, 1)dl\bar{p}(1-\bar{p})^2/2l_c^2(1)$. This expression can be generalized to k number of original segments. Then, the total probability density to have a segment of length l composed from any number of original segments can be calculated as $p(l, \bar{p}) = \bar{p}p(l, 1)\sum_{k=0}^{\infty}((1-\bar{p})l/l_c(1))^k/k!$, which leads to $p(l, \bar{p}) = \bar{p}/l_c(1)\exp(-\bar{p}l/\ l_c(1))$. Note that, while in the fully cross-linked network the probability density of having a segment of length l is $p(l, 1)$, the equivalent quantity in the network with $\bar{p} < 1$ is $p_0 = p(l, 1)\bar{p}$. The analysis indicates that the distribution function for any cross-link density remains Poisson, with its mean related to the mean of the fully cross-linked network distribution through $l_c(\bar{p}) = l_c(1)\bar{p}$. Figure 1 shows $p(l, \bar{p})$ for several values of $\bar{p}$, with the horizontal axis normalized by $l_c(\bar{p})$ in order to allow the means of all distributions to overlap at 1.This result is expected, given that both network generation and cross-linking are random, uncorrelated stochastic processes.

It should be observed that for a sparsely cross-linked network, the density ρ does not determine unequivocally the mean segment length as in the Corte-Kallmes relation, rather an additional parameter, such as $\bar{p}$, must be considered as, $l_c(\bar{p}) = \pi/2\rho\bar{p}$.

The elasticity of networks with various parameters l_b, ρ and $\bar{p}$ was investigated. Six networks with $L_0 = 0.5$, l_b in the range $(10^{-7}, 10^{-2})$ and $\rho = 100$ were generated and probed by imposing a prescribed uniaxial strain. The cross-linking density was varied by changing parameter $\bar{p}$ from 1 to 0.5; six values of $\bar{p}$ in this range were considered. For each of these 36 systems, ten replicas were generated and the results reported here are averages over these replicas. The data for all these systems are shown in Figure 2. The vertical axis shows the Young's modulus of the network, E, normalized with $\rho E_f A$ and a constant, α, which is a dimensionless quantity equal to 0.38. The variable of the horizontal axis is $w = \log_{10}((L_0/l_c(\bar{p}))^x(l_b/L_0)^y)$. The exponents x and y are changed until the data collapse on a master curve and we obtain $x = 7$ and $y = 2$. The blue (diamond) symbols correspond to the fully cross-linked case, $\bar{p} = 1$. The red (triangles)

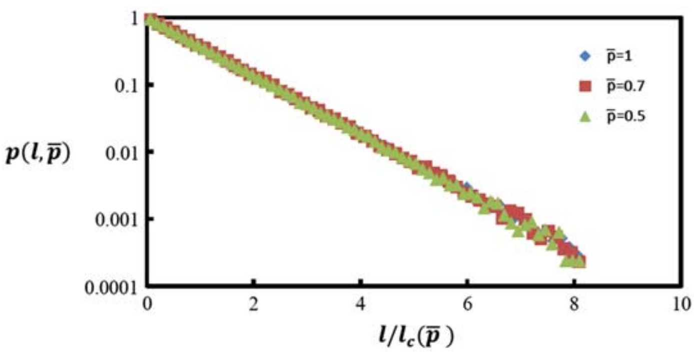

Figure 1. Probability distribution functions of segment lengths for networks with different crosslinking probabilities.

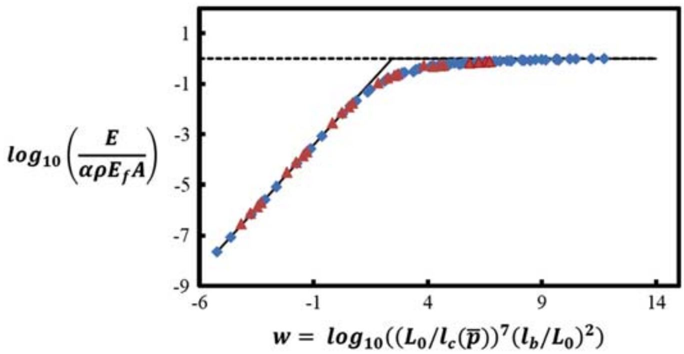

Figure 2. Master curve of Young's modulus E of networks with various sets of parameters ρ, L_0, l_b and $\bar{p}$. The blue (diamond) symbols correspond to fully cross-linked networks, $\bar{p} = 1$, while the red (triangles) symbols correspond to sparsely cross-lined network with $0.5 < \bar{p} < 1$.

represent sparsely cross-linked networks with $\bar{p} < 1$. The data collapse is excellent and it appears that one may define a unique master curve valid for all sparsely cross-linked networks above the stiffness percolation threshold.

In order to underline the novelty of the present work, it is necessary to review the literature on this subject. Master curves of this type have been reported in several publications [9–12]. Fully cross-linked networks ($\bar{p} = 1$) were considered in all these works. In this case, the classical Corte-Kallmes relation holds, and one can write the variable of the horizontal axis as $w = \log_{10}((\rho L_0)^x (l_b/L_0)^y)$, that is, the only relevant parameters are l_b and ρ. The novelty of this work is the observation that if one uses $l_c(\bar{p})$ in place of $l_c(1)$ in w, all data for sparsely cross-linked systems overlap on a unique master curve. The number of independent parameters in w now increases from 3 to 4. It should be noted that the normalization of the vertical axis is independent of $\bar{p}$.

Although it has been discussed in the cited works [9–12], reviewing the physical interpretation of the master curve is useful at this point. The curve has two well-defined regimes. At large values of w, that is for large l_b, large L_0 and/or small $l_c(\bar{p})$, the curve asymptotes to a horizontal, which indicates that $E \sim \rho E_f A$. Note the independence of E of L_0, l_b and $\bar{p}$. In this regime, the deformation is approximately affine and the strain energy is stored predominantly in the axial deformation mode of the fibres. This is reflected in the linear scaling of E with the axial stiffness of fibres, $E_f A$. At low values of w, it results that $E \sim (L_0/l_c(\bar{p}))^7 (E_f I/L_0^2)\rho \sim \rho^8 \bar{p}^7 L_0^5 E_f I$. In this regime, the deformation is highly non-affine and the strain energy is stored primarily in the bending mode of fibres. This reflects in the linear scaling of E with the bending stiffness of fibres, $E_f I$. The very strong dependence of the modulus on the density and on L_0 was discussed before [11]. The transition from the affine to non-affine behaviour is controlled by two non-dimensional parameters, that is $L_0/l_c(\bar{p})$ and l_b/L_0 present in w. The parameter $L_0/l_c(\bar{p})$, which is equivalent to the average number of cross-links per fibre, replaces parameter ρL_0 that appears in the constitutive relation in the fully cross-linked case. The results also show that in the non-affine regime, the elasticity is dictated by the number of cross-links per fibre, $L_0/l_c(\bar{p})$, which is in agreement with the previous theoretical work referring to fully cross-linked networks [18].

In the case of sparsely cross-linked networks, the modulus also depends strongly on parameter $\bar{p}$. A realization of the network, with given density, would deform non-affinely at low l_b and low cross-linking density, while at large l_b or/and large $\bar{p}$, would deform affinely. Given the strong dependence of w on $\bar{p}$, small variations in the cross-linking density has large effects on the degree of non-affinity of the deformation and implicitly on the nature of the constitutive equation of the network.

4. Conclusion

Sparsely cross-linked networks behave similarly with fully cross-linked networks and a unique master curve characterizing the behaviour of systems with any value of $\bar{p}$ has been defined. To make this unifying picture possible, one has to use the mean segment length, which is a function of degree of cross-linking, $\bar{p}$, in the formulation in place of the fibre density, ρ. The elastic modulus is independent of the degree of cross-linking in the affine limit, but is very sensitive to this parameter ($E \sim \bar{p}^7$) in the non-affine regime.

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