

Crosslinking Structure of Keratin: III. Rubberlike Elasticity Originating from Non-Uniform Structures of the Swollen Hair and Wool Fibers

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SYNOPSIS

Hair and wool fibers treated with an 11 *M* LiBr solution containing *N*-ethylmaleimide showed typical rubberlike elasticity in a solution composed of equal volumes of 8 *M* LiBr and diethylene glycol monobutyl ether. Stress-strain relations of the swollen fibers were treated with a two-phase structural model: a mechanically stable phase of higher crosslinked domains and a rubbery phase with lower crosslink density. Stress-strain curves were analyzed by applying non-Gaussian chain statistics to the swollen keratin network, including microdomains, which act as reinforcing filler particles in rubber. Swollen hair showed about 2.3 times higher modulus than wool. It has been suggested that: (1) the difference in the modulus between the two keratins is attributable to the difference in the volume fraction of domains, and (2) the crosslink density of rubbery phase in hair is virtually identical to that in wool.

INTRODUCTION

The fibrous components of wool and hair consist of intermediate filaments (IF) that are embedded in a matrix of protein chains so-called intermediate filament associated proteins (IFAP). The disulfide linkages in the proteins are responsible for the chemical inertness of the α -keratin materials and for their characteristics mechanical properties. The pattern of the disulfide bonding within the fiber is still a largely unresolved area.

Recently, the disulfide bonding with the IF and IFAP was discussed on the basis of the sequential and conformational structure of the proteins.¹ The macrofibril, which consists of microfibrils and matrix, might be considered a heavily crosslinked network polymer. The crosslinking structure of the disulfide linkages in the intact protein polymer has remained an interesting uncharted problem.² In this context, rubber elasticity theories have been applied to assess crosslinking in keratin.³⁻⁷

It has been reported that the swollen hair and wool keratin fibers prepared by the treatment with an 11 *M* LiBr solution containing *N*-ethylmaleimide show typical rubberlike elasticity in a mixed solution composed of equal volumes of 8 *M* LiBr and diethylene glycol mono-*n*-butyl ether. Further the retractive forces of the swollen fibers are nearly entropic so far as the extension ratios do not exceed the values of ca. 1.30, and no crystallization occurs at higher extensions.^{6,8} However, a well-known non-isotropic molecular structure of keratin made up of low-sulfur (α -helical) and high-sulfur (globular) regions still remains even when the fiber reached to a highly swollen state. Owing to the deviation from random network, application of elastic equation of state derived from conventional rubber elasticity theory to such a heterogeneous and densely crosslinked system becomes clearly inaccurate.

From the results of thermodynamical and non-Gaussian treatments of the stress-strain relationships for the swollen keratins, it has been suggested that the swollen keratin fiber consists of the two-phase structure similar to A-B-A block copolymers⁸: one is a mechanically stable phase of a densely crosslinked domain and the other is a continuous rubbery phase with a lower crosslink density.

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It has been demonstrated further that a simple elastic equation is applicable to chemically modified keratins such as hair and wool fibers treated with aqueous potassium cyanide, and reduced with tri-*n*-butylphosphine solutions.^{8,9} These chemical treatments lead to considerable decreases in the structural nonuniformity and, as a result, nearly random network is formed.

This paper deals with the application of the non-Gaussian theory to the equilibrium stress-strain curves obtained for swollen fibers in the diluent, and takes into account the filler effect of the domains on the network elasticity. The aim of this study is to estimate the volume fraction of domains in the fiber, and the number average molecular weight between crosslinks in rubbery regions, and to make a brief discussion on the crosslinking structures between different keratins.

THEORY

In treating elastic properties of swollen keratin, it is primarily assumed that densely crosslinked globular regions attributable to the stable domains cannot be deformed during the swelling and fiber extensions, namely, swelling and deformation of keratin fiber are only related to the randomly crosslinked rubbery phase with lower crosslink density.

The retractive force f for swollen rubber at constant volume V and temperature T is related to the entropy of elastic deformation, S_e , as in eq. (1):

$$f = -T(\partial S_e / \partial L_r)_{T,V}, \quad (1)$$

where L_r is the stretched length of the swollen rubber.

For the two-phase system including domains, the length L_r pertains only to that portion of the sample actually comprised of elastically active chain. If a cube of a swollen sample of the length L_s is stretched by a force f along the z -axis, it will be converted into a parallelepiped of reduced dimension under constant volume.

The volume of swollen sample, L_s^3 can be written by eq. (2):

$$L_s^3 = (L_{rs} + L_d)^3 = V_{rs} + V_d, \quad (2)$$

where L_{rs} and L_d are the effective length of rubber matrix and domain for stretching of the swollen sample with cross-sectional area L_s^2 and V_{rs} and V_d

are the corresponding volume in the swollen unstretched sample, respectively.

From eq. (2), we obtain eqs. (3) and (4):

$$V_{rs} = L_{rs}(L_{rs} + L_d)^2 = L_{rs}L_s^2 \quad (3)$$

and

$$V_d = L_d(L_{rs} + L_d)^2 = L_dL_s^2. \quad (4)$$

Here, the stretching ratio α for rubber matrix is represented as eq. (5):

$$\alpha = L_r / L_{rs}. \quad (5)$$

The stretching ratio λ for swollen sample is given by eq. (6):

$$\begin{aligned} \lambda &= L / L_s = (L_r + L_d) / (L_{rs} + L_d) \\ &= (\alpha + L_d / L_{rs}) / (1 + L_d / L_{rs}), \end{aligned} \quad (6)$$

where L is the elongated length of the swollen sample.

From eqs. (3), (4), and (6), we obtain the relation between α and λ in a simple form as given by eq. (7):

$$\alpha = \lambda(1 + R_d) - R_d, \quad (7)$$

where $R_d = V_d / V_{rs}$.

Again, from eqs. (1) and (5), the force f can be rewritten by eq. (8):

$$f = -(T / L_{rs})(\partial S_e / \partial \alpha)_{T,V}. \quad (8)$$

For simple extension of the swollen sample including domain, entropy change in rubbery phase, $\partial S_e / \partial \alpha$ is given by an usual rubber elasticity theory for swollen polymer network as eq. (9):

$$(\partial S_e / \partial \alpha)_{T,V} = -R\nu\phi_2^{-2/3}(\alpha - \alpha^{-2}), \quad (9)$$

where ν is the number of chains in rubbery phase and ϕ_2 is defined by eq. (10):

$$\phi_2 = V_{0,r} / V_{rs}, \quad (10)$$

where $V_{0,r}$ is the rubber volume in the unswollen sample.

From eqs. (8) and (9), we obtain eq. (11):

$$f = (RT\nu / L_{rs})\phi_2^{-2/3}(\alpha - \alpha^{-2}). \quad (11)$$

Dividing by the initial swollen cross-sectional area L_s^2 , the retractive force per unit swollen cross-sectional area, τ , can be written by eq. (12):

$$\tau = (RT\nu/L_{rs}L_s^2)\phi_2^{-2/3}(\alpha - \alpha^{-2}). \quad (12)$$

Again, from eqs. (3), (10), and (12), we obtain eqs. (13) and (14):

$$\tau = (RT\nu/V_{rs})\phi_2^{-2/3}(\alpha - \alpha^{-2}) \quad (13)$$

and

$$\tau = (RT\nu/V_{0,r})\phi_2^{1/3}(\alpha - \alpha^{-2}). \quad (14)$$

The volume fraction of dry sample to the swollen sample, v_2 , is experimentally obtainable value, and is given by eqs. (15) and (16):

$$v_2 = (\phi_2 + R_d)/(1 + R_d) \quad (15)$$

and

$$\phi_2 = v_2(1 + R_d) - R_d. \quad (16)$$

Thus, from eqs. (14) and (16), using the crosslink density in rubbery phase, we obtain eq. (17):

$$\tau = (\rho RT/M_c)[v_2(1 + R_d) - R_d]^{1/3}(\alpha - \alpha^{-2}), \quad (17)$$

where ρ is the density of the rubber matrix in unswollen state and M_c is the number average molecular weight between crosslinks on protein chains in rubber regions.

In considering the filler effect of microdomains, which act as filler particles dispersed in the rubbery network and influence overall elastic properties as reinforcing the elastomer, the resulting reinforcement has been treated by Guth¹⁰ and recently by Leonard¹¹ and ΔS_e^* the entropy change of elastic deformation of rubbery phase including domain has been written as eq. (18):

$$\Delta S_e^* = \Delta S_e \gamma(\kappa, \phi_d), \quad (18)$$

where $\gamma = 1 + a\kappa\phi_d + b\kappa^2\phi_d^2$. Here, ϕ_d is the volume fraction of domain in the swollen sample, which equals to $R_d/(1 + R_d)$, κ is the shape factor as the length: breadth ratio for rod-like filler, and a and b are constants. Guth shows empirically that for $\kappa \approx 1$ in the case of spherical filler particle in a GR—S rubber carbon black system, $a = 2.5$ and $b = 14.1$,

while for $\kappa \gg 1$, $a = 0.67$ and $b = 1.62$, respectively.¹⁰ We may assume for $\kappa \geq 1$ the values of two constants are equal to those in the case of spherical shape.

As reported previously,⁸ Mooney–Rivlin plots for swollen keratins tend to deviate from the straight line even at lower extension ranges. This implies that the swollen keratin chain is non-Gaussian. A three-chain model theory¹² derived from non-Gaussian chain statistics might be considered applicable for rubber elasticity of the swollen keratins. For analysis of the stress–strain curve of the swollen fiber including domain, non-Gaussian expression term, $(\sqrt{n}/3)[\mathcal{L}^{-1}(\alpha/\sqrt{n}) - \alpha^{-3/2}\mathcal{L}^{-1}(1/\sqrt{\alpha n})]$, a correction term for network defects as dangling ends, $(1 - 2M_c/M)$, and filler effects represented by eq. (18) are introduced into eq. (17).

A modified equation can be obtained for $\kappa \geq 1$ as eq. (19):

$$\begin{aligned} \tau^* &= (\rho RT/M_c)[v_2(1 + R_d) - R_d]^{1/3} \\ &\times (1 - 2M_c/M)(\sqrt{n}/3)[\mathcal{L}^{-1}(\alpha/\sqrt{n}) \\ &\quad - \alpha^{3/2}\mathcal{L}^{-1}(1/\sqrt{\alpha n})]\gamma \quad (19) \\ \alpha &= \lambda(1 + R_d) - R_d \\ \gamma &= 1 + 2.5\kappa[R_d/(1 + R_d)] \\ &\quad + 14.1\kappa^2[R_d/(1 + R_d)]^2, \end{aligned}$$

where τ^* is the retracative forces at the extension ratios λ for swollen sample, n is the number of segments equivalent to random chain, $\mathcal{L}^{-1}(X)$ is the inverse Langevin function, and M is the number average molecular weight of primary molecule forming rubber matrix. The non-Gaussian expression may be reduced to $(\alpha - \alpha^{-2})$ for small deformation of the network.

EXPERIMENTAL

Materials

Purified human hair and Lincoln wool were prepared as reported previously.⁸ Tri-*n*-butyl phosphine (TBP) and *N*-ethylmaleimide (NEMI) used were special reagent grade. Diethylene glycol mono-*n*-butyl ether (BC) were obtained by distillation of commercial products under reduced pressure in the presence of a small amount of sodium hydroxide after dehydration with anhydrous sodium sulfate overnight.

Reduced with TBP and subsequently *S*- β -cyanoethylated human hairs were prepared as described in a previous paper.⁸

Preparation of Swollen Fibers

The fibers (50 mg) were treated with an 11 *M* LiBr aqueous solution containing 10^{-2} *M* NEMI (2 mL) at 90°C for 1 h, and subsequently immersed in a mixed solution composed of equal volumes of 8 *M* LiBr and BC at room temperature. The swollen fibers thus obtained were subjected to mechanical tests.

Mechanical Tests for Swollen Fibers

The stress-strain relations for the swollen fibers were obtained in the mixed solution at 50°C. The sample was elongated at a rate of ca. 10% min to ca. 40% extension for hair and 50% for wool, and conditioned by repeated loading and unloading. Equilibrium forces were measured at constant elongations at the intervals of ca. 2–4% extension. The sample was elongated at a constant length *L*, which corresponds to the extension ratio λ , and allowed to relax for a time until an equilibrium force was obtained. The relaxation times required for measurement of equilibrium forces were different among the fibers under extension at different strain ratios. The longest relaxation time observed was ca. 1 h at the highest extension of swollen hair.

Stresses referred to the average cross-sectional areas of the swollen and unstrained fiber, τ^* , were used for construction of stress-strain curve. The average cross-sectional area was calculated by assuming a circular cross-section of the sample from the average value of the swollen diameter measured directly under a microscope at room temperature, since the bulk coefficient of thermal expansion of the swollen fiber was substantially zero in the range from 20–70°C.⁸

The volume fraction of keratin materials in swollen sample, v_2 , was calculated by the equation: $v_2 = (d_D/d_S)^2 (l_D/l_S)$, where d_D and d_S are the diameters of dry and swollen state, respectively, and l_D and l_S are the corresponding lengths of unstrained fiber. Detailed methods for determination of these values were described in a previous paper.⁸

RESULTS

Random Network System

For the system with no domain, $R_d = 0$ in eq. (19), then $\alpha = \lambda$ and $\gamma = 1$, we obtain eq. (20):

$$\tau^* = G(\sqrt{n}/3) [\mathcal{L}^{-1}(\lambda/\sqrt{n}) - \lambda^{-3/2} \mathcal{L}^{-1}(1/\sqrt{\gamma n})], \quad (20)$$

where the shear modulus of swollen fiber, $G = (\rho RT/M_c)v_2^{1/3}(1 - 2M_c/M)$.

If our swollen keratin system is a random network with no domain, eq. (20) may be applicable over the whole extension range of fiber. Here, the Langevin function $Y = \mathcal{L}(X)$ is written by eq. (21) and the relation between *X* and *Y* as being the asymptotic approach to unity is as shown in Figure 1.

$$Y = \mathcal{L}(X) = \coth X - (1/X). \quad (21)$$

The corresponding inverse Langevin function $X = \mathcal{L}^{-1}(Y)$ can be usually obtained by series expansion. The curve for series expansion to the fourth term is also shown in Figure 1. These results show that in the series expansion to the fourth term, a good approximation can be obtained in the range of *Y*-value from 0 to about 0.6, and the approximation, however, becomes inadequate over the values of the above range. Application of eq. (20) for a system of a relatively high degree of crosslink density such as swollen keratin, which is expected to be comprised of molecules with an equivalent random link *n* less than 5, clearly needs the use of the expansion series including more higher terms. It is more convenient to evaluate the *X* values from the table of the function $Y = \mathcal{L}(X)$ made up on a computer rather than from the series expansion. A detailed table was constructed by dividing into 2,000 intervals for *Y*-axis between the values of 0 and 1.

Figure 2 shows the stress-strain curves of human hair, Lincoln wool, and reduced human hair. Fitting the experimental data for eq. (20) with suitable choice of parameters M_c and *n*, we can evaluate the values of these parameters. It was attempted with

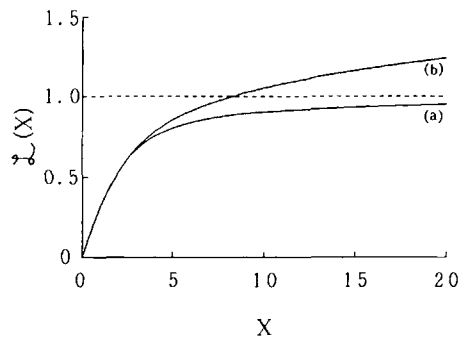


Figure 1 Relationships between *X* and *Y* of the Langevin function $Y = \mathcal{L}(X)$: curve (a), the Langevin function representing asymptotic approach to unity; curve (b), the Langevin function obtained from series expansion of inverse Langevin function to the fourth term, $X = \mathcal{L}^{-1}(Y) = 3Y + (9/5)Y^3 + (295/175)Y^5 + (1539/875)Y^7$.

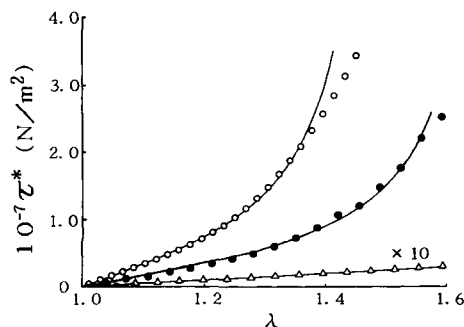


Figure 2 Relationships between equilibrium stress and strain for swollen human hair, Lincoln wool, and reduced and subsequently *S*- β -cyanoethylated human hair: (○), human hair; (●), Lincoln wool; (△), reduced and *S*- β -cyanoethylated human hair; (—), lines fitted to experimental data by eq. (20).

the aid of a computer to make fit the equation, [eq. (20)], to experimental data with these adjustable parameters using a Damping–Gauss method of non-linear least squares. These parameters can be obtained by using the data over the whole range of entropy-dependent extensions that correspond to about 25% for hair, 30% for wool, and 60% for reduced hair, respectively.⁸ The results fit well to experimental data and are shown by the solid lines in Figure 2. The values obtained for parameters are shown in Table I. Here, the number average molecular weight of primary molecule of the network chains is assumed as 5.0×10^4 for the molecular weight of low-sulfur proteins in wool keratin.¹³

The values obtained for M_c , n , and the number of amino acid residues per segment n_r are also shown in Table I. The n_r values were calculated by the equation: $n_r = M_c/nM_0$, where M_0 (=115) is the average molecular weight of amino acid residues of the low-sulfur protein in wool.¹³ The length equivalent to random chain segment is dependent on primary structure of macromolecule, namely, the composition and the sequence of amino acid residues in protein.

The number of amino acid residues per segment that equals the characteristic ratio, b ($=\langle r_0^2 \rangle / n_b l_b^2$), is in the range 9.0 ± 0.5 for a number of homopolymeric polypeptides.¹⁴ In this expression, $\langle r_0^2 \rangle$ is the unperturbed mean-square end-to-end length of the free polymer chains, n_b the number of peptide units, and l_b the distance between successive α -carbon atoms. A large variety of denatured globular proteins in which disulfide linkages are broken by reduction occur in random coil form and the corresponding value, which equals ~ 4.2 ,^{15,16} was also found to be approximately constant.

The n_r values obtained for unreduced human hair and Lincoln wool (Table I) are considerably less than the values reported on various proteins in a variety of solvents.^{14,15} We may also expect that the ratio of M_c/n or n_r value is constant for both reduced and unreduced keratins. The results shown in Table I are, however, significantly different between the reduced and unreduced keratins. These results clearly indicate, therefore, that application of eq. (20) is inaccurate for the swollen unreduced keratin systems. On the other hand, it has been evidenced that from a variety of experimental sources the reduced hair and wool have an elasticity from randomly crosslinked network.^{8,9} The n_r value obtained as 10.9 for the reduced hair is ca. 2.6 times larger than those of usual globular proteins in random form. This seems to be appropriate for the keratin molecules in the diluent since the disulfide crosslinks may restrict the rotational motion of the chains near the crosslinks.

Two-Phase System

It has been shown that the swollen keratin is composed of densely crosslinked domains embedded in continuous, lightly crosslinked rubbery phase, and the elastic equation of state for the two-phase system is derived as eq. (19). Fitting the experimental data, τ^* , λ , and v_2 for eq. (19) with suitable choice of parameters, R_d , M_c , and κ , we can evaluate these parameters. It was assumed, here, that the segment

Table I Results Obtained from eq. (20)

Samples	Disulfide Content* ($\mu\text{mol/g}$)	v_2	M_c (g/mol)	n	M_c/n (g/mol)	n_r
Reduced and <i>S</i> - β -cyanoethylated human hair	91.6	0.209	7,920	6.34	1,250	10.9
Human hair	662.5	0.703	607	2.30	264	2.3
Lincoln wool	407.0	0.603	832	2.88	289	2.5

* Ref. 8.

length (M_c/n) of the keratin chains is the same for both reduced and unreduced keratins. It appears to be reasonable to take the value of 1,250 as the segment length obtained for the reduced hair (Table I). The κ -value was determined by well fitting for eq. (19) to give a value of 1.6 for both hair and wool keratins. The other parameters evaluated are shown in Table II. The shear modulus of the swollen fiber, G , is largely dependent on the volume fraction of domains, ϕ_d , rather than the value of M_c or crosslink density ρ/M_c in the rubbery regions. Here, the density of the rubbery phase is assumed for calculation to be equal to the fiber density, ρ . It is notable that the number of crosslinks in the rubbery phase is approximately the same for the unreduced keratins.

DISCUSSION

Modulus of Swollen Fiber

The results in Table II suggest why hair has higher modulus than wool. It has been shown that the shear modulus of swollen keratins is proportional to their cystine content.⁸ The present results clearly show that the difference in modulus between the keratins is due to the difference in the volume fraction of domains and to their reinforcing effects as filler particles dispersed within the rubber matrix.

Number of Crosslinks in Rubber Regions

It has been believed that the soluble *S*-carboxymethylated high-sulfur proteins (SCMKB) from keratin originate from the globular matrix and the soluble *S*-carboxymethylated low-sulfur proteins (SCMKA) originate from the crystalline microfibrils. The molecular weight of SCMKA proteins ranging from 45,000–60,000 has been reported.¹⁷ It is appropriate now to consider that the low-sulfur protein chains pertain to the rubbery phase in the swollen fiber. Crewther and Dowling reported¹⁸ that SCM-cysteine content in SCMKA fractions from

Merino wool ranged from 33–41 residues per 1,000 amino acid residues, which corresponds to 14–18 mol per chain with the mean molecular weight of 50,000 and the mean residue weight of 115.¹³

From the M_c value of the wool shown in Table II, the average number of crosslinking sites can be calculated to be about 12 mol (= 50,000/4,020) per chain by assuming a random distribution of the crosslinks. This value seems to be reasonable for the following reasons: (1) the actual number of cystine crosslinks is less than the analytical values for SCM-cysteine, which include the entities from free cysteine residues existing in the intact proteins; (2) the number of crosslinks estimated from the mechanical measurement is less than the amount of chemically analyzed cystines when the intramolecular cystine crosslinks are involved; and (3) the distribution of crosslinks is not random and some cystine residues occur in too near sites to play a role as different intermolecular crosslinks.¹⁹

Further studies will be needed to clarify whether the number of crosslinks present in rubber is almost the same or not for a variety of keratins.

Volume Fraction of Domains in Keratin

Keratin fiber consists of various morphological components: two major components of orthocortex and paracortex, and minor components of cuticles, nuclear remnants, intramacrofibillar materials, cell membrane complex. With extension of the swollen fiber, microfibrillar aggregates in cortex regions may probably be considered to act as force-bearing components. It seems unlikely that the minor components amounting to about 25.9% of the fiber (fine wool)²⁰ are greatly concerned with the stress-strain properties. Little contribution of the scale structures to the stress-strain behavior of the swollen fiber has been found for wool and for human hair, which has multiple layers of cells in the cuticle.⁸

With respect to the amounts of microfibrils and matrix in different type of cortex, it has been shown

Table II Results Obtained from eq. (19)

Samples	ρ^a (g/cm ³)	$10^{-6}G$ (N/m ²)	R_d	ϕ_d	M_c (g/mol)	$10^4\rho/M_c$ (mol/cm ³)	n	ϕ'_d
Reduced and <i>S</i> - β -cyanoethylated								
human hair	1.28	0.19	0.000	0.000	7,920	1.62	6.34	0.000
Human hair	1.30	11.3	0.659	0.397	4,050	3.21	3.24	0.562
Lincoln wool	1.30	4.95	0.359	0.264	4,020	3.23	3.22	0.438

^a Ref. 8.

that: (1) the proportion of paracortex in fine wool is about 30–50% of the total amount of the cortex, and it increases in coarse fiber,^{20–23} and (2) the percentage of volume occupied by microfibrils in the paracortex and the orthocortex are about 45 and 74%, respectively.²⁰ Bradbury also showed that the volume ratio of microfibrils to matrix is about 60 : 40 for fine Merino wool. The ratio for Lincoln wool in coarser than Merino wool is, therefore, expected to be less than that for Merino wool.²⁴ At present, there has been no available information for human hair.

Here, the volume fraction of domains in unswollen sample, ϕ'_d , can be calculated by eq. (22):

$$\phi'_d = R_d/v_2(1 + R_d). \quad (22)$$

The calculated values are also shown in Table II. This result in value of 48.3% for Lincoln wool appears to be very reasonable from the above discussion. The ϕ'_d value for hair is about 1.3 times larger than that for wool. It is emphasized that these results can be explained by the structure of keratin, although assumption has been made that the domains are rigid and stable to the swelling and the deformation of fiber.

Strict interpretations of the shape factor, κ , and the interaction between domain surface and rubbery network chains remain further investigations.

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