Supplementary Information to:

Multi-scale Progressive Failure Mechanism and Mechanical Properties of Nanofibrous

Polyurea Aerogels

Chenglin Wu,^{a*}, Tahereh Taghvaee^b, Congjie Wei^a, Arman Ghasemi^c, Genda Chen^a, Nicholas

Leventis^b, Wei Gao^c

 ^a Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO 65401,

^b Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401

^c Department of Mechanical Engineering, The University of Texas at San Antonio, San Antonio,

TX, 78249, United States

*Corresponding Author, Email: wuch@mst.edu

Submitted to Soft Matter April 2018

Note 1: Molecular Dynamics Modelling

N1.1 Force field The individual components of the total force field energy are:

where N_{bond} , N_{angle} , $N_{torsion}$ and N are the numbers of bonds, angles, dihedrals and atoms, respectively; r_{ij} and K_{bij} are the distance and coefficient of bond between particles *i* and *j*, respectively; θ_{ijk} and K_{aijk} are the angle and coefficient of angle formed among particles *i*, j and k, respectively; ϕ_{ijkl} and K_{nijkl} are the dihedral angle and coefficient of dihedral among particles i, j, k and l, respectively. For the Lenard-Jones contribution, ϵ_{ij} is the depth of the potential and σ_{ij} is the finite distance at which the inter-particle potential is zero. They can be determined from geometric combination rules such as $\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{\frac{1}{2}}$ and $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{\frac{1}{2}}$. For the Coulomb electrostatic interactions, q, is charge and ϵ is the dielectric constant.

All atoms optimized potential for liquid simulation (OPLS- AA) contains functional forms for bond, angle, and dihedral deformations among bonded interactions. We use this force field for all our MD calculation since it was found in close agreement with the density functional theory [32-34]. For any atom type in the polyurea structure, force field parameters were chosen by matching the atom type with its corresponding atom defined in the OPLS parameter database. The cut-off for all MD simulations was also considered as 10 Angstrom.

N1.2 Molecular structures and properties Polyurea aerogels (PUAs) result from the reaction of aliphatic triisocyanates and water [3, 4], forming interconnected polymer chains with isocyanurate cores and urea linkage as illustrated in Fig. S1a-b. By comparing the atomic structures simulated from molecular dynamics with x-ray diffraction results, about eight polymer chains were identified in a primary particle as shown in Fig. S1c. The polymer chains of various primary particles were entangled together to form bonding, eventually giving rise to a secondary particle as illustrated in Fig. 3d. The open polymer chains in the outer primary particles of each secondary particle were randomly connected to form a fibrous structure of PUA, as illustrated in Fig. S1e. As the basic building block, the primary particle is the material genome for the mechanical properties, which will be the focus of the MD simulation.



Fig. S1 Hierarchical structures of PUAs: (a) chemical structure of isocyanurate core with urea linkages, (b) interconnected polymer chains, (c) primary particle formed with cluster of polymer chains, (d) secondary particle formed with cluster of primary particles, (e) network nanostructure of PUAs formed with linked secondary particles.

For the primary particle, our system of study consists of 8 layers of third generation aromatic polyurea chains (Fig. S2a). ant it has an initial configuration as it shown in Fig. S2b, in which, two stacks of layers are perpendicular together, where, each stack consists of four layers and the distance between the layers is equal to 4 Angstrom as illustrated in Fig. S2b. As shown in Fig. S2c-f, the polymer chains start to tangle at the beginning stages (30 ps and before), as time elapses, the tangled chains form a sphere, which has radius approximately 6.4 nm. This is quite close to the 7-nm estimation from experiment. To demonstrate the strong interactions between the primary particles, we conducted a tension simulation by fixing the box size and applying a uniaxial stretch of two primary particles of with different overlapping distances as shown in Fig. S1g. All of the force-distance responses show linear, nonlinear ascending stages followed by a peak strength and the slow force-decreasing force stage. The failure was found to initiate when the stable distance for LJ potentials between particles was exceeded in the contact zone between two particles. The residual strength mainly comes from the polymer chain entanglement. In addition, the tensile and residual strength increase with the increasing overlapping distance. This indicates that the polymer chain entanglement mainly contributes to the strength of the PUA nanostructures. However, the elastic stiffness, which is the slope of the linear ascending stage, does not vary significantly. This indicates that the elastic modulus of all PUA is constant due to the same internal structure of the primary particle. Therefore, we can assume a constant elastic's modulus for the base materials of all PUAs. However,

without knowing the exact overlapping distance, the specific yield and residual strength remain undetermined from MD results. It also should be noted here that the viscoelasticity was not modelled since the modelling time is relative short. However, this approximation will not reverse the claimed assumption that the base material properties should be same given the same primary particle structure.



Fig. S2 Determine primary structure of PUA: (a) aromatic chain monomer component and structure, the brown, red, green and blue colors indicate carbon, oxygen, nitrogen, and hydrogen atoms, respectively, (b) initial configuration of stacked chain structure for

primary particle, (c) primary particle structure at t = 0 s prior to annealing, (d) t = 90 ps, (e) t = 200 ps, (f) t = 2ns after annealing. (g) Force-distance relationship of two primary particles with overlapping distances of: 2 nm (red), 4 nm (black), and 6.4 nm (blue), insert shows failure process and evolution of connecting radius during separation.

Note 2: Extraction of Elastic Relaxation Modulus

From the proposed approach by Huang and Lu [16], the force (P) and displacement ($^{\delta}$) relation for a linearly ramped displacement loading, $^{\delta}(t) = \delta_{0}t$, can be expressed as,

$$P(t) = \frac{4\delta_0^2}{\pi (1 - v^2) tan\alpha} \int_0^t E(t - \xi) \xi d\xi$$
(S1)

where $\alpha \approx 70.5^{\circ}$ for Berkovich tip, which can be re-written as,

$$E(t) = \frac{\pi (1 - v^2) tan \alpha d^2 P(t)}{4 d\delta^2}$$
(S2)

Therefore, by selecting the form for the relaxation modulus, we have

$$E(t) = E_{\infty} + \sum_{i=1}^{N} E_i e^{-\lambda_i t}$$
(S3)

Where E_{∞} is the time independent elastic modulus, E_i and λ_i are the time dependent coefficients. By fitting the experimental data as illustrated in Fig. S3, the extracted values for PUA-11, 16, and 24 are,

$$E(t)_{11} = E_{\infty,11}(1 + C_{11}e^{-0.1t} + D_{11}e^{-0.01t})$$
(S4a)

$$E(t)_{16} = E_{\infty,16} (1 + C_{16} e^{-0.1t} + D_{16} e^{-0.01t})$$
(S4b)

$$E(t)_{11} = E_{\infty,24} (1 + C_{24} e^{-0.1t} + D_{24} e^{-0.01t})$$
(S4c)

After fitting all experimental data, it was found that E_{∞} varies with indentation depths while *C* and *D* remains almost constant for each type of PUA. The extracted values for *C* and *D* are listed in Table S1. We also found that these coefficients change slightly for different type of PUAs.

Table S1 Time-dependent coefficients for PUAs

	PUA-11	PUA-16	PUA-24
С	0.051±0.005	0.045±0.003	0.048 ± 0.006
D	0.11±0.002	0.12±0.007	0.11±0.004





Fig. S3 Extraction of elastic relaxation modulus (a) typical force-displacement response,(b) fitting between experiment and analytical values.

Note 3: Porosity Dependent Strain Hardening

The isotropic strain hardening is coupled with the porosity variation. In this model, the total elastic strain energy density of a material integration point W_e at the onset of yield for a hydrostatically pressurized condition is,

$$w_e = \int_{0}^{\varepsilon_{ij}} \sigma_{ij} d\varepsilon_{ij} = \int_{0}^{\varepsilon_{ij}} (s_{ij} + p\delta_{ij}) (de_{ij} + d\epsilon\delta_{ij}),$$
(S5)

where σ_{ij} is the total stress tensor; ε_{ij} is the total elastic strain tensor, $p = \frac{1}{3}\sigma_{kk}$ is the

hydrostatic pressure, δ_{ij} is Kronecker delta, e_{ij} is the deviatoric strain tensor; $\epsilon = \frac{1}{3} \varepsilon_{kk}$ is the hydrostatic strain. The dot product of the deviatoric tensor gives the strain energy density,

$$w_e = \frac{1}{E} \left(\frac{1}{1 + (\eta/3)^2} \right) \left(\sigma_e^2 + \eta^2 p^2 \right)$$
(S6)

Where $\sigma_e = \left(\frac{3}{2}S_{ij}S_{ij}\right)^{1/2}$ is von Mises stress, S_{ij} is the stress deviator, η defines the ellipcity of the yield surface, which is defined by an equation of plastic Poisson's ratio

$$\eta = \sqrt{\frac{9(1-2v_p)}{2(1+v_p)}}$$
, the plastic Poisson's ratio $v_p \stackrel{\text{def}}{=} -\frac{d\varepsilon_{p11}}{d\varepsilon_{p33}}$, with ε_{p11} , ε_{p33} are the transverse and loading directional component of the plastic strain tensor respectively under uniaxial compression. Note that when $v_p \approx 0$ (which was found to be the case based the uniaxial compression experiment [19]), $\eta = \sqrt{4.5}$, which is significantly higher than the case of incompressible von Mises plasticity where $\eta = 0$.

At uniaxially stressed state, the total elastic strain energy density is then $w_e = \frac{\bar{\sigma}^2}{2E}$, where $\bar{\sigma}$ is the uniaxial stress. If we assume the critical value for the elastic strain energy density remains the same for different stress-states, then the uniaxial yield stress can be expressed as,

$$\bar{\sigma} = \sqrt{\left(\frac{1}{1+(\eta/3)^2}\right)} \left(\sigma_e^2 + \eta^2 p^2\right).$$
(S7)

This gives us the yield function for multi-axial loading in the form of

$$\Phi = \sqrt{\frac{1}{1 + (\eta/3)^2}} (\sigma_e^2 + \eta^2 p^2) - \sigma_e = 0.$$
(S8)

Given this yield function, the plastic strain ε_{ij}^p is normal to the yield surface and is then defined under the flow-rule with the consistency requirement as,

$$d\varepsilon_{ij}^{p} = \frac{1}{H_{p}\partial S_{ij}\partial S_{kl}} dS_{kl}.$$
(S9)

Where $H_p = \frac{d\overline{\sigma}}{d\overline{\varepsilon}_p}$ is tangent hardening modulus which can be obtained from uniaxial stress versus the plastic strain relationship.

Note 4: Characteristics of PUA Nanostructures

Table 1 summarizes material characterization data pertinent to this work. Bulk densities (ρ_b) increased from 0.123 g cm-3 to 0.244 g cm-4 for PUA-11 to PUA-24. Skeletal densities (ρ_s) remained constant, as expected from open porosity, Π , which, therefore, decreased in reverse order to ρ_b . The skeletal framework consists of interconnected fibres, which at higher magnification appear as strings of fused beads in all three types of samples. By SANS, all three skeletal frameworks consist of about same-size primary particles (7 nm in radius) with fuzzy interfaces (high-Q slope>4.00 – Q: scattering vector). From the SANS results, the primary particles formed closely-packed secondary particles (within a low-Q slope of 3.0). The radius of the secondary particles ranged from 17 to 24 nm, which is in good agreement with the average size of the beads (about 40 nm in diameter) as observed from SEM. From these SEM images, all PUA share similar geometrical features in terms of randomness in cell shapes and size as shown in Fig.2. Each ligament of the network structure has a slenderness ratio (length over radius) above 10. Together with the interconnected structures, a bending dominant deformation mechanism is expected under compression.

The post-indentation sites as illustrated in Fig. S4a were scanned using atomic force microscopy (AFM). No significant pile-ups were observed from both SEM and AFM images. The distinctive ridges following the shape of the Berkovich tip also indicate strong plastic behaviors as indicated from force-displacement responses. Fig. S4a-c showed the typical deformed profiles after indentations of PUA-11, 16, and 24. The linearly fitted lines (dashed lines in Fig. S4d)

describe the anticipated indentation profiles following the Berkovich tip geometry. Comparing to the experimental results (symbols), the actual deformed profiles are deeper. This indicates an absence of the pile-up behavior usually caused by confinement of adjacent materials.



Fig. S4 AFM scan of deformation profiles: (a) PUA-11, (b) 16, (c) 24, arrows show cross-section location, (e) cross-sectional profile along the arrows

Note 5: Finite Element Modeling Details

A three-dimensional half-structure model of indentation was generated as shown in Fig. S5a. A friction-free contact was assumed between the indenter and PUA. The radius of the tip is set at 100 nm. The element size is controlled at 25 nm at the contact area and gradually increased as moving away from the contact area as shown in Fig. S5b-d.

From the equivalent plastic strain contours of PUA-11, 16, and 24, concentrations are shown under the tip with high value of 0.8-0.9. This means the remaining porosity is very low since most of the ligaments are collapsed, forming particle contacts, penetrations or fusing. Sharp transition is also found between the plastic and elastic zone. This demonstrates the localized compressive behavior due to the missing lateral confinement.



Fig. S5 Finite element modelling: (a) half-structure model, (b-d) plastic strain contours near contact for PUA-11, 16, and 24.