Electronic Supplementary Information for

A novel degradation mechanism of the elastic modulus of wet polymer substrates under nanoindentation

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1 Materials and Methods

1.1 Preparation process of wet polymer substrate

Based on the dry polymer substrate, the construct processes of the wet polymer substrate were as follows (Fig. S1). Firstly, the same volume of water bulk and dry polymer were superimposed in order to avoid the influence of the swelling of the aqueous polymer on its elastic modulus. Then, with each polymer monomer as the center of the sphere, water molecules within a certain radius were removed, thereby eliminating the positional overlap between water molecules and polymer monomers. Finally, by adjusting the radius of the sphere, the wet polymer substrate with different water content was obtained. The water content (*wct*) of the polymer substrate ranged from 0.5% to 20% in this study

1.2 Potential functions of the simulation system

In this study, the hydrogen bond breaking phenomena occurring after the polymer molecules encounter water were not considered. Therefore, the interaction between the two adjacent bonding monomers on the same chain of the polymer substrate was described by finitely-extended nonlinear elastic (FENE) potential.[35,36]

$$U_{FENE}=\begin{cases} -0.5kR_0^2\ln\left[1-\left((r_1-l_0)/R_0\right)^2\right], & |r_1-l_0|\le R_0 \\ \infty , & |r_1-l_0|>R_0 \end{cases} \qquad (S-1)$$

Meanwhile, the interaction between nonbonding monomers was described by the 12-6 Lennard-Jones (LJ) potential.

$$U_{LJ}=\begin{cases} 4\varepsilon_1\left[(\sigma_1/r_1)^{12}-(\sigma_1/r_1)^{6}\right], & r_1\le 2.5\sigma_1 \\ 0 , & r_1>2.5\sigma_1 \end{cases} \qquad (S-2)$$

where r_1 is the bond length between the two adjacent bonding monomers or the distance between non-bonding monomers. l_0, which is equals to $1.5\sigma_1$, is the equilibrium bond length. R_0, which is equals to $0.5\sigma_1$, is the maximum expansion range of the spring. k, which is equals to $10\varepsilon_1/\sigma_1^2$, is the spring constant. ε_1 and σ_1 are the energy units and length units of the Lennard-Jones potential, respectively. Finally, interactions of polymer-Si and polymer-H_2O were also described by Lennard-Jones potential as equation S-2, respectively. The parameter values of polymer-Si potential was obtained by our previous study.[36] And the parameter values of polymer-H_2O potential were obtained by Lorentz-Berthelot mixing rules[41] based on polymer-polymer potential and Van der Waals force term between oxygen atoms in TIP4P potential function. The values of relevant parameters of Lennard-Jones potential in this study were listed in Table S1.

1.3 Identification of confined zone between the indenter and the polymer substrate

To determine the confined zone between shown in Fig.2, firstly, a cross section through the centroid of the indenter and parallel to the YZ plane was selected.

Secondly, the section was divided by the grid of 12Å × 8Å × 8Å. For every grid, the local density of the polymer substrate without consideration of water molecules was calculated based on the equation S-3 and the corresponding density distribution could be obtained (Fig. 2b).

$$\rho = \sum_{i=1}^{N} m_i \Big/ V \qquad (S-3)$$

where ρ and V were the density and volume of the grid, respectively. *N* was the number of polymer monomers in the grid. m_i was the mass of the $i-th$ polymer monomer. In order to reduce the statistical error, each grid was separated in the $y-$ or $z-\ direction$ by 2 Å. So, each grid was partially overlapped.

Thirdly, the confined zone was defined as the area between the indenter and polymer substrate and its height was less than h_0 according to the density distribution of polymer substrate (Fig. 2b). h_0 was the initial height along *z* direction of the polymer substrate, as shown in Fig. 1.

1.4 Calculations of local density and pressure of the confined water film

Firstly, the same water section as the polymer section was chosen to calculate the local density and pressure of confined water film. And the water section was divided by the grid of 12Å × 5Å × 3.5Å. And each grid was also separated in the *y*- or *z*- direction by 2Å.

Then, the local pressure of water film in each gird could be obtained based on equation S-4. [36,41,42]

$$P = \left\{ \left[\sum_{1}^{N} m_i \times \left(\vec{v}_i - \vec{v}_c \right)^2 \right] + \left[\sum_{i=1}^{N} \left(\vec{\omega}_i^b \cdot \vec{I}_i^b \cdot \vec{\omega}_i^b \right) \right] - \frac{1}{2} \sum_{i=1}^{N} \left(\sum_{j=1}^{M} \vec{f}_{ij} \cdot \vec{r}_{ij} \right) \right\} \Big/ (3.0 \times V) \qquad (S-4)$$

where *P* is the pressure of water molecules in the grid. $\vec{v}_i$ and $\vec{\omega}_i^b$ are the translational velocity and rotational angular velocity of the *i-th* water molecule, respectively. $\vec{v}_c$ is the centroid velocity of the water molecules in the grid. m_i are $\vec{I}_i^b$ the mass and moment of inertia of the *i-th* water molecule, respectively. $\vec{f}_{ij}$ represents the force exerted by *j-th* water molecule on *i-th* water molecule. $\vec{r}_{ij}$ is the displacement from the center of mass position of *i-th* water molecule to the center of mass position of *j-th* water molecule. V is the volume of the grid. In addition, similar to the calculation of polymer substrate, the local density of the water film could also be calculated based on the equation S-3. So, the corresponding the local pressure and density distributions of the water film at the section could be obtained, as shown in Fig. S2.

Finally, the average pressure (P^{wat}_{ave}) and density (ρ^{wat}_{ave}), the maximum pressure (P^{wat}_{max}) and density (ρ^{wat}_{max}) of the confined water film at the maximum indentation depth could be obtained by calculating the local pressure and density of water film at the confined zone based on the definition of confined zone.

1.5 Smooth process of load-displacement curves of the indenter

Firstly, the corresponding loads and displacements of the indenter at the every moment were recorded. So, the instantaneous load curve corresponding to each displacement was obtained. Then, in order to reduce the noise of this load-displacement curve, the load-displacement curve was smoothed by us. Specially, the load and displacement data corresponding to the period of [t, $t+\Delta t$] were averaged. In this study, Δt was chosen as 75 fs. Finally, based on the indentation processes on the polymer substrate under different water contents, the corresponding load-displacement curves of the indenter after smoothing treatments could be obtained, as shown in Fig. 3.

1.6 Calculations of elastic modulus and hardness of polymer substrate under indent load

(1) Calculations of E_c and H_c

According to the load-displacement curves, the calculation processes of E_c and H_c based on Oliver-Pharr nano-indentation method were as follows.[43-45]

Firstly, the coefficients B and m in equation S-5 were obtained by unloading curve fitting in Fig. 3. And the parameter h_f in the equation S-5 represented the final residual indentation depth after fully unloading.

$$F_z = B\left(h - h_f\right)^m \qquad (S-5)$$

Secondly, the initial unloading contact siffness S was given as equation S-6

$$S = \left(dF_z/dh\right)|_{h = h_{max}} = Bm\left(h_{max} - h_f\right)^{m-1}. \qquad (S-6)$$

Thirdly, based on the peak load F_{zmax} and the maximal indentation depth h_{max}, the contact depth h_c was given by equation S-7.

$$h_c = h_{max} - \varepsilon F_{zmax}/S \qquad (S-7)$$

where the geometric constant ε =0.75 for the spherical indenter. So, the corresponding the projected area of the elastic contact A could be obtained according to equation S-8.

$$A = \pi\left(R^2 - \left(R - h_c\right)^2\right) \qquad (S-8)$$

Fianlly, the reduced modulus E_r was given by equation S-9 and equaiton S-10

$$E_r = S\sqrt{\pi}/(2\sqrt{A}) \quad . \qquad (S-9)$$

$$1/E_r = \left(1 - v_{indent}^2\right)/E_{indent} + \left(1 - v_{poly}^2\right)/E_c \qquad (S-10)$$

where E_{indent} and v_{indent} were the elastic modulus and Poission's ratio for the indenter, and v_{poly} was Poission's ratio for the polymer substrate. For the rigid indenter, E_{indent} was much larger than E_{poly}. Therefore, the relationship between E_c and E_r could be simplified into equation S-11.

$$E_c \approx E_r\left(1 - v_{poly}^2\right) . \qquad (S-11)$$

To obtain v_{poly}, the tensile stress-strain process of the dry polymer matrix was performed by MD simulations. Then the stress tensor of the polymer matrix system could be calculated. Finally, v_{poly} and E_{poly} of the dry polymer matrix under tensile loads were obtained based on the generalized Hooke's law and were about 0.25 and 0.998GPa.

Meanwhile, H_c was obtained according to the equation S-12.

$$H_c = F_{zmax}/A \qquad (S-12)$$

(2) Calculations of E_w and H_w

Based on the calculation process of E_c and H_c, E_w and H_w can be obtained as follows.

Firstly, the contact depth h_c^{wet} was given by equation S-13 based on the assumption that the contact stiffness of the wet substrate was equal to the contact stiffness *S* in equation.

$$h_c^{wet} = h_{max} + \delta - \varepsilon F_{zmax}/S \qquad (S-13)$$

Then, the corresponding projected area A_{wet} could be obtained according to equation S-14.

$$A_{wet} = \pi\left((R+\delta)^2 - \left((R+\delta) - h_c^{wet}\right)^2\right) \qquad (S-14)$$

Subseqently, the reduced modulus E_r was given by equation S-15.

$$E_r^{wet} = S\sqrt{\pi}/\left(2\sqrt{A_{wet}}\right) \quad . \qquad (S-15)$$

Finally, E_w and H_w was given by the equations S-16 and S-17.

$$E_w \approx E_r^{wet}\left(1 - v_{poly}^2\right) . \qquad (S-16)$$

$$H_w = F_{zmax}/A_{wet} \qquad (S-17)$$

1.7 Calculations of the spatial probability distribution function of monolayer water molecules

The spatial probability distribution function *G*(*x, y*)[46] represented the probability of finding another molecule *j* at a distance of *r* (*x, y*) near molecule *i.* The calculation process of *G*(*x, y*) of a layer of water molecules were as follows.

$$G(x,y) = DA(x,y)/DA_0 , \qquad (S-18)$$

where $DA(x,y)$ was the local water molecular density in the rectangular micro-region at a distance of *r* (*x, y*) near molecule A. DA_0 was the average water molecular density in the plane of the entire water layer.

Therefore, $DA(x,y)$ and DA_0 were given as equation S-19 and S-20, respectively.

$$DA(x,y) = n(x,y)/\Delta A = n(x,y)/(dx \times dy) \qquad (S-19)$$

$$DA_0 = N_L/A_L \qquad (S-20)$$

where $n(x,y)$ and N_L represented the number of water molecules in the rectangular micro-region and the entire water layer, respectively. ΔA represented the area of the rectangular micro-region with side lengths dx and dy. A_L was the planar area of the entire water layer.

Finally, the spatial distribution function based on simulation ensemble was given as equation S-21.

$$G(x,y) = A_L \times \sum_{i=1}^{N_L} BIN_i(x,y) \Big/ \left(N_L^2 \times \tau_{run} \times dx \times dy\right) \qquad (S-21)$$

where τ_{run} was the number of simulation time steps used in calculating distribution functions. $BIN_i(x,y)$ represented the total number of water molecule pairs at a distance of $r(x, y)$ in the whole water layer plane within the time steps of τ_{run}.

2 SUPPLEMENTARY FIGURES

Figure S1.

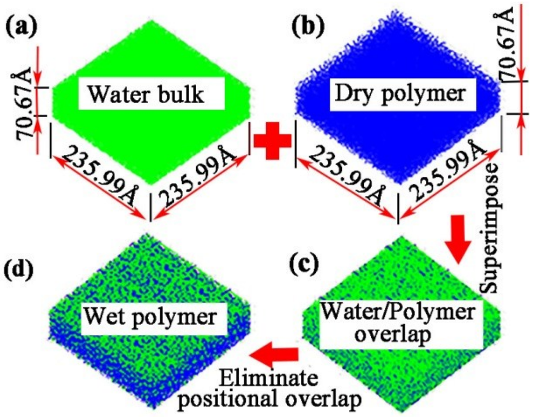

Fig. S1 The preparation of the wet polymer substrate. (a) Water bulk.(b) Dry polymer substrate.(c) Overlap of water bulk and dry polymer substrate.(d) Wet polymer substrate by eliminating the positional overlap of the water molecules and the polymer monomer.

Figure S2.

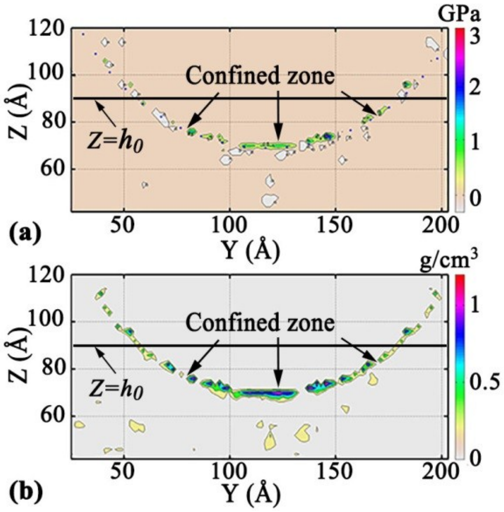

Fig. S2 (a) and (b) were the local pressure and density distribution of the water film diagram at the maximum indentation depth when the water content was 10%, respectively.

Figure S3.

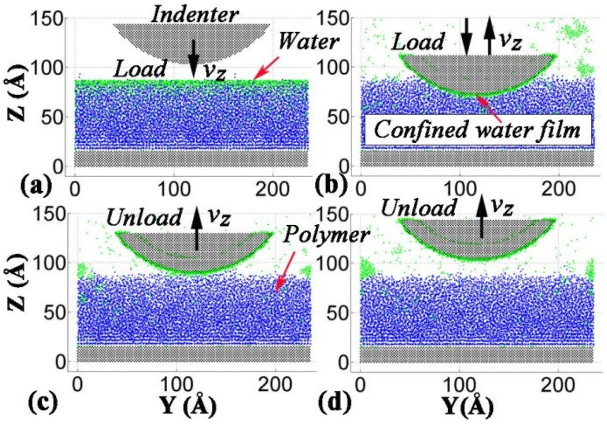

Fig. S3 The side cross-section views of atomic positions at the different moments during indentation process when the water content was 7%. The blue dots and green dots presented polymer monomers and water molecules, respectively. The rest of atoms presented silicon atoms. (a) The initial moment, (b) The moment of maximum indentation depth, (c) The moment of indenter just left from the polymer substrate. (d) The moment of indenter back to the initial position.

Figure S4.

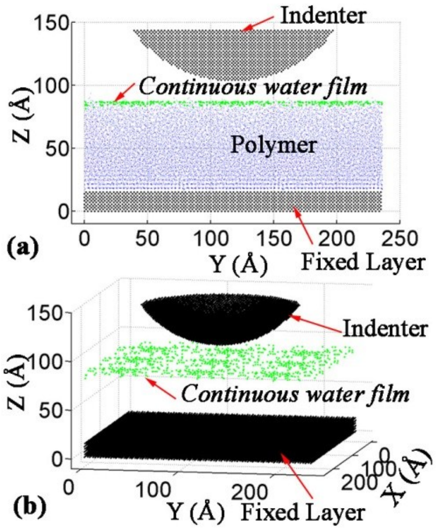

Fig. S4 A continuous water film layer on the polymer surface occurred when the water content was 0.5%. (a) YZ two-dimensional projection, (b) XYZ three-dimensional projection. And the polymer substrate was ignored to make a clear comparison.

Table S1.

Table S1 The values of parameters in 12-6 Lennard-Jones potential functions. And the potential function was expressed by $U_{LJ} = 4\varepsilon_1\left[(\sigma_1/r_1)^{12} - (\sigma_1/r_1)^6\right]$.

	ε_1(erg/pair atom)	σ_1(Å)	cutoff (Å)
Polymer-Polymer[35,36]	1.3806×10^{-14}	4.017	10.0425
Polymer-Silicon[36]	1.3806×10^{-14}	4.017	10.0425
Polymer-Water[36,39,41]	1.4333×10^{-14}	3.2795	8.1988
Si^{2+} - Water[40]	8.9139×10^{-14}	1.381	8.47
Si^{4+}-Water[40]	1.5425×10^{-14}	3.388	8.47