



# Interfacial Interactions of Polyurethane-based Polymer Coatings: A Molecular Simulations Study

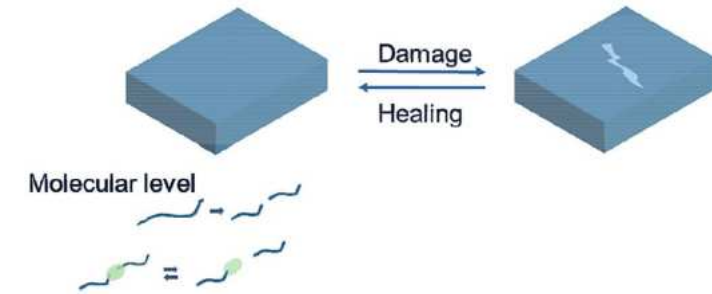
Gokhan Kacar  
Trakya University  
Edirne, Turkey

# Smart coatings

- Wide use of polymers → Forced them to extend their service life and gain new functionalities
- Conventional engineering approach → **Damage prevention**
  - Stronger material = Long lasting material
- Smart polymer approach → **Damage management**
  - Dealing with the damage

*or*

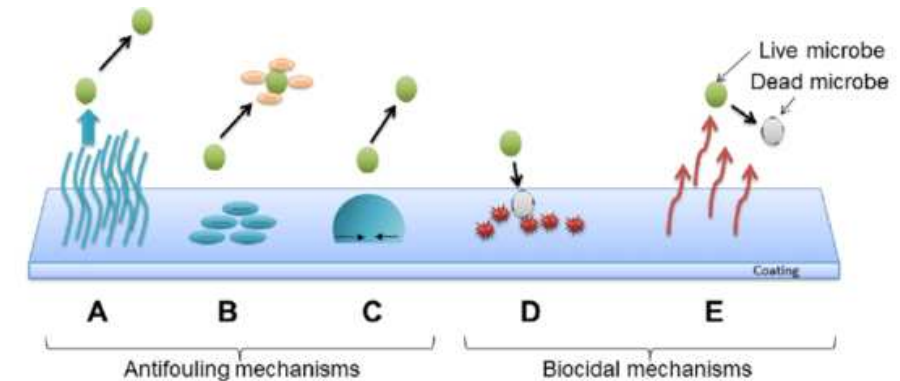
  - **Providing the desired function to the material** (depends on environment)



**Source:** Hager M.D. & Zechel S., Self-healing polymers: from general basics to mechanistic aspects, Chapter 3.

# Why smart coatings?

- **Mimics the surface behavior in nature** (biologically inspired materials)
  - Self-healing, self-cleaning, hydrophilic/hydrophobic characteristics etc.
- Potential of forming functional *or* multifunctional surfaces
  - Autonomous mechanisms → Sustainable functionality
  - Esteves C. et al. reported,
    - Addition of PEG segments to PPG coating causes low friction and lubricity on surface<sup>1</sup>

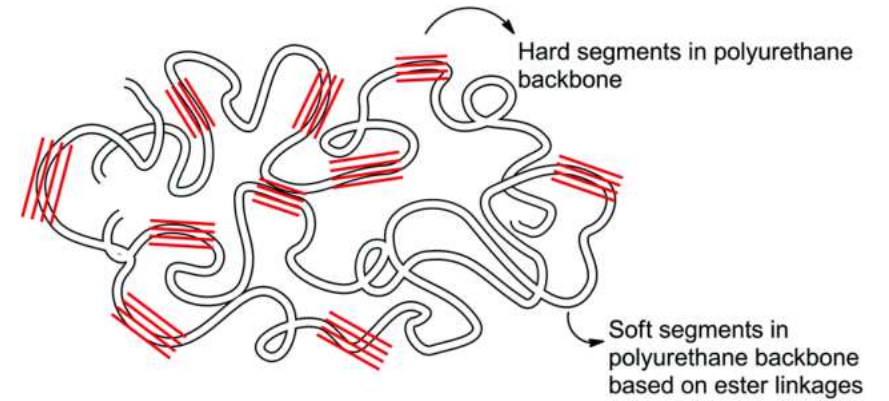


Source: Singha P., Locklin J., Handa H., Acta Biomaterialia, 2015.

- **Eco-friendly** & wide range of use in various industries
  - Biomedical applications, paint industry, marine engineering etc.

# PU-based coatings

- **Di/Tri-isocyanate + Polyol → Polyurethane**
  - Isocyanate: *Hard* segments
  - Long flexible polyol chains: *Soft* segments



Source: RSCAdv., 2020,10,3029

- Ideal structures to attach dangling chains (availability of reactive ends -NCO, -OH)
- **Segmented structure + functional dangling chains + wide range of  $T_g$** 
  - Results in superior properties compared to conventional PU
- Protective barrier by dangling chains → Keeps weathering/biological elements away

# Dual functional coatings with dangling chains

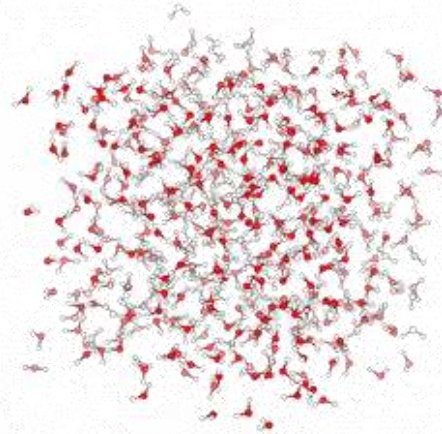
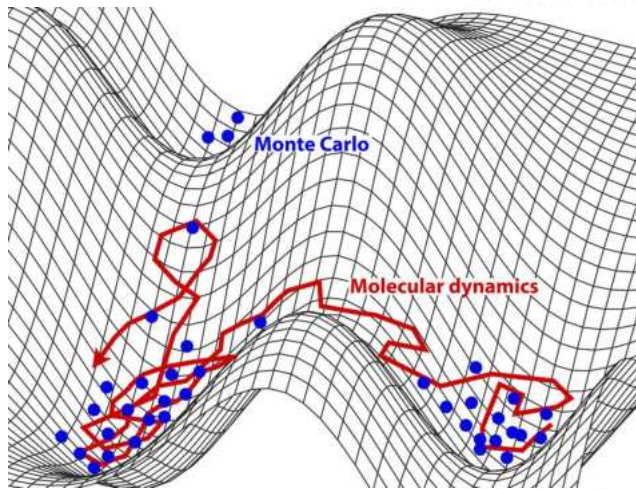
- The majority of PU coatings are hydrophobic
  - Smart behaviour can be maintained by additional dangling chains
  - Hydrophilic dangling chains (e.g., PEG) → Lubricious surface

In fact,

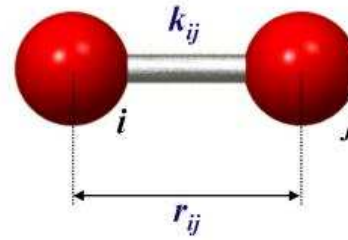
- Use of **PEG** in monofunctional PU coatings may cause **swelling** and loosening of network  
→ **Solution:** Combined use of hydrophilic and hydrophobic groups
- Dual chemical nature of hydrophilic and hydrophobic compound
  - Promoting the migration of PEGs to surface: Benefiting from hydrophilic surface property efficiently
  - **Low friction** on coating surface

# Molecular Simulations

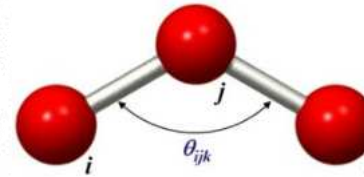
- Solve Newton's equation of motions
  - $f^T = ma$
- Predefined (semiempirical, empirical) force fields to compute  $f^T$



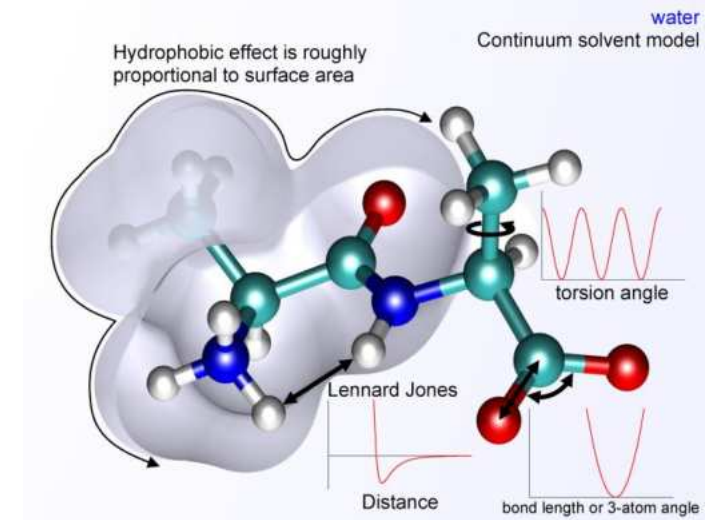
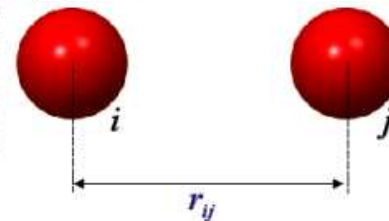
Bonded potential



Angle potential



Non-bonded potential



wikipedia.org

$$V_{vdW} = 4 \epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$

# Method: Dissipative Particle Dynamics (DPD)

- Conventional DPD parameterization is appropriate for using similar bead sizes
  - Chemical structures of polymers include various size of groups
  - Preferred an **alternative parameterization** which allows **different bead sizes**

- **C**onservative, **R**andom and **D**issipative forces

$$\mathbf{F}^T = m\mathbf{a}$$

- **C** force characterizes the equilibrium structure

$$\mathbf{F}^T = \mathbf{F}^C + \mathbf{F}^R + \mathbf{F}^D$$

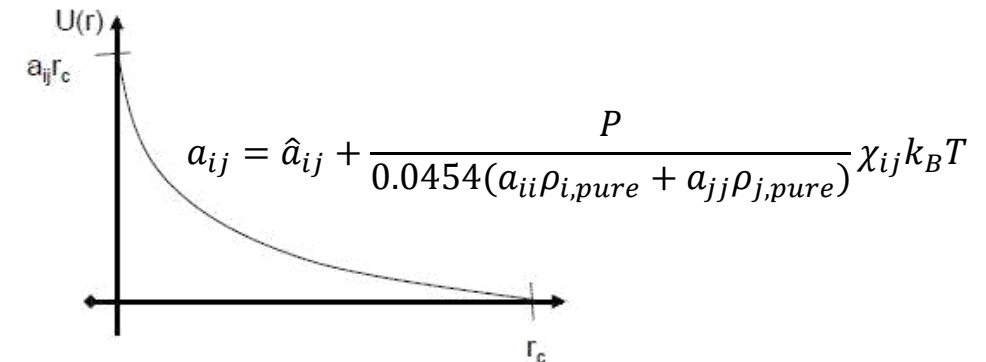
- **R** and **D** forces are coupled and act as a thermostat

- **Hydrogen bonds** in DPD?

$$\vec{f}^T = \vec{f}^C + \vec{f}^R + \vec{f}^D + \vec{f}^{Morse}$$

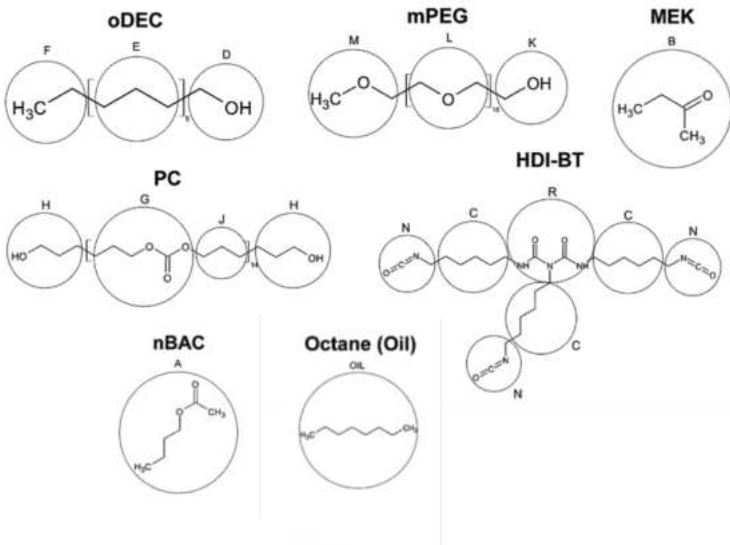
$$E = D_0 \left[ e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right] \quad r < r_c$$

$$D_0(x) \equiv E_{H-bond}(x) = E_{Pot,Mix}(x) - E_{Pot,A} - E_{Pot,W}$$

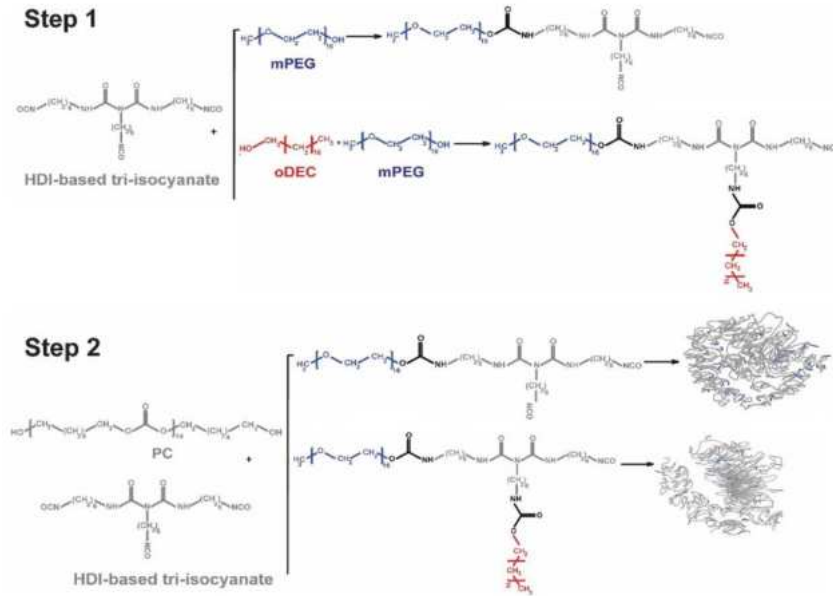


# Materials

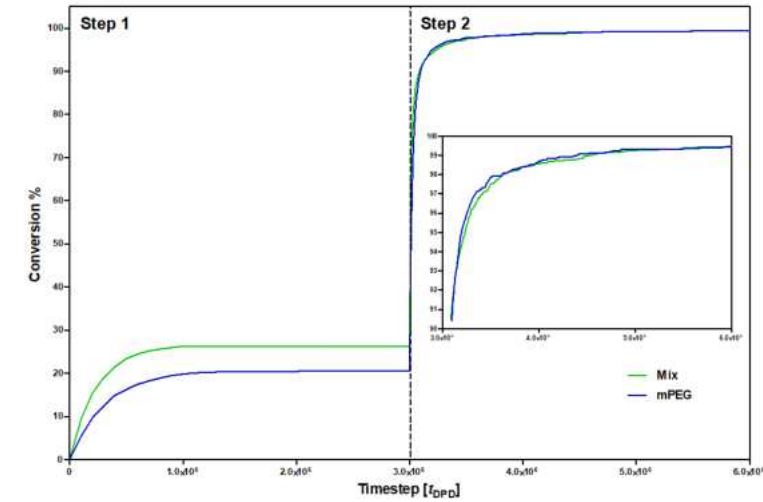
## Coarse-grained forms of molecules



## Two-step polymerization



## Cross-link conversion

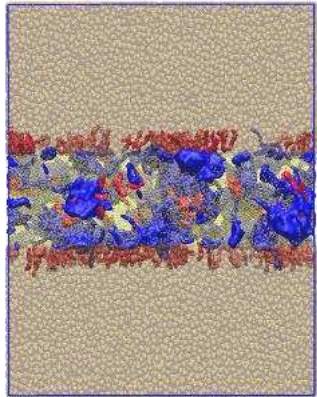


Mix: 99.48%  
mPEG: 99.44%

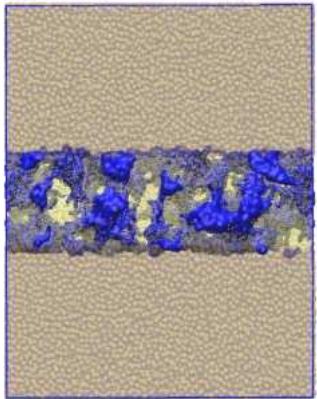


# Switchab

oil



mix



mPEG



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Progress in Organic Coatings

journal homepage: [www.elsevier.com/locate/porgcoat](http://www.elsevier.com/locate/porgcoat)



## Modeling surface segregation of smart PU coatings at hydrophilic and hydrophobic interfaces via coarse-grained molecular dynamics and mesoscopic simulations

Deniz Kizilkaya<sup>a,1</sup>, Hassan Ghermezcheshme<sup>b,1</sup>, Sepide Eslami Sabzevar<sup>b</sup>, Hesam Makki<sup>b,c,\*</sup>, Gokhan Kacar<sup>a,\*\*</sup>

<sup>a</sup> Department of Genetics and Bioengineering, Faculty of Engineering, Trakya University, 22030 Edirne, Turkey

<sup>b</sup> Department of Polymer and Color Engineering, Amirkabir University of Technology, 424 Hafez Ave., Tehran, Iran

<sup>c</sup> Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

### ARTICLE INFO

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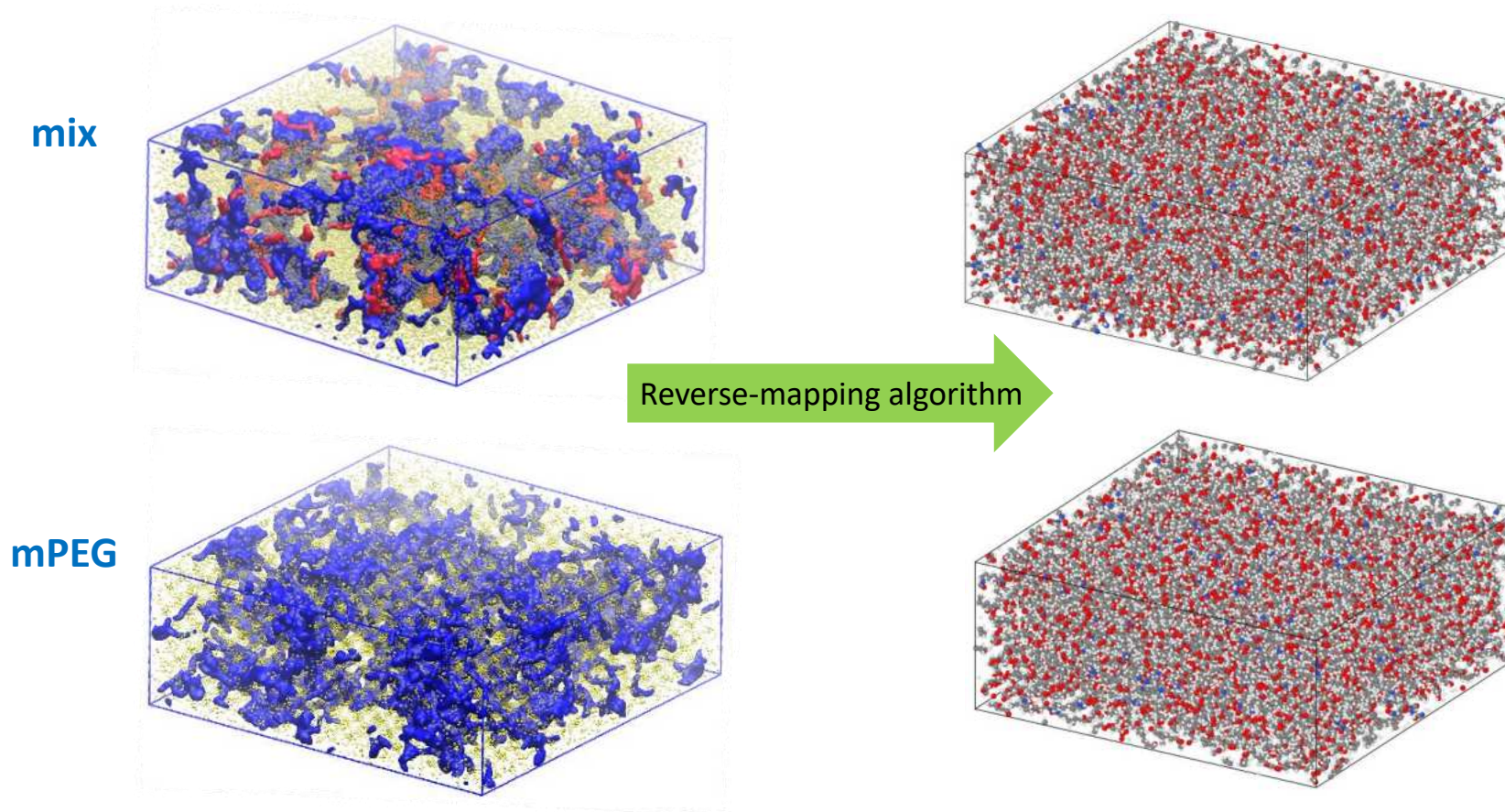
Smart coating  
Polyurethane network  
Surface responsive coatings  
MARTINI model  
DPD simulation

### ABSTRACT

Developing adaptive coatings having desired functionalities at targeted interfaces is one of the major efforts in the coatings science area. The adaptation of the surface functionality to the changing surface conditions can be maintained by introducing dangling chains with different properties to the cross-linked polymer coatings. In this work, we strive to investigate the change in interfacial morphology of PU coatings as exposed to hydrophilic (HPI) and hydrophobic (HPB) interfaces by employing molecular simulations at the coarse-grained and mesoscopic levels. The molecular structure and surface segregation dynamics are studied for PU coatings having pure HPI, mixture of HPI and HPB, and amphiphilic dangling chains. The dual-scale simulations, Dissipative Particle Dynamics (DPD) and MARTINI model, yield results about the dangling chain structures at the interface in terms of their end-to-end distances, where HPI chains adopt a more extended conformation in water in comparison to oil interfaces. The reverse is observed to be valid for the HPB chains. Regarding the dangling chain dynamics, a swift migration towards the interfaces is noticed at about 10 ns for both of the simulation methods. The structures of the dangling chains and their interaction with the interfaces are also characterized by computing the radial distribution function (RDF) profiles. Preferential interactions between the HPI/water and HPB/oil are clearly noted. The switchability of the surfaces is also studied by simulating the system in cycles, such that the interface is changed from water to oil and back to water. The migration of HPI groups in the dangling chains towards water and vice versa in each cycle is clearly shown by the simulations. In all, the inherent structure and dynamics of the dangling chains is obtained at the molecular level by the dual-scale molecular simulations. Our findings reveal a significant level of understanding about interfacial morphology of thermoset coatings modified by dangling chains, where the results can be extended to find applications in guiding the experimental studies.

of dangling chains are from integrals of is ngling chains to ces (hydrophilic-water, -oil)

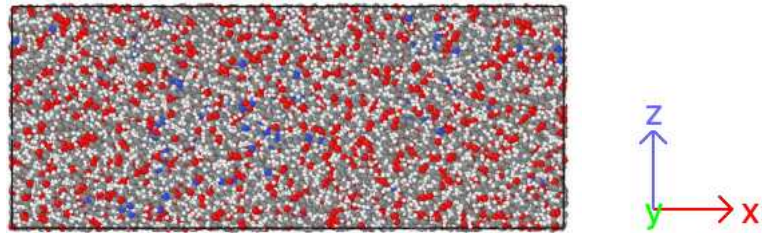
# Reverse-mapping (Coarse-grained $\rightarrow$ Atomistic)



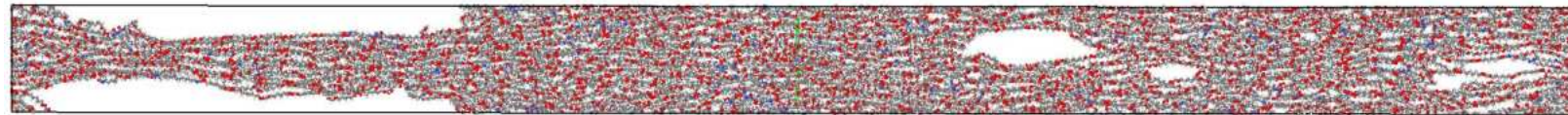
- Obtaining atomistic coordinates from DPD results *via* reverse-mapping algorithm
- $\rightarrow$  Computing mechanical properties of PU coatings are from all atom MD simulations

# Uniaxial tensile test on bulk PU

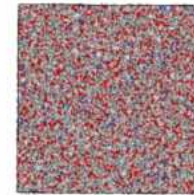
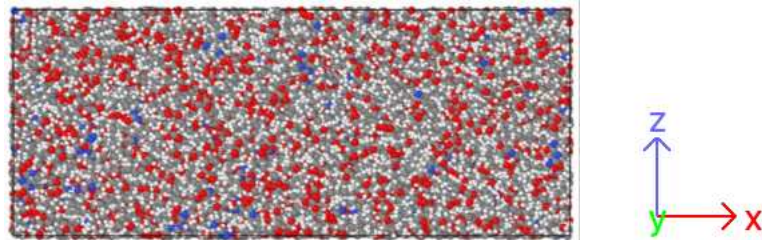
mix



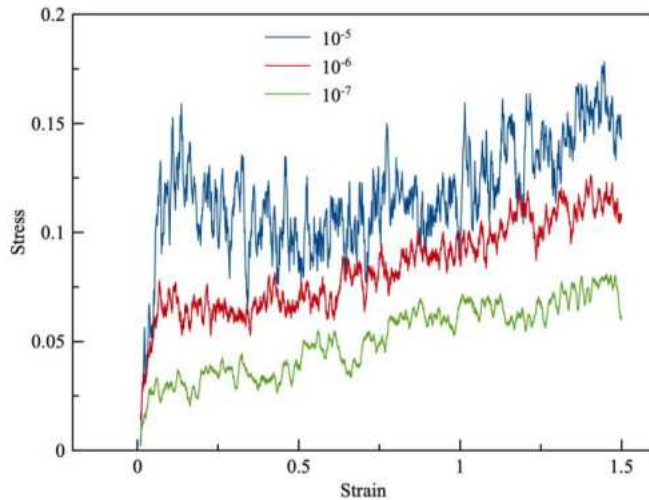
- Stretching the bulk at a constant rate in x-direction
- Strain rate:  $10^{-7}$  1/fs



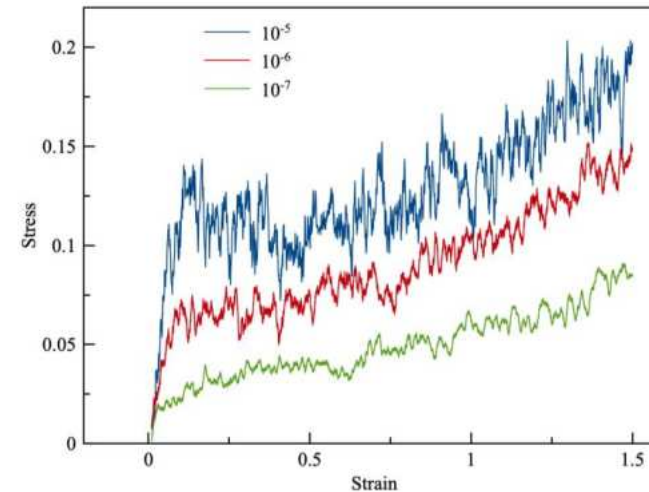
mPEG



# Elastic modulus and strain rate effect



mPEG <i>E</i> Modulus	
Strain Rate (s <sup>-1</sup> )	Stress (GPa)
<b>10<sup>10</sup></b>	1.6175
<b>10<sup>9</sup></b>	1.4186
<b>10<sup>8</sup></b>	0.6789
<b>10<sup>6</sup></b>	0.0522



Mix <i>E</i> Modulus	
Strain Rate (s <sup>-1</sup> )	Stress (GPa)
<b>10<sup>10</sup></b>	1.1192
<b>10<sup>9</sup></b>	0.9654
<b>10<sup>8</sup></b>	0.6237
<b>10<sup>6</sup></b>	0.0482

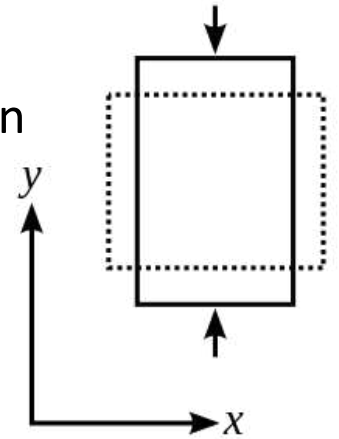
- Elastic modulus computed from uniaxial deformation of bulk polymers
- According to Modi and Karttunen 10<sup>8</sup>/s for polymers  
<https://doi.org/10.3390/nano12193379>
- **Lower** elastic modulus with more rigid **Mix** system

# Poisson's ratio

- Poisson's ratio computed from uniaxial deformation of bulk polymers
  - Poisson's ratio ( $\nu$ ) is the deformation of a material perpendicular to the loading direction
- Negative ratio of transverse strain to axial strain

mPEG	mix
0.29298	0.33491

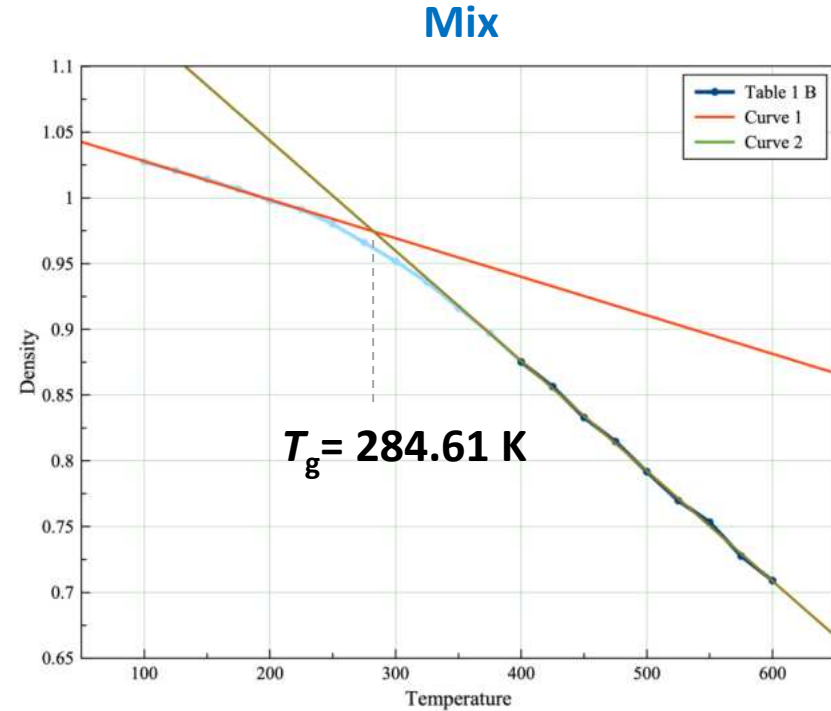
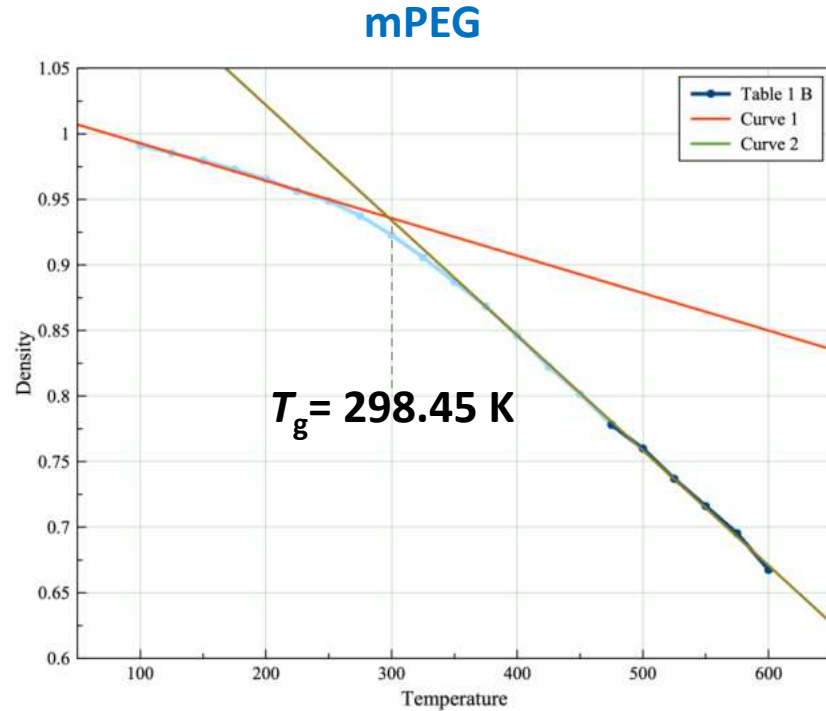
- **Lower** Poisson's ratio with less complex **mPEG** system



$$\nu = -\frac{d\varepsilon_{\text{trans}}}{d\varepsilon_{\text{axial}}} = -\frac{d\varepsilon_y}{d\varepsilon_x} = -\frac{d\varepsilon_z}{d\varepsilon_x}$$

- Poisson's ratio
- transverse strain
- axial strain

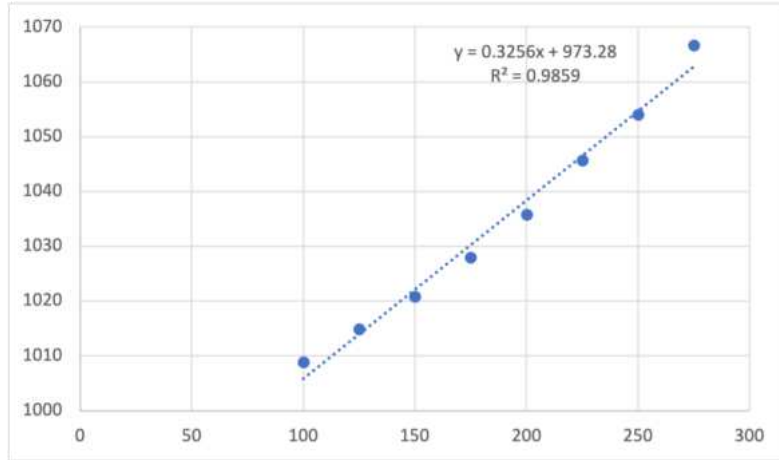
# Glass transition temperature ( $T_g$ )



- Lower  $T_g$  in more rigid **Mix** system

# Coefficient of Thermal Expansion (CTE)

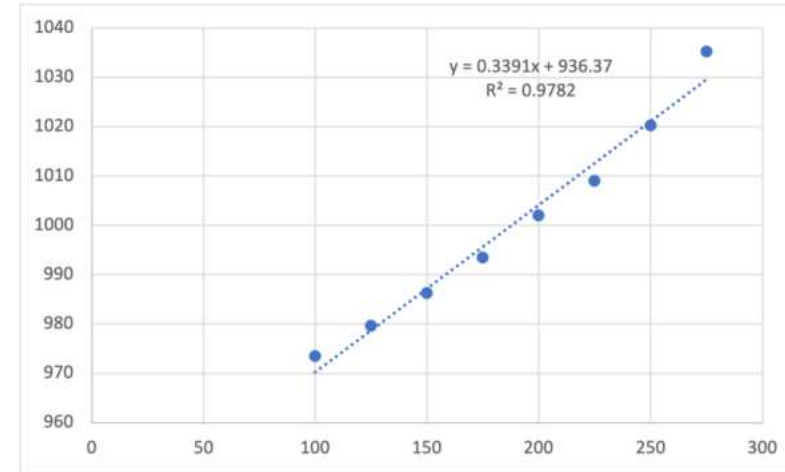
mPEG



$V_0$ : 0.4799 m<sup>3</sup>

**CET**:  $0.3256 / 0.4799 = \mathbf{0.6783}$

Mix



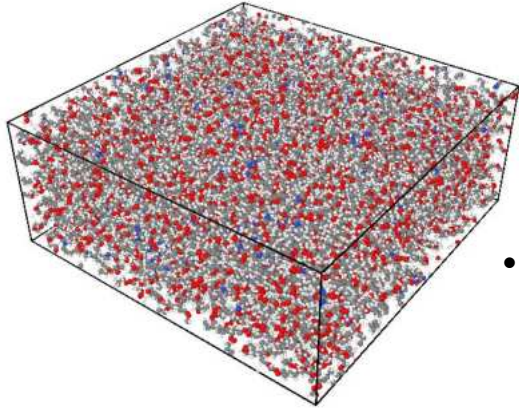
$V_0$ : 0.4667 m<sup>3</sup>

**CET**:  $0.3391 / 0.4667 = \mathbf{0.7265}$

→ The slope in the temperature range 100–275 K was used for CTE → below  $T_g$

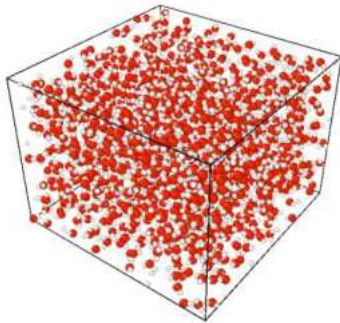
# Current: Modelling of wettability behavior

mPEG

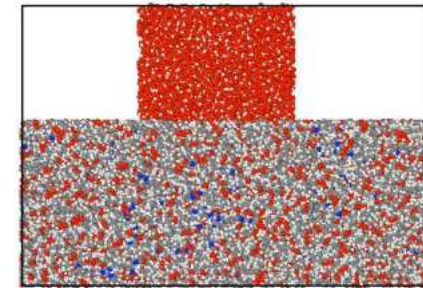
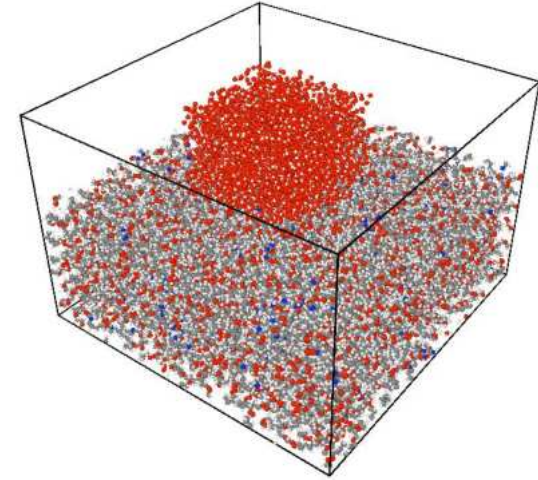


- Box size: 106.263 Å x 106.263 Å x 42.5052 Å

water



- Box size: 40 Å x 40 Å x 30 Å
- SPC/E water model





# Summary

- *in silico* description of polyurethane coatings with proper chemical nature
- Equilibrated cross-linked structure at molecular scale realized
- Reverse-mapped coordinates result in all-atom structure
- Mechanical and thermodynamic properties estimated
- Estimating surface properties (e.g. tension, adhesion strength) on the go
  
- Experimental verification needed
- Remove pull-test strain rate effect?
- Develop approaches for better simulation-experiment comparison
- Automated computational coatings design

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**Computational  
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Research Group  
@TrakyaUniv**

Deniz Kizilkaya (Ph.D.)  
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Aysu Erdim (M.Sc.)  
Ceyda Kimil (M.Sc.)

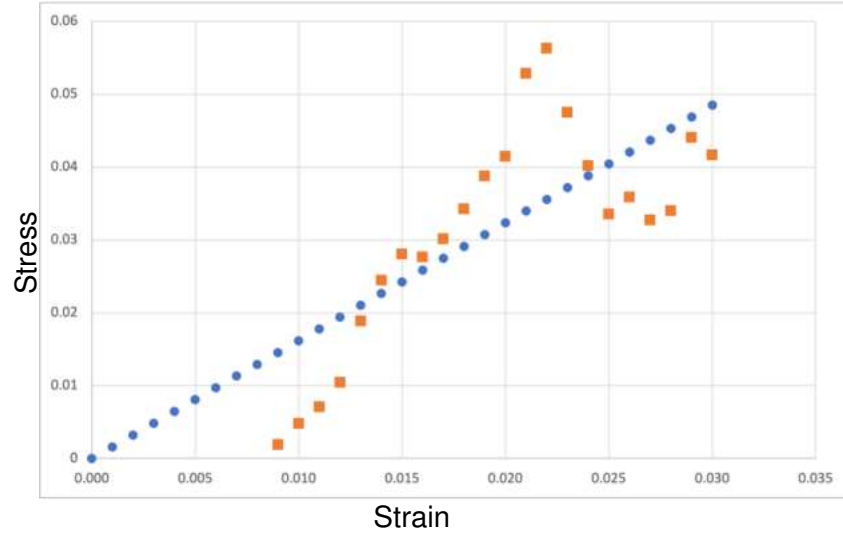


Any questions?

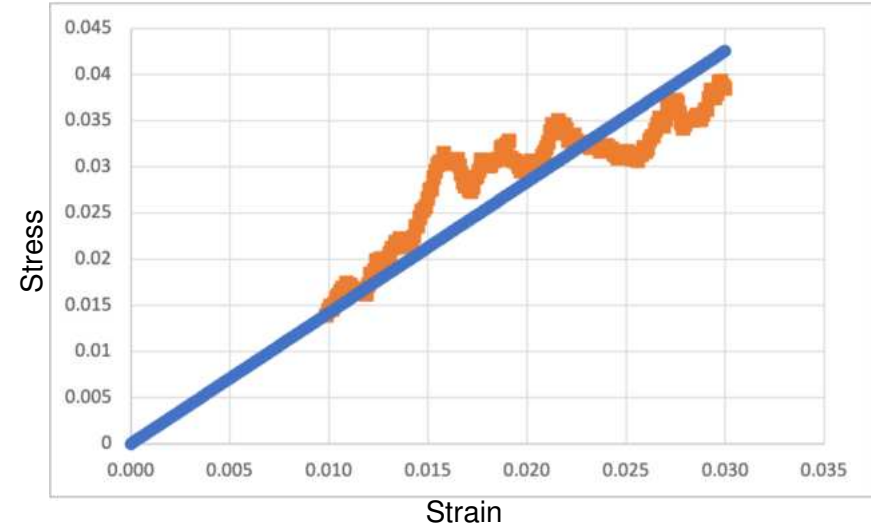
# mpeg system

!!!!!!  
0-0.03

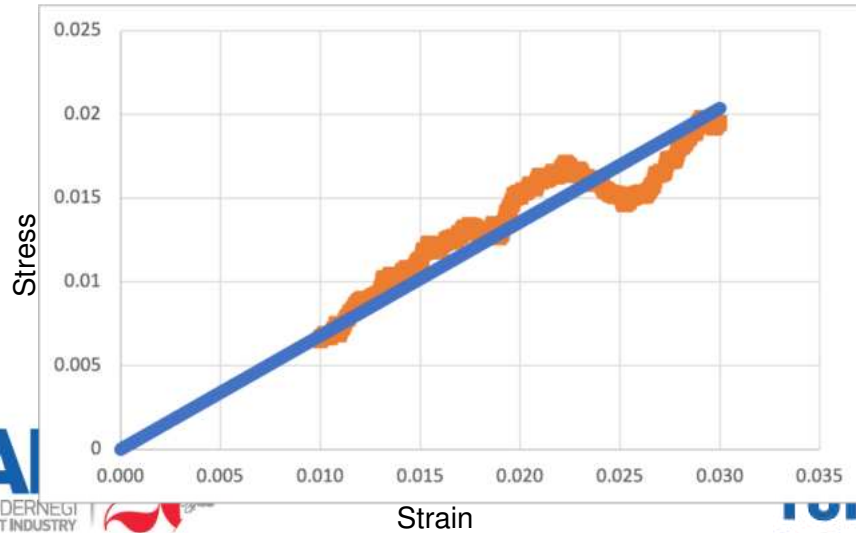
### Strain Rate: $10^{-5}$ 1/fs



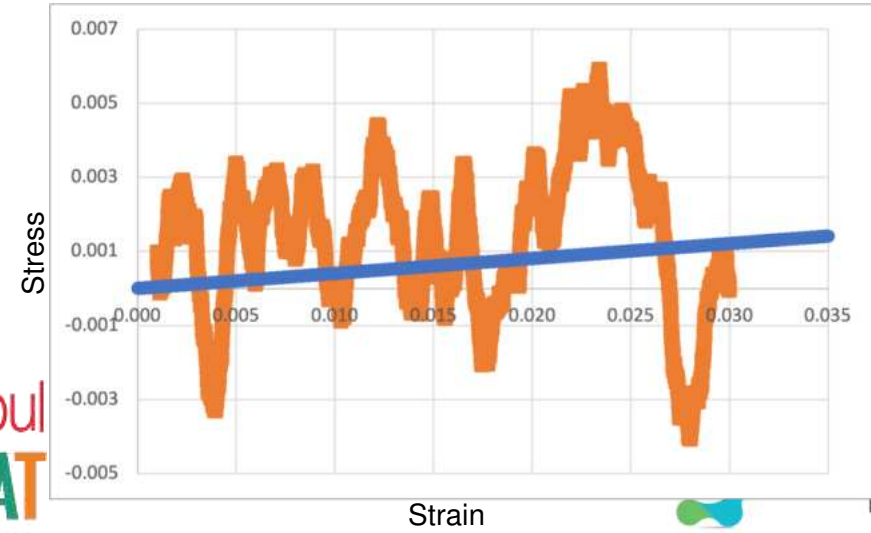
### Strain Rate: $10^{-6}$ 1/fs



### Strain Rate: $10^{-7}$ 1/fs



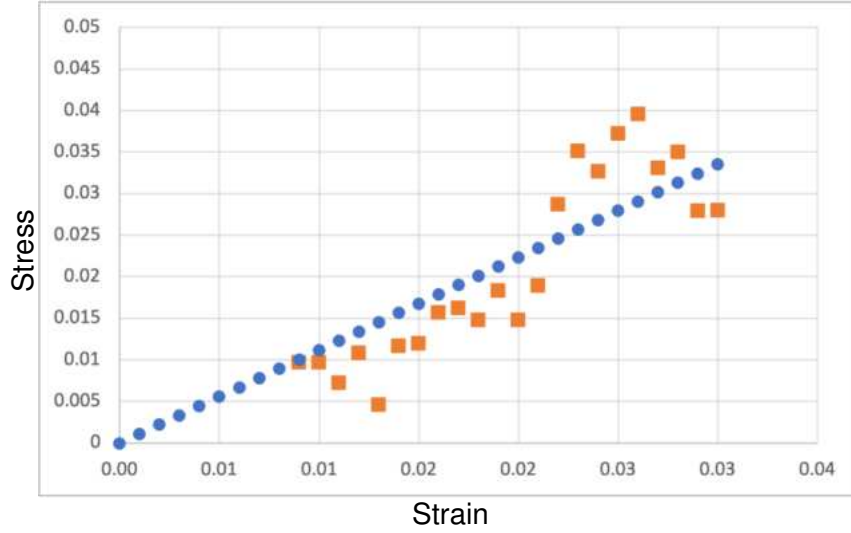
### Strain Rate: $10^{-9}$ 1/fs



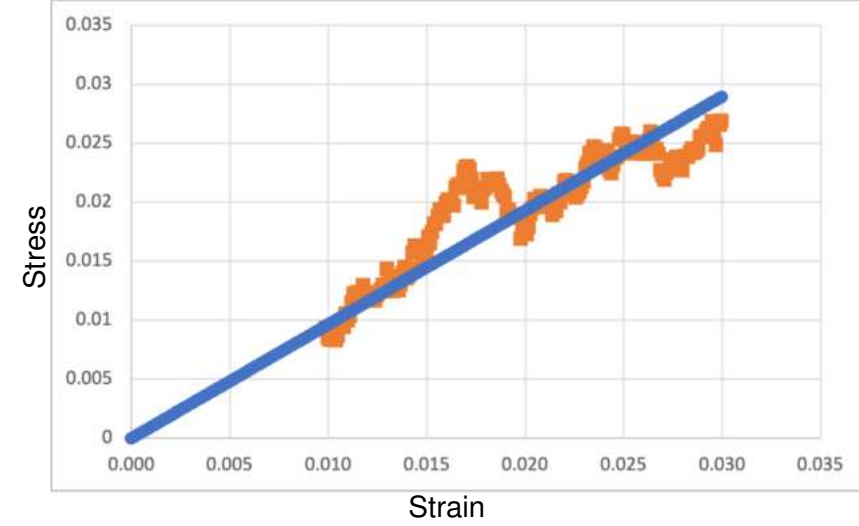
# mix system

!!!!  
0-0.03

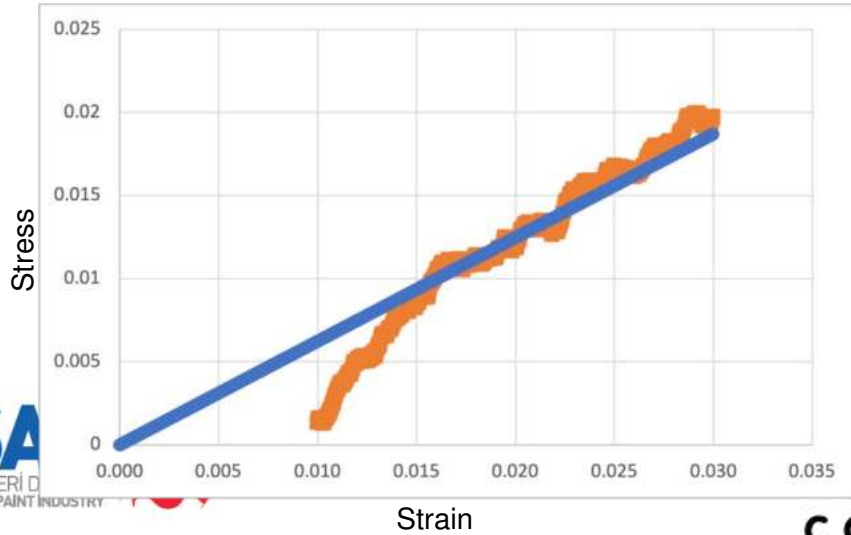
### Strain Rate: $10^{-5}$ 1/fs



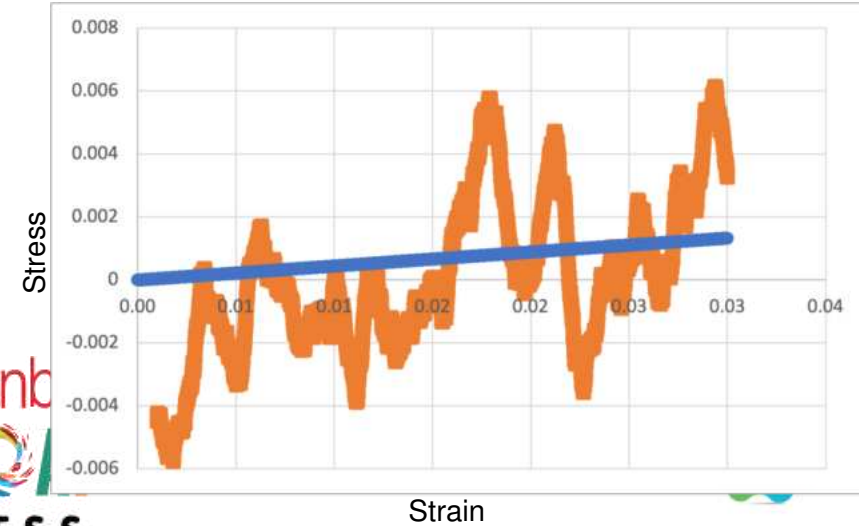
### Strain Rate: $10^{-6}$ 1/fs



### Strain Rate: $10^{-7}$ 1/fs



### Strain Rate: $10^{-9}$ 1/fs



# Computed Elastic Modulus for mPEG in Different Dragging Directions

- To assess isotropic behavior, we deformed the polyurethane sample in the x, y, and z directions.
- Isotropic behavior implies consistent material response, regardless of the direction of deformation.

mPEG E Modulus			
Strain Rate (1/fs)	Drag-x	Drag-y	Drag-z
$10^{-5}$	1.6175	2.4643	1.7195
$10^{-6}$	1.4186	1.2077	1.2538
$10^{-7}$	0.6789	0.6321	0.8328

### Removing strain rate dependency

PU Systems	$E$ Modulus (GPa)
mPEG	0.33802213
Mix	0.36906218

$$E^{-1} = \frac{\bar{V}}{k_B T} \langle (\varepsilon_z - \langle \varepsilon_z \rangle)^2 \rangle$$