Screen the best ionic liquids for keratin dissolution by using COSMO-RS

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Screen the best ionic liquid for keratin dissolution by using COSMO-RS

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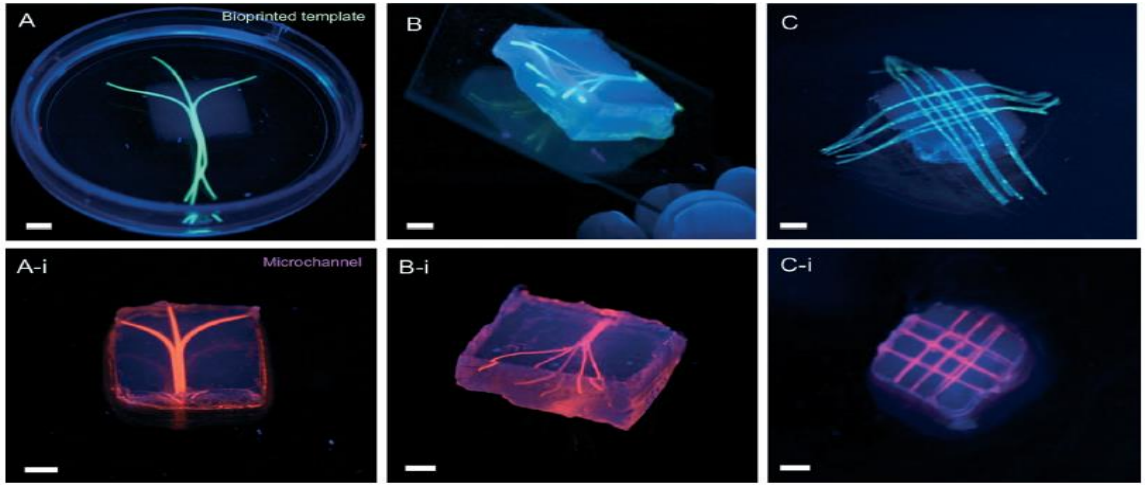
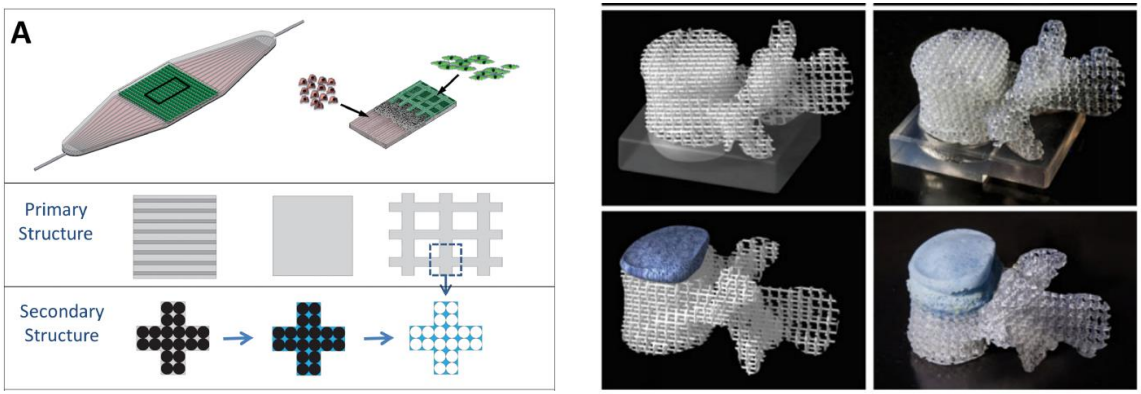
Application of PDMS in tissue engineering





- Most PDMS used in tissue engineering applications are nonpolar, inert and highly hydrophobic, which lead to the low biocompatibility and interaction responses between implantations and cells.

1) Morgan, Kathy Ye, et al. Advanced functional materials 26.32 (2016): 5873-5883. 2)Bertassoni, Luiz E., et al. Lab on a Chip 14.13 (2014): 2202-2211.
3) Lantada, Andrés Díaz, et al. Springer, Cham, 2016. 331-349.

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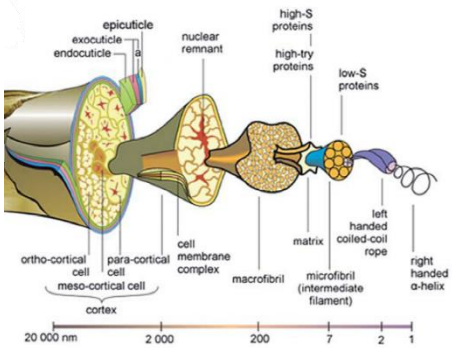
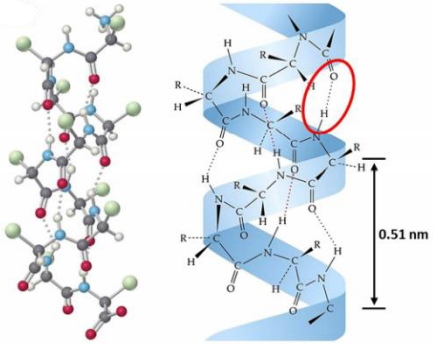
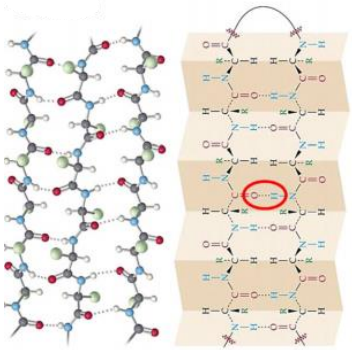
Structure of keratin and application of keratin in elastomer

Structure of keratin





α- helix



β- sheet

Application of keratin in elastomer

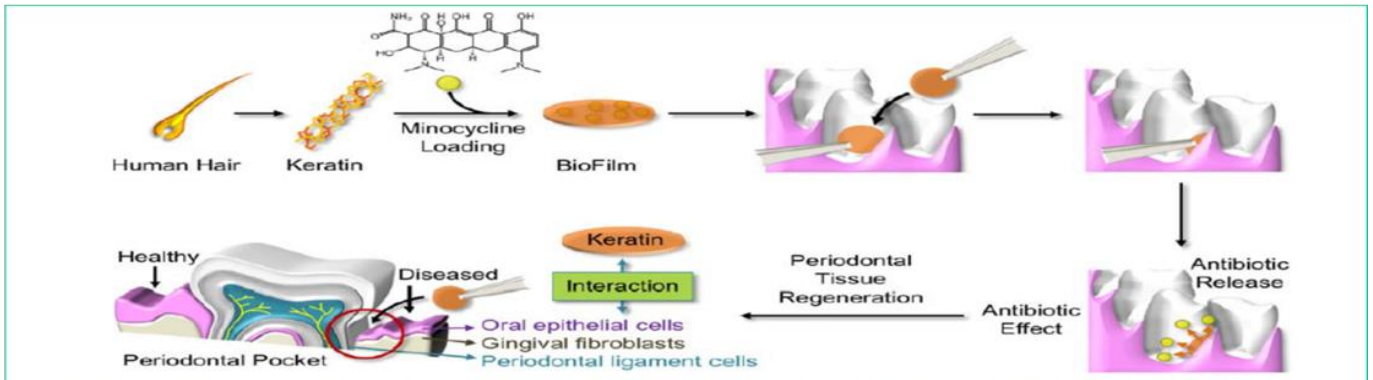


Figure 1. A schematic description of intrapocket antibiotic-eluting human hair keratin-based film for periodontal tissue regeneration.

Lee, Hanna, et al. Macromolecular Research 23.3 (2015): 300-308.

- Keratin molecules have many inter- and intra-molecular strong bonds and also have no regular repeating units, which lead to it difficult to be dissolved by traditional solvent
- Keratin has the special amino acid sequence for cell adhesion, which can increase susceptibility to bio-decomposition
- Keratin can improve the mechanical properties of composites

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Keratin dissolution in ionic liquids

Ionic liquid (IL) is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature

Properties of ILs

- High chemical stability and thermal stability
- Wider liquid state, Non-volatile
- Low vapor pressure
- Tunable structure and properties
- Wide electrochemical windows
- high electrical conductivity

Advantages of ILs in dissolving keratin

- Higher solubility
- It can be recycled with high recovery rate
- Less damage to keratin structure
- Tunable structure and properties

- It is nevertheless a challenge to identify the best ILs for keratin dissolution;
- Experimental measurement of all these systems is not practically feasible;
- A rapid and a priori screening method to predict the keratin solubility capacity for ILs is needed

Study of keratin dissolution in ionic liquids

Author	ILs	Temperature ℃	Time	Solubility
Yimei Ji	[Bmim]Cl/Na_2SO_3/H_2O	90	1h	6.6
	[Bmim]Cl	100	10h	4
	[Bmim]Cl	130	10h	11
	[Amim]Cl	130	10h	8
Haibo Xie	[Bmim]Br	130	10h	2
	[Bmim]BF_4	130	24h	ND
	[Bmim]PF_6	130	24h	ND
Yun-Xian Wang	[HOEmim]NTf_2/$NaHSO_3$	80	4h	2.5
	[Bmim]Cl	130	10h	50
	[Amim]Cl	130	10h	50
Azlia Idris	[Choline][thioglycolate]	130	10h	45
	Bis-(2-ethylhexyl) ammonium[thioglycolate]	130	10h	ND
Shuangshuang Zheng	[Bmim]Cl	130	5h	8
	[BPy]Cl	130	24h	ND
	[P_{444}]Cl	130	24h	ND
	[N_{444}]Cl	130	24	ND
	[N_{2221}]DMP	130	3h	8
	[Emim]DMP	130	1.5h	8
	[Bmim]OAc	130	10min	8
	[Bmim]SCN	130	15h	8
	[Bmim]$FeCl_4$	130	24	ND
	[Bmim]DMP	130	1.5h	8

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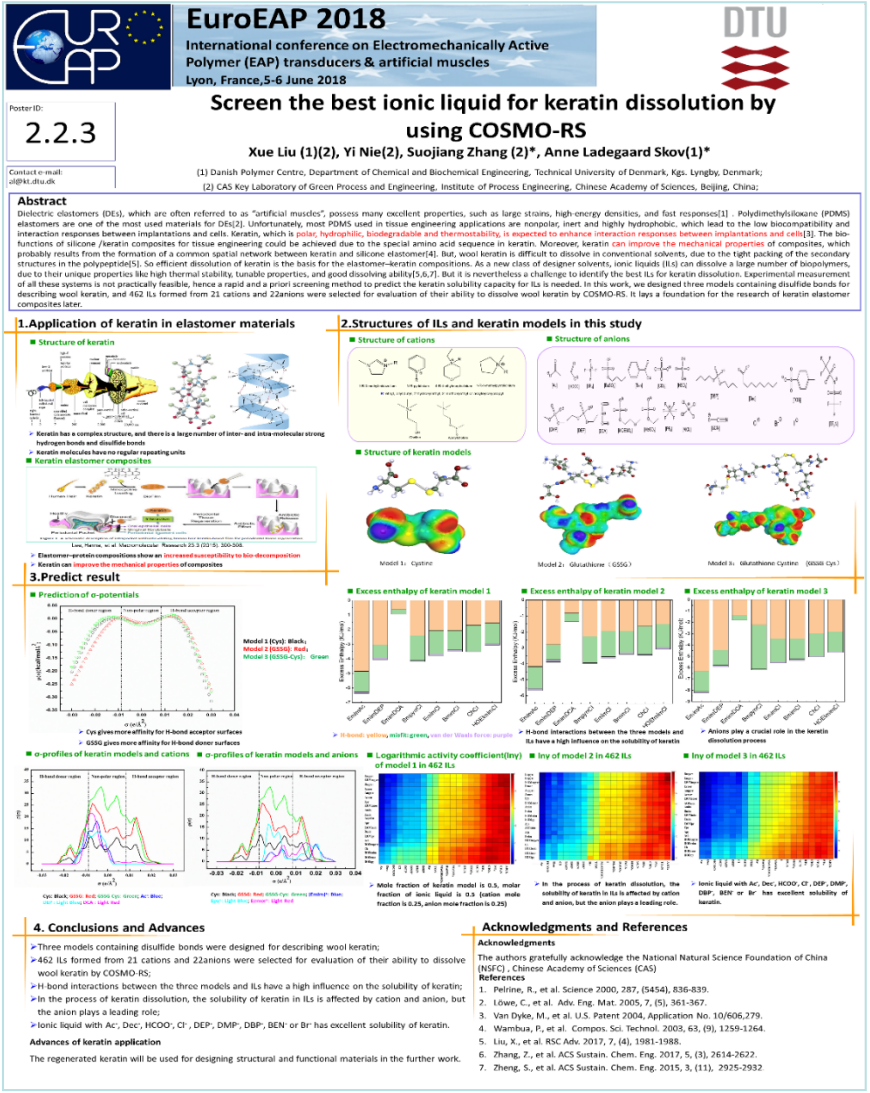

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Abstract

Dielectric elastomers (DEs), which are often referred to as "artificial muscles", possess many excellent properties, such as large strains, high-energy densities, and fast responses[1] . Polydimethylsiloxane (PDMS) elastomers are one of the most used materials for DEs[2]. Unfortunately, most PDMS used in tissue engineering applications are nonpolar, inert and highly hydrophobic, which lead to the low biocompatibility and interaction responses between implantations and cells. Keratin, which is polar, hydrophilic, biodegradable and thermostability, is expected to enhance interaction responses between implantations and cells[3]. The bio-functions of silicone /keratin composites for tissue engineering could be achieved due to the special amino acid sequence in keratin. Moreover, keratin can improve the mechanical properties of composites, which probably results from the formation of a common spatial network between keratin and silicone elastomer[4]. But, wool keratin is difficult to dissolve in conventional solvents, due to the tight packing of the secondary structures in the polypeptide[5]. So efficient dissolution of keratin is the basis for the elastomer–keratin compositions. As a new class of designer solvents, ionic liquids (ILs) can dissolve a large number of biopolymers, due to their unique properties like high thermal stability, tunable properties, and good dissolving ability[5,6,7]. But it is nevertheless a challenge to identify the best ILs for keratin dissolution. Experimental measurement of all these systems is not practically feasible, hence a rapid and a priori screening method to predict the keratin solubility capacity for ILs is needed. In this work, we designed three models containing disulfide bonds for describing wool keratin, and 462 ILs formed from 21 cations and 22anions were selected for evaluation of their ability to dissolve wool keratin by COSMO-RS. It lays a foundation for the research of keratin elastomer composites later.

1.Application of keratin in elastomer materials

- Structure of keratin
- Keratin has a complex structure, and there is a large number of inter- and intra-molecular strong hydrogen bonds and disulfide bonds
- Keratin molecules have no regular repeating units
- Keratin elastomer composites
- Elastomer–protein compositions show an increased susceptibility to bio-decomposition
- Keratin can improve the mechanical properties of composites

2.Structures of ILs and keratin models in this study

- Structure of cations
- Structure of anions
- Structure of keratin models

Model 1: Cystine; Model 2: Glutathione (GSSG); Model 3: Glutathione Cystine (GSSG Cys)

3.Predict result

- Prediction of σ-potentials
- Excess enthalpy of keratin model 1
- Excess enthalpy of keratin model 2
- Excess enthalpy of keratin model 3

Model 1 (Cys): Black; Model 2 (GSSG): Red; Model 3 (GSSG-Cys): Green

- Cys gives more affinity for H-bond acceptor surfaces
- GSSG gives more affinity for H-bond donor surfaces
- H-bond: yellow, misfit: green, van der Waals force: purple
- H-bond interactions between the three models and ILs have a high influence on the solubility of keratin
- Anions play a crucial role in the keratin dissolution process

- σ-profiles of keratin models and cations
- σ-profiles of keratin models and anions
- Logarithmic activity coefficient(lny) of model 1 in 462 ILs
- lny of model 2 in 462 ILs
- lny of model 3 in 462 ILs

Cys: Black; GSSG: Red; GSSG Cys: Green; Ac: Blue; Cl: light Blue; Br: light red

Cys: Black; GSSG: Red; GSSG Cys: Green; Cl-Anion: Blue; Cl: light Blue; Br-Anion: light Red

- Mole fraction of keratin model is 0.5, molar fraction of ionic liquid is 0.5 (cation mole fraction is 0.25, anion mole fraction is 0.25)
- In the process of keratin dissolution, the solubility of keratin in ILs is affected by cation and anion, but the anion plays a leading role.
- Ionic liquid with Ac^-, Dec^-, $HCOO^-$, Cl^-, DEP^-, DMP^-, DBP^-, BEN^- or Br^- has excellent solubility of keratin.

4. Conclusions and Advances

- Three models containing disulfide bonds were designed for describing wool keratin;
- 462 ILs formed from 21 cations and 22anions were selected for evaluation of their ability to dissolve wool keratin by COSMO-RS;
- H-bond interactions between the three models and ILs have a high influence on the solubility of keratin;
- In the process of keratin dissolution, the solubility of keratin in ILs is affected by cation and anion, but the anion plays a leading role;
- Ionic liquid with Ac^-, Dec^-, $HCOO^-$, Cl^-, DEP^-, DMP^-, DBP^-, BEN^- or Br^- has excellent solubility of keratin.

Advances of keratin application

The regenerated keratin will be used for designing structural and functional materials in the further work.

Acknowledgments

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Thank You!