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14. ABSTRACT

Via computational modeling, we investigate the mechanism of strain recovery in dual cross-linked polymer grafted nanoparticle networks. The individual nanoparticles are composed of a rigid spherical core and a corona of grafted polymers that encompass reactive end groups. With the overlap of the coronas on adjacent particles, the reactive end groups form permanent or labile bonds, and thus form a “dual cross-linked” network. We consider the strain recovery of the material after it is allowed to relax from the application of a tensile force. Notably, the existing labile bonds can break and new bonds can form in the course of deformation. Hence, a damaged material could be

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Report Title

MODELING THE RESPONSE OF DUAL CROSS-LINKED NANOPARTICLE NETWORKS TO MECHANICHAL DEFORMATION

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Via computational modeling, we investigate the mechanism of strain recovery in dual cross-linked polymer grafted nanoparticle networks. The individual nanoparticles are composed of a rigid spherical core and a corona of grafted polymers that encompass reactive end groups. With the overlap of the coronas on adjacent particles, the reactive end groups form permanent or labile bonds, and thus form a “dual cross-linked” network. We consider the strain recovery of the material after it is allowed to relax from the application of a tensile force. Notably, the existing labile bonds can break and new bonds can form in the course of deformation. Hence, a damaged material could be “rejuvenated” both in terms of the recovery of strain and the number of bonds, if the relaxation occurs over a sufficiently long time. We show that this rejuvenation depends on the fraction of permanent bonds, strength of labile bonds, and maximal strain. Specifically, we show that while an increase in the labile bond energy leads to formation of a tough material, it also leads to delayed strain recovery. Further, we show that an increase in the fraction of permanent bonds not only enables faster recovery but also yields improved recovery even after multiple stretch-relaxation cycles.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/31/2014	7.00	Balaji V. S. Iyer, Victor V. Yashin, Tomasz Kowalewski, Krzysztof Matyjaszewski, Anna C. Balazs. Strain recovery and self-healing in dual cross-linked nanoparticle networks, Polymer Chemistry, (03 2013): 0. doi: 10.1039/c3py00075c
01/31/2014	8.00	Olga Kuksenok, Pratyush Dayal, Amitabh Bhattacharya, Victor V. Yashin, Debabrata Deb, Irene C. Chen, Krystyn J. Van Vliet, Anna C. Balazs. Chemo-responsive, self-oscillating gels that undergo biomimetic communication, Chemical Society Reviews, (2013): 0. doi: 10.1039/c3cs35497k
01/31/2014	9.00	Peixi Yuan, Olga Kuksenok, Dustin E. Gross, Anna C. Balazs, Jeffrey S. Moore, Ralph G. Nuzzo. UV patternable thin film chemistry for shape and functionally versatile self-oscillating gels, Soft Matter, (2013): 0. doi: 10.1039/c2sm27100a
01/31/2014	10.00	P. Dayal, O. Kuksenok, A. C. Balazs. Reconfigurable assemblies of active, autochemotactic gels, Proceedings of the National Academy of Sciences, (12 2012): 0. doi: 10.1073/pnas.1213432110
01/31/2014	11.00	Orit Peleg, Thierry Savin, German V. Kolmakov, Isaac G. Salib, Anna C. Balazs, Martin Kröger, Viola Vogel. Fibers with Integrated Mechanochemical Switches: Minimalistic Design Principles Derived from Fibronectin, Biophysical Journal, (11 2012): 0. doi: 10.1016/j.bpj.2012.09.028
01/31/2014	12.00	Balaji V. S. Iyer, Isaac G. Salib, Victor V. Yashin, Tomasz Kowalewski, Krzysztof Matyjaszewski, Anna C. Balazs. Modeling the response of dual cross-linked nanoparticle networks to mechanical deformation, Soft Matter, (2013): 0. doi: 10.1039/c2sm27121d
08/28/2011	1.00	Isaac G. Salib, German V. Kolmakov, Chet N. Gnegy, Krzysztof Matyjaszewski, Anna C. Balazs. Role of Parallel Reformable Bonds in the Self-Healing of Cross-Linked Nanogel Particles, Langmuir, (04 2011): 0. doi: 10.1021/la104609t
08/29/2012	2.00	Pratyush Dayal, Olga Kuksenok, Amitabh Bhattacharya, Anna C. Balazs. Chemically-mediated communication in self-oscillating, biomimetic cilia, Journal of Materials Chemistry, (2012): 0. doi: 10.1039/c1jm13787e
08/29/2012	3.00	Irene Chou Chen, Olga Kuksenok, Victor V. Yashin, Anna C. Balazs, Krystyn J. Van Vliet. Mechanical Resuscitation of Chemical Oscillations in Belousov-Zhabotinsky Gels, Advanced Functional Materials, (06 2012): 0. doi: 10.1002/adfm.201103036
08/29/2012	4.00	Victor V Yashin, Olga Kuksenok, Pratyush Dayal, Anna C Balazs. Mechano-chemical oscillations and waves in reactive gels, Reports on Progress in Physics, (06 2012): 0. doi: 10.1088/0034-4885/75/6/066601
08/29/2012	5.00	Victor V. Yashin, Seiichi Suzuki, Ryo Yoshida, Anna C. Balazs. Controlling the dynamic behavior of heterogeneous self-oscillating gels, Journal of Materials Chemistry, (2012): 0. doi: 10.1039/c2jm32065g

TOTAL: **11**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

MRS Fall Meeting, Boston, MA, Dec. 1-6, 2013. Symposium on "Modeling and Theory-Driven Design of Soft Materials". "Designing Self-regenerating Polymer Gels"

348. Composites at Lake Louise Conference, Lake Louise, Alberta, Canada, Nov. 3-7, 2013. "Self-healing in Dual Cross-linked Nanoparticle Composites".

347. Rushmore Plaza Civic Center, Rapid City, SD, Oct. 3, 2013. Mines Medal. "Designing Materials that Appear to 'Think'"

346. Chemical & Biological Engineering Dept., South Dakota School of Mines, Rapid City, SD, Oct. 3, 2013. "Designing Biomimetic Self-Healing Materials"

345. Journey Museum, Rapid City, SD, Oct. 1, 2013. "Amazing Science Lecture Series", "The Amazing Behavior of Self-Oscillating Gels"

344. South Dakota School of Mines, Rapid City, SD, Oct. 1, 2013. Student Convocation— Guest Speaker: "The Amazing Behavior of Self-Oscillating Gels"

343. 246th ACS National Meeting, Indianapolis, IN, Sept. 8-12, 2013. "Modeling the response of dual cross-linked nanoparticle networks to mechanical deformation".

342. DOE Biomaterials Contractors Meeting, Gaithersburg, MD., Aug. 19-21, 2013, "Modeling Self-healing Behavior in Biomimetic Materials".

341. 34th Australian Polymer Society Meeting, Darwin, Australia, July 7-10, 2013. "Modeling Active Polymer Gels".

340. Isaac Newton Institute for Mathematical Sciences, Workshop on Dynamics of Suspensions, Gels, Cells and Tissues, Cambridge, UK, June 24-28, 2013. "Reconfigurable Assemblies of Active, Auto-chemotactic Gels".

339. Fourth International Conference on Self-healing Materials, Ghent, Belgium, June 16-20, 2013. "Modeling self-healing in dual cross-linked nanoparticle networks".

338. Cambridge University, Cavendish Laboratories, Cambridge, UK, March 8, 2013. "Reconfigurable Assemblies of Active, Auto-chemotactic Gels".

337. Pennsylvania State University, Center for Nanoscale Science/MRSEC, State College, PA, Feb. 25, 2013. "Reconfigurable Assemblies of Active, Auto-chemotactic Gels".

Number of Presentations: 13.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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01/31/2014	6.00	. Modeling Polymer Grafted Nanoparticle Networks Reinforced by High-strength Chains, Soft Matter (08 2013)

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Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Mines Medal, South Dakota School of Mines, 2013.

Fellow, Royal Society of Chemistry, 2010.

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Balaji Iyer	0.50
Victor Yashin	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Anna Balazs	0.25	
FTE Equivalent:	**0.25**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Emily Crabb	1.00	
Nick Moeller	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

MODELING THE RESPONSE OF DUAL CROSS-LINKED NANOPARTICLE NETWORKS TO MECHANICHAL DEFORMATION

Anna C. Balazs

1 Introduction

Advances in the grafting of polymer chains onto nanoparticles now permit significant control over the type and number of chains that can be anchored on the particles. Through the appropriate functionalization of these grafted chains, the coated nanoparticles can be interconnected into extensive networks. Recent studies have revealed that these nanoparticle networks can exhibit remarkable mechanical properties [1]. There are, however, few theoretical or computational models [2,3], that can provide useful guidelines for tailoring the properties of the functionalized chains to yield the desired mechanical properties in networks of polymer grafted nanoparticles (or “PGNs”).

The problem becomes particularly challenging due to a number of issues that must be addressed in designing advantageous PGN networks. For instance, while conventional soft nanogels provide a useful degree of elasticity, the polymers grafted onto the rigid nanoparticles must now impart the desired flexibility. Furthermore, the grafted polymers must be functionalized with the appropriate reactive groups in order to achieve an effective dual cross-linking. These constraints introduce a number of design variables, such as the length of the grafted chains and the interaction energies between reactive groups; these play an important role in dictating the overall mechanical behavior of the composite.

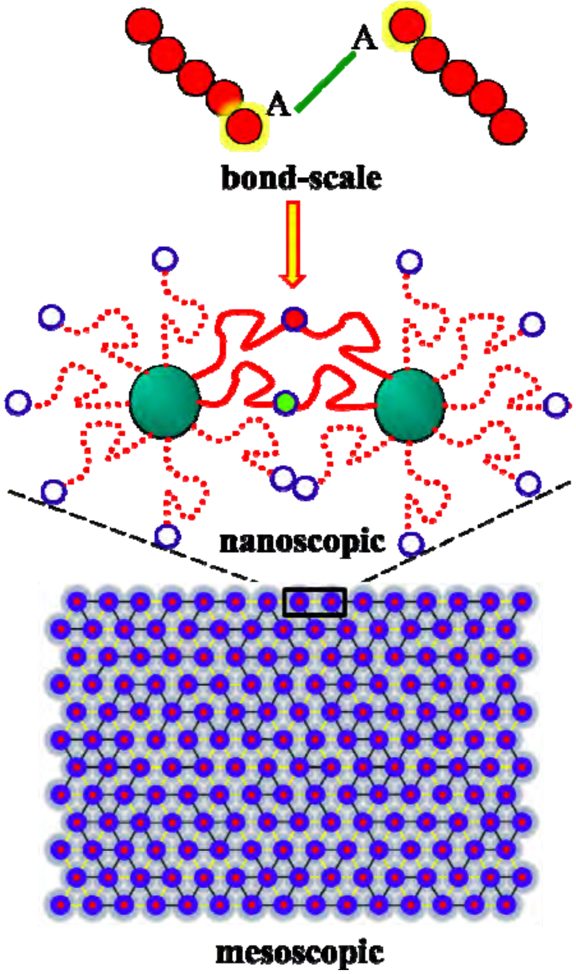
The appropriate computational models would greatly facilitate the design of such hybrids materials. Such computational studies are challenging because all the relevant length and time scales should be captured in one specific model. Namely, the model must span a range of architectural features and temporal events. Herein, we develop an approach that encompasses the essential features to establish guidelines for tailoring the strength and toughness of PGN networks [4].

2 Model & Simulation Methodology

We develop a hybrid computational model for the behavior of a network of cross-linked polymer-grafted nanoparticles (PGNs). The individual nanoparticles are composed of a rigid core and a corona of grafted polymers that encompass reactive end groups (Fig 1). With the overlap of the coronas on adjacent particles, the reactive end groups can form permanent or labile bonds, which lead to the formation of a “dual cross-linked” network (Fig 1). To capture these multi-scale interactions, our approach integrates the essential structural features of the polymer grafted nanoparticles, the interactions between the overlapping coronas, and the kinetics of bond formation and rupture between the reactive groups on the chain ends.

The interaction between two PGNs is modeled through a sum of interaction potentials and is given by $U_{\text{int}} = U_{rep} + U_{coh} + U_{link}$. The first term, U_{rep} , characterizes the repulsive interactions between the grafted nanoparticles that decays exponentially at large separations and exhibits a logarithmic growth when the particles are brought close to each other [5]. The second term in the potential, U_{coh} , describes the attractive cohesive interaction between the coated particles. This term is constant for small inter-particle separations, but balances the repulsion at the edges of the corona to allow for the overlap between neighboring coronas [5]. The final term, U_{link} , describes the attractive interaction [6] between the particles linked by the bonded polymer arms and depends on the number of bonds, N_b , formed between the given pair of particles.

The number of bonds formed, N_b, depends on the maximum number of bonding pairs, $N_{\max}$, available in the corona overlap volume, and on the rates of formation and rupture of individual bonds. The rate of formation depends on the probability of contact of two chain ends that, in turn, depends on the free-end distribution in the corona. At the individual bond level, we use the Bell model [7] to describe the rupture and re-formation of bonds due to thermal fluctuations.



Via this model, we determine the tensile properties of the dual cross-linked samples in a two-step simulation. In the first step, we numerically evolve the equation for the number of bonds, N_b. In the next step, we use this value of N_b to calculate the spring force and integrate numerically the equation of motion: $d\mathbf{x}/dt = \mu\mathbf{F}_{tot}$ where, μ, is the mobility and $\mathbf{F}_{tot}$ is the total force on the grafted particle.

3 Results & Conclusion

We find that the mechanical behavior of the network can be tailored by altering the bond energies of the labile bonds, the fraction of permanent bonds in the network and the thickness of the polymer corona. In particular, for a network with weaker labile bonds, an increase in fraction of permanent bonds and the contour length of the chain can yield a tough network that behaves like a polymeric material, which exhibits cold drawing/necking. On the other hand, similar changes to the network with stronger labile bonds lead to an increase in toughness, with the network characteristics being similar to that of a purely ductile material. Variations in the ratio between the strain rate and the bond rupture rate are also found to affect the response of the networks. Our model provides a powerful approach for predicting how critical features of the system affect the performance of cross-linked polymer-grafted nanoparticle networks.

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