Plenary 2

Progress in multi-scaled structure and related properties of elastomer nanocomposites explored by molecular dynamics simulation

Liqun Zhang^{1,2,3}

¹*Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials*

²*Beijing Engineering Research Center of Advanced Elastomers and*

³*State Key Laboratory of Organic-Inorganic Composites,
Beijing University of Chemical Technology, Beijing 100029,
People's Republic of China*

E-mail: zhanglq@mail.buct.edu.cn

Prof Zhang has been very active in the research field of polymer science and technology for over 25 years since his bachelor thesis in 1989 and has been leading the Center of Advanced Elastomer Materials (www.caem.buct.edu.cn), which holds a leading position in China in the field of elastomeric polymer science and technology and possesses an internationally well recognized fame. He is the Dean of College of Materials Science and Engineering at Beijing University of Chemical Technology, also the head of Key Lab. of Beijing City on Preparation and Processing of Novel Polymer Materials, the head of Engineering Research Center of Ministry of Education on Energy and Resource Saved Elastomers, and associate head of State Key Lab of Organic-Inorganic Composites, China. He is the fellow of China Chemistry Industry and Engineering Society, the fellow of China Materials Research Society, the fellow of China Composite Materials Society, the fellow of China Nano Science and Technology Society, vice president of China Rubber Division, vice president of China Polymer Materials Engineering Division, and vice president of China Micro-Nano Composites Division, etc. Currently, he is serving as an editorial board member of "Expressed Polymer Letter", "Mini Reviews in Medicinal Chemistry (USA)", "Journal of Applied Polymer Science (USA)", "Rubber Chemistry and Technology (USA)", "Plastics, Rubber and Composites: Molecular Engineering (UK)", "Elastomers and Composites (Korea)" and other 9 Chinese scientific journals.

He has published over 300 international papers on above subjects and some of them are in highly reputed journals such as Advanced Functional Materials, ACS Nano, Biomaterials, Biomacromolecules, Macromolecules, Langmuir, Polymer, and Progress in Polymer Science. His papers have been cited by peers in a positive manner for over 7000 times (Web of Science) with an H-index of 40. He is a (co-) author of 8 books (chapters) and has given over 80 plenary/keynote/invited lectures in international conferences. He and his team members have filed 160 Chinese patents. He has received many high reputed scientific awards from relative Association, Society, Ministry and Committee of China including prestigious "9th China Youth Scientific Award" and "National Invention Award".

In 2012, he received Spark-Thomas Award from ACS Rubber Division, Asia Research Award from Society of Chemical Engineering of Japan. In 2014, he got the Morand Lambla Award from International Polymer Processing Society, which was due to his important contributions to elastomeric polymer science and technology.

Abstract

In this talk I will systematically present some important simulated results of elastomer nanocomposites (ENCs) via molecular dynamics simulation. First, we studied the dispersion and aggregation behavior of bare nanoparticles (NPs) with different geometries such as spherical, sheet-like and rod-like on the molecular scale. To model small ligands used in experiments to realize better dispersion, we investigated the dispersion of NPs end-grafted with polymer chains by varying the grafted chain length and grafting density. In addition, the effect of the middle- and end-functionalization on the dispersion of NPs is also covered. Second, we probed the translational and relaxation dynamics at the chain and segmental length scales of the interfacial regions, hoping to elucidate whether "glassy polymer layers" exist around NPs. Meanwhile, the formation mechanism of bound rubber is as well included. Third, we simulated the enhancement of the stress-strain and fracture toughness induced by NPs, providing a molecular reinforcing mechanism. Fourth, the famous "Payne effect", namely the decrease of the storage modulus as a function of the strain amplitude was examined, uncovering the underlying reason responsible for this non-linear behavior, and meanwhile how the introduced carbon nano-springs can effectively reduce the dynamic hysteresis of ENCs is illustrated. Fifth, through simulation synthesis approach, we put forward a new and achievable approach to design and prepare a nanoparticle chemical network, with the NPs acting as "giant cross-linkers" or netpoints to chemically connect the

dual end-groups of each polymer chain to form a network. We find this new network structure possesses excellent static and dynamic mechanical properties, highlighting a ultralow dynamic hysteresis loss tailored for green automobile tires. In general, computer simulation is shown to have the capability to obtain some fundamental understanding of ENC, in hopes of providing some design principles for synthesizing and fabricating multi-functional and high performance ENCs.

1. Introduction

It is well known that elastomer nanocomposites possess a complicated multi-scaled structure, such as from the repeating unit ($\approx 1nm$), the segment length ($\approx 5-10nm$) to the radius of gyration and end-to-end distance ($\approx 50-100nm$) of polymer chains, and the primary particle ($\approx 20-50nm$), the aggregate ($\approx 100-200nm$) to the agglomerate ($\approx 10^4-10^6 nm$) of the spherical nanoparticles (NPs). It is always difficult to characterize this multi-scaled structure through experimental tools, and molecular dynamics simulation, as a powerful computational simulation approach, can be employed to overcome this challenge. Besides this multi-scaled structure, to establish the structure-property relation is also lacking, particularly about the static and dynamic mechanical properties. Molecular dynamics simulation can be utilized to conveniently vary a large space of structural parameters such as the size, shape and volume fraction of NPs, the physical and chemical interfacial interaction, the conformation, the molecular weight and its distribution of polymer chains, different dispersion state and morphology, and so on. In order to achieve this target, we need to develop a multi-scale simulation technique to combine the molecular dynamics simulation at the molecular level with the finite element analysis at the microscopic level.

2. Simulation techniques

We use the coarse-grained model, and the polymer chains are modeled through the standard bead-spring model. We note that although these polymeric chains are rather short, they have already shown the static and dynamic behavior characteristic of long chains. By mapping the coarse-grained model to the real one, each bond corresponds to $n \approx 3-6$ covalent bonds along the backbone of a realistic chemical chain. Since it is not our aim to study any specific polymer, the mass m and diameter σ of each bead is set to be unit, which indicates that all calculated quantities are dimensionless. The non-bonded interaction between all polymer beads is modeled through the truncated and shifted Lennard-Jones (LJ) equation as follows:

$$U(r) = \begin{cases} 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] + C & r < r_{cutoff} \\ 0 & r \geq r_{cutoff} \end{cases} \quad (1)$$

where the LJ interaction is cut off at the distance $r = r_{cutoff}$ and C is a constant, which guarantees that the potential energy is continuous at the cutoff distance. r is the separation distance between two polymer beads. σ defines the length scale and ϵ is the energy scale of our model. The interaction between the adjacent bonded beads is modeled by a harmonic potential:

$$U_{bond} = \frac{1}{2} K (r - r_0)^2 \quad (2)$$

Where $K = 500\epsilon/\sigma^2$ and $r_0 = 1.0\sigma$, guaranteeing a certain stiffness of the bonds while avoiding the high-frequency modes and chain crossing. r is the separation distance between two connected polymer beads.

The NPT ensemble is adopted in our MD simulations, where the temperature is mostly fixed at $T^* = 1.0$, and the pressure is set to be $P^* = 0.01$ by using the Nose-Hoover thermostat and barostat. The velocity-Verlet algorithm is used to integrate the equations of motion with a time step $\delta t = 0.001$, where the time is reduced by τ (τ is the unit time of the simulation). The periodic boundary condition is used in all three directions. Before the cross-linking, the obtained structures are equilibrated under the NPT ensemble over a long time so that each chain has moved at least $2R_g$. To produce the cross-linked bonds, we randomly select pairs of beads within a distance of 1.25σ of each other as a function of the simulation time, and tether them together by means of the harmonic potential. After the cross-linking process, the obtained structures are further equilibrated with the NPT ensemble, guaranteeing that our simulated systems have been fully and properly equilibrated. All MD runs are carried out through the large scale atomic/molecular massively parallel simulator (LAMMPS), which is developed by Sandia National Laboratories. More simulation details can be found in our previous work.

3. Results and Discussion

3.1 We studied the dispersion and aggregation behavior of bare nanoparticles (NPs) with different geometries such as spherical, sheet-like and rod-like on the molecular scale. In the case of spherical NPs, a moderate interfacial interaction strength exists to achieve the best dispersion state, as illustrated in Figure 1. To model small ligands used in experiments to realize better dispersion, we investigated the dispersion of NPs end-grafted with polymer chains by varying the grafted chain length and grafting density. In addition, the effect of the middle- and end-functionalization on the dispersion of NPs is also covered.

Figure 1. Snapshots of the dispersion state of the nanoparticles (NPs) as a function of the polymer-filler interaction strength ϵ_{np} . Note that the red spheres denote spherical NPs, and the blue points represent the polymer matrix.

3.2 We probed the translational and relaxation dynamics at the chain and segmental length scales of the interfacial regions, hoping to elucidate whether “glassy polymer layers” exist around NPs. Meanwhile, the formation mechanism of bound rubber is as well simulated.

Figure 2. (a) The adsorption state of a single polymer chain on the surface of the filler in the case of weakly attractive $\epsilon_{np}=2.0$ and strongly attractive $\epsilon_{np}=10.0$ polymer-filler interaction strength. The orientation of polymer chains on the (b) bond and (c) segmental length scales as a function of the distance from the mass center of the filler for three different cases of polymer-filler interaction strength such as purely repulsive, weakly attractive and strongly attractively.

3.3 We simulated the enhancement of the stress-strain and fracture toughness induced by NPs, providing a molecular reinforcing mechanism.

Figure 3. Snapshot of the uniaxial tensile deformation. The red spheres denote the spherical NPs, and the blue beads stand for polymer chains.

3.4 The famous “Payne effect”, namely the decrease of the storage modulus as a function of the strain amplitude was examined, uncovering the underlying reason responsible for this non-linear behavior, and meanwhile how the introduced carbon nano-springs can effectively reduce the dynamic hysteresis of ENC is illustrated.

Figure 4. Snapshots of the dynamic shear deformation, with the increase of the strain amplitude.

3.5 Through simulation synthesis approach, we put forward a new and achievable approach to design and prepare a nanoparticle chemical network, with the NPs acting as “giant cross-linkers” or netpoints to chemically connect the dual end-groups of each polymer chain to form a network. We find this new network structure possesses excellent static and dynamic mechanical properties, highlighting a ultralow dynamic hysteresis loss tailored for green automobile tires. As shown in Figure 5 (a), we have schematically shown three typical nanoscale frictions such as polymer-nanoparticle sliding, nanoparticle-nanoparticle sliding and polymer-polymer sliding. The dynamic mechanical properties are further compared for styrene-butadiene-styrene (SBS), thermoplastic polyurethane (TPU), end-linked PDMS, NR/silica and NR/carbon black systems in Figure 5 (b) and (c).

Figure 5. (a) Schematics of the three nanoscale frictions such as polymer-nanoparticle sliding, nanoparticle-nanoparticle sliding and polymer-polymer sliding. Comparison of the storage modulus (b) and loss factor (c) as a function of the strain amplitude for styrene-butadiene-styrene (SBS), thermoplastic polyurethane (TPU), end-linked PDMS, NR/silica and NR/carbon black systems. (d) Comparison of the loss factor at the strain amplitude equal to 7%.

3.6 To effectively establish the relation between multi-scaled structure and property of elastomer nanocomposites, we aim to develop an approach that bridges molecular dynamics simulation at the molecular level with finite element analysis at the microscopic level.

4. Conclusions

We focus our attention on the dispersion of the fillers, the polymer-filler interaction interfacial interaction, the static mechanical reinforcement such as the stress-strain and the fracture behavior, the Payne effect and the dynamic mechanical properties. More efforts should be devoted to developing the multi-scale simulation technique by combining molecular dynamics simulation and finite element analysis.

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