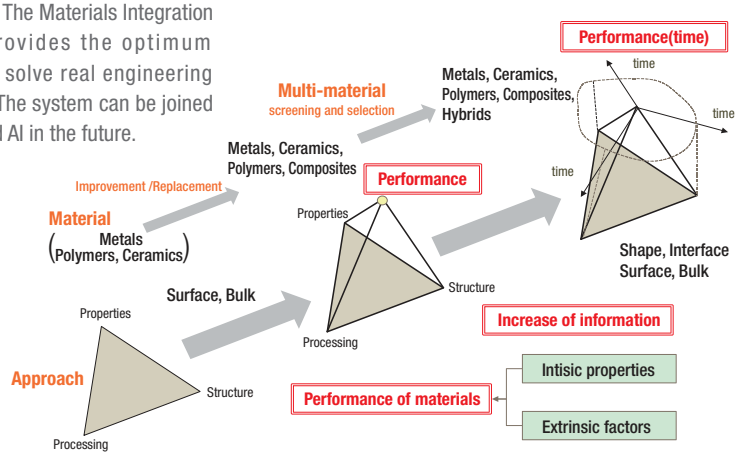
SIP-SM'4
Structural Materials for Innovation

MATERIALS INTEGRATION FOR ENGINEERING POLYMERS

Aiming at breakthroughs via Merger of Different Fields

The number of materials and variety of academic tools are increasing. The Materials Integration system provides the optimum solution to solve real engineering problems. The system can be joined with IoT and AI in the future.

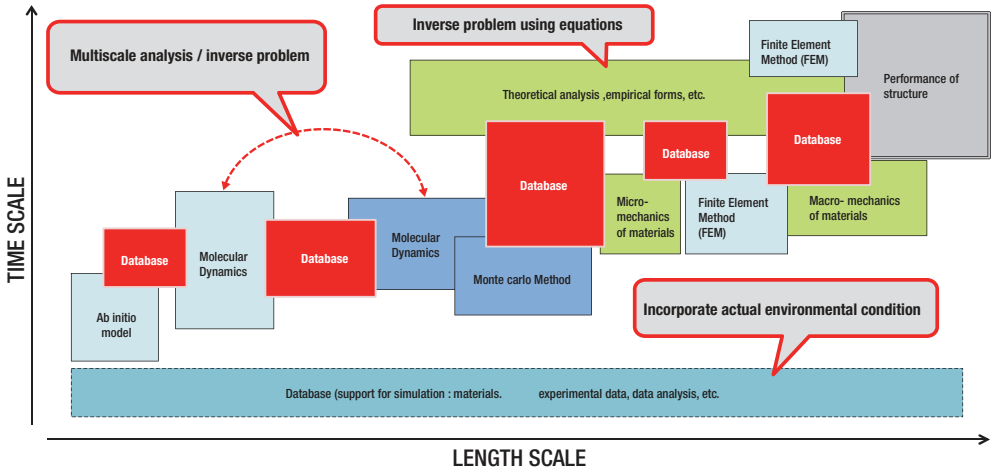


Materials Integration uses all scientific knowledge to help research and development of materials and structures. The system is designed from an engineering point of view. The system also provides information on the effect of service environment on the performance of materials and components. These computer-based estimations help to save research and development time.

Structural Materials for Innovation

SIP Cross-ministerial Strategic Innovation Promotion Program

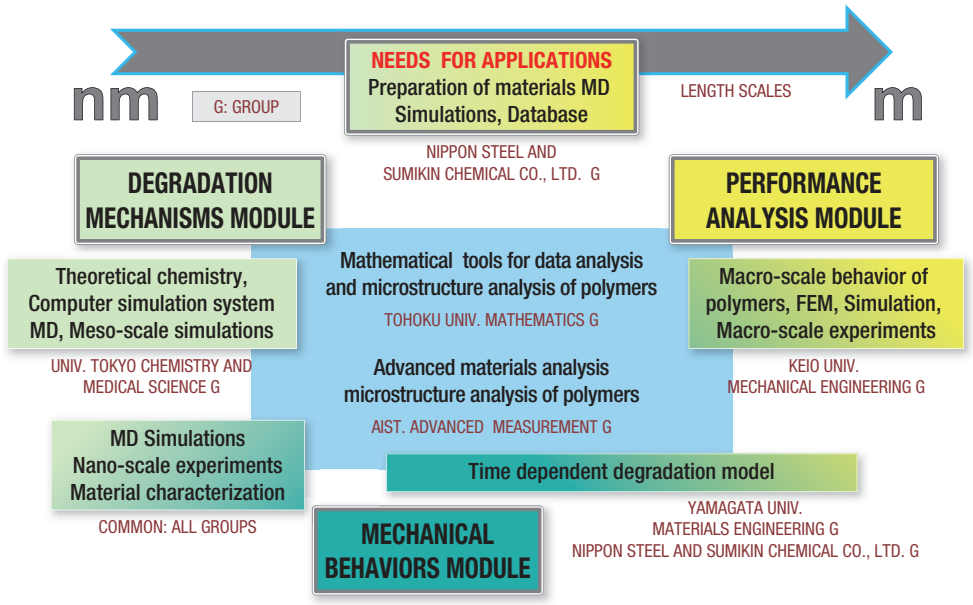
Concept & Approach



Materials Integration (MI) for engineering polymer materials combines different length scale and time scale behaviors via a new database system. The MI system is expected to understand the relationship between processing, structures, properties and performance of the engineering polymer materials from any length scale and time scales. Materials Integration for engineering polymers aims to bridge all scientific knowledge and tools of related fields. The tools include analysis, simulations, experiments, empirical forms, etc.

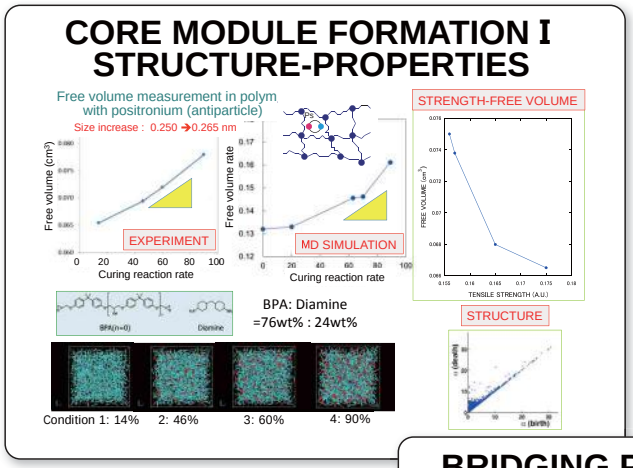
Unique formation of research fields in the researchers in MI for engineering polymers covers mathematics, medicine, materials science, chemistry, physics, etc. Inverse problems is expected to solve using the MI system, this is especially effective for shortening of R&D time of related materials fields.

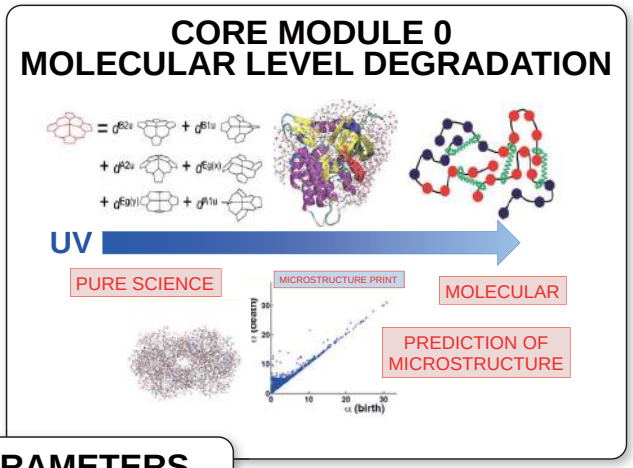
Team Members and Roles

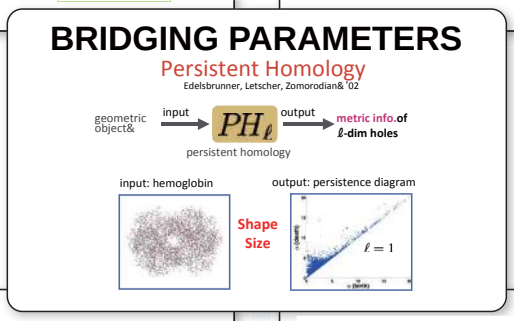


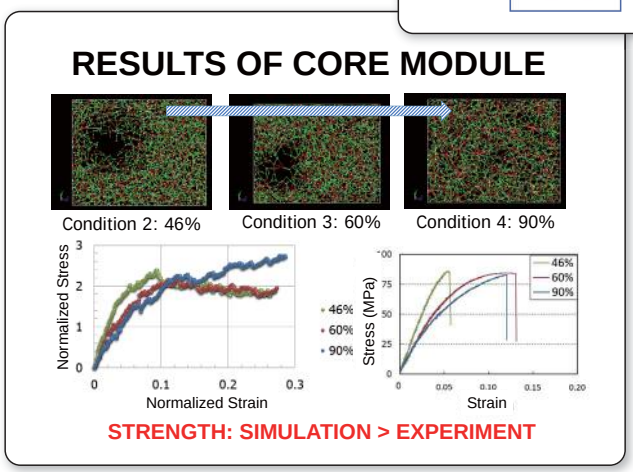
The team organization for Materials Integration of polymer materials is performed following the selection of individual research proposals. Thus, members did not know the actual task before team formation. This point is especially important to achieve the high potential MI systems for engineering polymers. The team is expected to bring new approaches and to form integration of research fields to achieve the goals of the MI system. Understanding of real engineering problems through the developed MI system is designed to address use industrial applications using open built-in databases and closed individual databases prepared by the user companies.

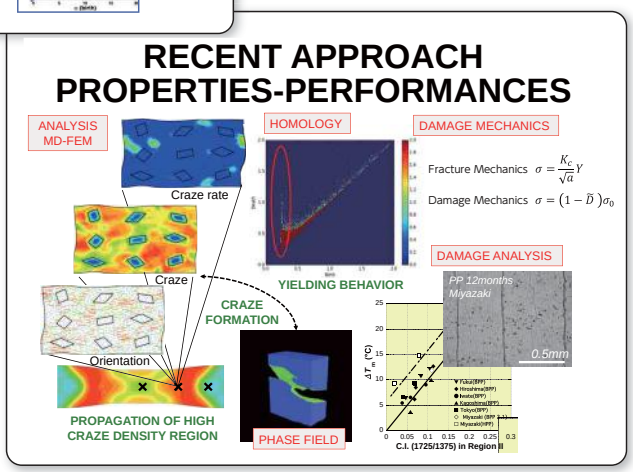
Research and Development of Polymer MI











Initially, we focused on structural epoxy polymers and prepared some model epoxy resin samples. Mechanical tests, positron annihilation-based free volume measurements, nano-palpation atomic force microscopy (AFM) analysis, and full atom and coarse-grained molecular dynamics (MD) simulations were conducted to clarify the relationship between molecular structures and mechanical properties. Additionally, the material heterogeneities were quantified via persistent homology analysis. Then, databases were created based on these results and applied to solve inverse problems.

The effects of conversion on mechanical properties were confirmed by subjecting the polymer samples to mechanical tests. The free volumes of the polymer samples increased as their conversion by positron annihilation increased. This finding is in good agreement with the MD simulation results.

The heterogeneities of the polymer materials are reflected in dynamic systems of the structural materials, including their fracture and damage mechanics. Therefore, we aim to develop a polymer materials integration (MI) system consisting of practical modules that can be used to correlate the spatial and temporal scales.

In addition to the conventional approaches used to study polymers, the development of approaches based on fresh perspectives has been enabled through the combined efforts of many researchers with expertise in various scientific and technological fields. Thus, our research and development have evolved, and we now pursue high-level, novel polymer MI studies. For example, the use of mathematical approaches enables combining different technical elements to define the components of polymer materials.

Breakthroughs via Merger of Different Fields

A mathematical approach for materials integration and its applications

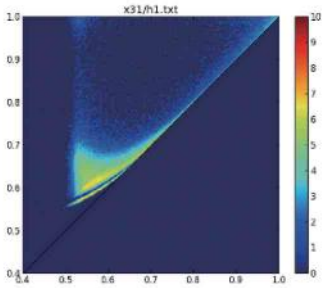
Mathematics

Keyword AFM, ABED, XFH, Phase- field method, Computational homology, Coarse-grained simulation

YASUMASA NISHIURA

Advanced Institute for Materials Research, Tohoku University

We will explore a new mathematical approach to clarify and predict the hierarchical dynamical structures of materials degradation and fracture. Coarse-grained simulations and the phase-field method will be used to describe the fracture dynamics in a complementary manner. A useful languages to describe the hierarchical structure of degradation and fill the micro-macro separation gap is computational topology, especially persistent homology, which not only counts the number of holes, but also distinguishes the sizes and shapes of complex morphologiesy. Cutting-edge measurements, such as AFM, ABED, and X-ray fluorescence holography (XFH), will be combined with these mathematical tools and integrated into a topological simulator that able to predict the onset of degradation and describe fracture propagation.



Performance prediction for polymers by nonlinear analysis

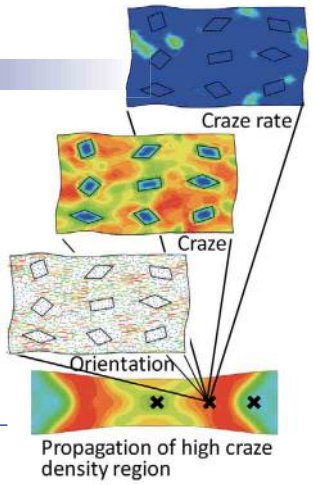
Mechanical engineering

Keyword Nonlinear solid mechanics, Multiscale FE analysis, Damage mechanics

KAZUYUKI SHIZAWA

Department of Mechanical Engineering, Keio University

Our research is classified into nonlinear solid mechanics to analyze large deformation of materials and materials science to investigate the microscopic behavior of polymers. Our group proposed the molecular-chain plasticity model to represent deformation behavior of polymers on the basis of crystal plasticity theory by assuming molecular-chain slip systems on molecular-chain entanglements. In this model, we adopted the Arrhenius-type inelastic response law based on change of local free volume and associated the deformation activation energy with the evolution behavior of craze that is a damage specific to polymers. Using this model, we performed the multiscale finite element (FE) analysis with a homogenization method and reproduced various phenomena computationally, such as propagation of a strain-rate shear band, molecular-chain orientation, nonlinear strain recovery during unloading and the propagation of a high-craze-density region (see the figure shown on the right). Our aim is to predict the mechanical performance of matrix for fiber-reinforced plastics by introducing ultraviolet degradation effects into our model.



Computational chemistry approaches

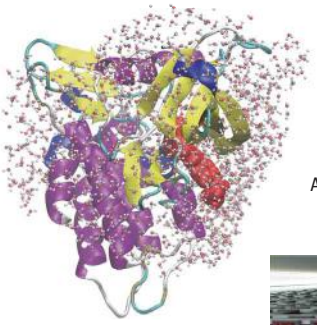
Medicine

Keyword molecular dynamics calculation, all-atom model, electronic state calculation, coarse-grained model

TAKEFUMI YAMASHITA

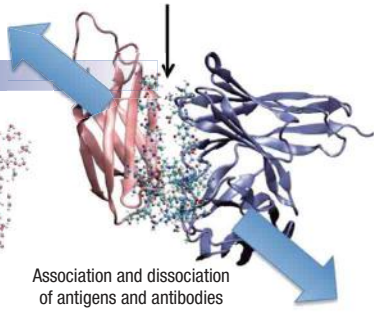
Research Center for Advanced Science and Technology, The University of Tokyo

Computational chemistry is a branch of science that aims at understanding and explaining the properties of matter via theoretical or computational studies at the atomic or molecular level. This branch of chemistry usually involves the use of three element technologies: all-atom molecular dynamics calculation for simulating the motions of all the atoms constituting a system, molecular orbital calculation for clarifying the electron motions that determine the nature of atoms, and coarse-grained model calculation for analyzing a large system by treating a large atom group as a single particle. We expect the aforementioned methods, individually or in combination, to be used as substitutes to difficult and complex experiments. Application of these methods to proteins, which are important macromolecules playing essential biological roles, has long been a difficult challenge. However, because of notable advances in the computational power , these methods based on computational chemistry have emerged as powerful analytical tools. For example, it is now possible to clarify atomic-level mechanisms underlying protein functions by means of all-atom molecular dynamics calculations. We plan to pursue further research to understand the nature of various polymer materials and enable their design from the viewpoint of computational chemistry.



Kinase (indicated by ribbons) and inhibitor (indicated by red balls)

Interface complementarity/water molecules located at the interface



Association and dissociation of antigens and antibodies

K computer
(RIKEN Advanced Institute for Computational Science)

Japan Science and Technology Agency

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Japan Science and Technology Agency(JST)
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http://www.jst.go.jp/sip/k03.html

2016.02

Expectation for Materials Integration of engineering polymers

Professor **Teruo Kishi**
Program Director

The main objective of Materials Integration (MI) for engineering polymers is to reduce the time needed for research and development of engineering materials. Materials Integration is expected to become a new concept tool different from traditional research and development. The MI system for engineering polymers is a new idea and the research result is expected to contribute to cutting-edge research and development of engineering polymers.

Materials Integration for engineering polymers

Professor **Yutaka Kagawa**
Deputy Program Director

Our research on Materials Integration of polymer materials uses all scientific tools such as theory, experiment, analyses, simulation, database, empirical forms, etc. to solve real engineering problems and reduce time for R&D. The team members have completely different specialty fields. The pioneer organization of an interdisciplinary team is expected to open new approaches of materials science and engineering of polymers in the near future.

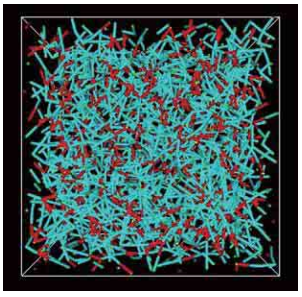
Chemistry

Development of practical optimal design and comprehensive evaluation support tool for advanced structural polymer materials

Nippon Steel & Sumikin Chemical Co., Ltd.
SHIN-ETSU FUJIMOTO **KEIICHI HAYASHI** **GENKI TAKEUCHI**

Keyword Polymer design, Computational science, Advanced measurement

We examine the relationship between molecular structures and the mechanical performance of structural thermosetting polymers. The molecular structures of epoxy polymers are calculated using molecular dynamics (MD) simulations, and a database of the simulation results is constructed using an advanced mathematical method. The database can provide the relationships between the molecular structures and material heterogeneities that affect the mechanical performance of the materials. The figure presents a simulation result obtained using a coarse-grained MD method. This simulation enables the determination of the effects of the molecular structures on the curing reaction. The relationships of the molecular structures and constitutive laws can be determined using a series of MD simulations with appropriate force field potentials as parameters. This information will be useful in assembling screening modules for the molecular structures and in designing advanced structural polymer materials.



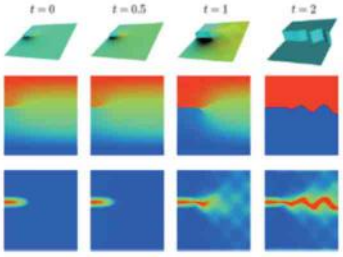
Mathematics

A new mathematical approach for fracture dynamics

YASUMASA NISHIURA Advanced Institute for Materials Research, Tohoku University

Keyword Phase separation, Phase-field approach, Computational homology

One of the key issues in materials science involves modeling the dynamical aspects of defects, interfaces, and fracture, which provides a seamless connection from the micro to macro level. A large challenge is understanding the development of the onset of microscopic degradation into macroscopic fracture. Using the data from cutting-edge measurements such as atomic force microscopy, ABED, and X-ray fluorescence holography combined with coarsened simulation and the phase-field approach, we develop a new dynamic mathematical model for degradation and fracture. Computational homology, which not only counts the number of holes but also distinguishes the size and shape of complex morphology, is a key tool used to understand the hierarchical structure of degradation and fill the gap in the micro–macro linkage of our targeted model.



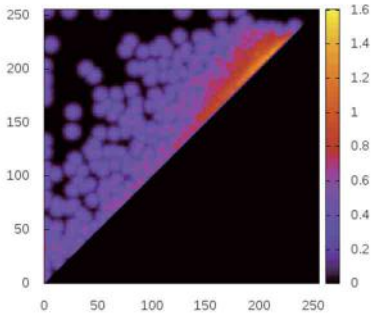
Mathematics

Theory and algorithm for spatiotemporal computational homology

YASUAKI HIRAOKA Advanced Institute for Materials Research, Tohoku University

Keyword: Computational homology, Persistence diagram, Topological data analysis

We have been developing descriptors for high-dimensional disordered structures in polymer materials. The inputs we treat are atomic locations obtained from molecular dynamics simulations and 2D/3D digital images obtained from experimental observations. Our tools are the so-called persistence diagrams (PDs), which capture topological and geometric information of the inputs. One of the significant properties of PDs is that it enables the characterization of hierarchical geometric features. From this property, it is highly expected that we can characterize the geometry of materials on a multiscale level and discover new correlations with physical properties. Furthermore, to characterize the aging and damage of materials, we have been developing spatiotemporal computational homological tools. Although our tools are universal, we mainly focus on epoxy resins in this project.



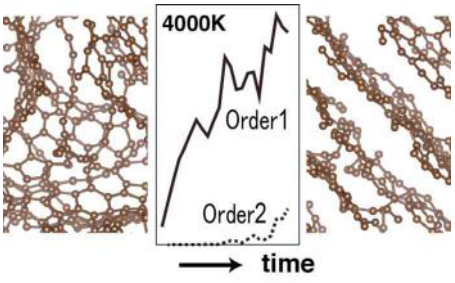
Mathematics

Deterioration prediction of materials based on computational science

KAZUTO AKAGI Advanced Institute for Materials Research, Tohoku University

Keyword: First-principles calculation, Multiscale simulation, Deterioration prediction

To identify microscopic causes (signs) leading to macroscopic results (deterioration, destruction), it is important to find strong correlations buried in data obtained by measurements (synchrotron radiation, electron microscope, etc.) and multiscale computer simulations. Mathematical methods such as topological analysis are applied here. To elucidate the physical and chemical origin of such strong correlations, first-principles density functional calculations are used. The findings are reduced to the materials integration platform by improving the parameters in multiscale simulations. Alloy systems are also treated for general understanding. The right figure presents an example of the quantitative evaluation of ordering (growth of the graphite structure) of amorphous carbon at high temperature.



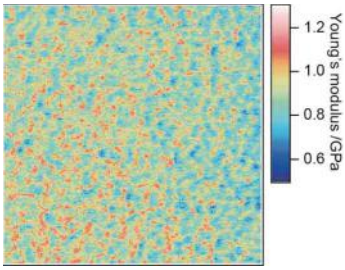
Chemistry

Nanoscale visualization of degradation and fracture of polymers

KEN NAKAJIMA Graduate School of Engineering, Tokyo Institute of Technology

Keyword: Nano-palpation atomic force microscopy, Nanoscale viscoelasticity mapping

A nanoscale visualization of the degradation and fracture of polymers is performed. Specifically, nanoscale viscoelastic mapping using a nano-palpation atomic force microscope is applied to analyze the structural and mechanical properties of epoxy resins under different curing conditions. The curing condition exhibits a strong correlation with the length scale of the nanoscopic inhomogeneous structure. The figure shows elastic modulus mapping of an epoxy resin with a certain curing condition (500 nm) that exhibits an inhomogeneous length scale of approximately 7.5 nm. It is possible to perform a similar measurement on samples under stretching and to visualize the craze network and stress chain network. This data will be provided to a mathematical analysis group to conduct data-assimilation coarse-graining simulations and/or persistent homology analysis.



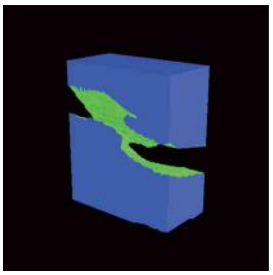
Mathematics

Mathematical model for sign of cracking

TAKESHI TAKAISHI Hiroshima Kokusai Gakuin University, Center for General Education

Keyword Phase-field method, FEM

The aim of this work is to construct a mathematical model of the macroscale cracking of polymer materials, which includes the effect of the sign of cracking. In this research, the phase field plays such an important role in the cracking, damage, and deterioration of the material. An evolutional model that describes the process of macroscale fracture induced by the inhomogeneous properties of the material will be developed. The relation between the topological properties of molecules and inhomogeneity of materials will clarify the relation between the molecular structure and sign of cracking. The figure presents the numerical result of the 3D crack propagation of a material with inhomogeneous toughness. It is possible to create a database by performing a series of simulations of the distribution of fracture toughness and initial damage.



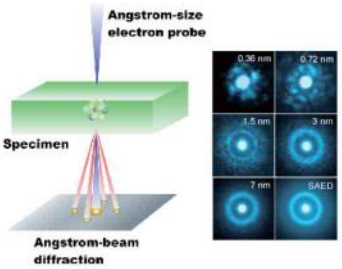
Materials

Analysis of structural defects using transmission electron microscopy

AKIHIKO HIRATA Advanced Institute for Materials Research, Tohoku University

Keyword Structural defects, Electron diffraction, Local structure, Crystal, Amorphous

To understand the early signs of material deterioration and failure, we develop a transmission electron microscopy methodology for detecting structural defects in both crystalline and amorphous materials. The developed nanoscale electron diffraction analysis for amorphous materials is shown in the right figure. This method enables us to obtain local structural information even for amorphous materials. It is also expected that reliable structural data will be available by combining with the other complementary methods. With this reliable structural data, elucidating the deterioration and failure mechanisms of materials becomes possible by working closely with computational and mathematical methods.



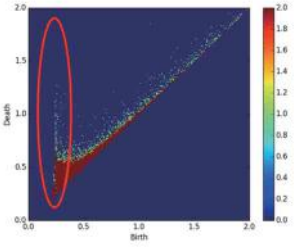
Medicine

Topological data analysis of the fracture process of polymer materials

TAKASHI ICHINOMIYA Gifu University School of Medicine

Keyword Topology, Applied mathematics, Molecular dynamics

We attempt to understand the fundamental process of the fracture of polymer materials. To this end, we employ persistence diagrams (PDs), a topological data analysis approach used to visualize the multiscale topology of atoms. The figure presents an example of a PD, which was obtained from a molecular dynamics simulation of fracture in a glassy polymer. The green and red points surrounded by the red circle represent the topological change of the structure accompanied by craze formation. The knowledge acquired from our research will contribute to the early detection of fracture and reliable estimation of material strength.



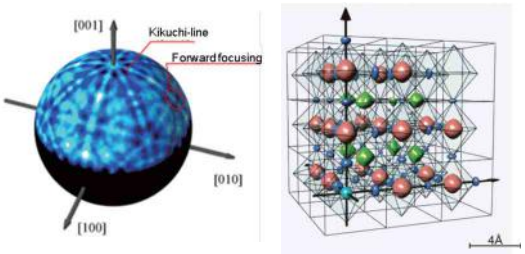
Materials

Observation of destruction precursors by using atomic resolution holography

KOICHI HAYASHI Nagoya Institute of Technology

Keyword X-ray fluorescence holography, Atomic imaging

We study atomic resolution holography by using X-ray and electron beams. The holograms produce accurate and high-resolution 3D atomic images with elemental sensitivities. Phase transitions are one cause of material embrittlement. The embrittlement of-titanium, which is a biomaterial, occurs via the precipitation of the-phase due to phase transition. However, the accurate structure of this-phase cannot be determined using X-ray diffraction because its grain size is on the order of a few nanometers. Unlike X-ray diffraction, atomic resolution holography can be used to analyze low-dimensional structures. To develop ideas for stopping such heterogeneities, we are trying to examine the precursors of material destruction with great sensitivity.



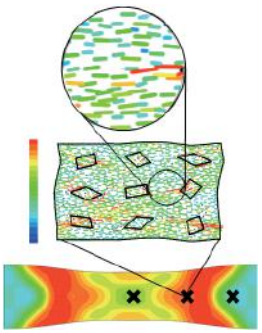
Mechanical engineering

Multiscale modeling of damage and degradation of thermosetting polymers

KAZUYUKI SHIZAWA Dept. Mech. Eng., Keio University

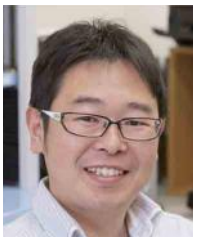
Keyword Molecular Chain Plasticity, Damage, Degradation, Multiscale Modeling

In the molecular chain plasticity model proposed by the author, the kink rotation in a molecular chain is thought to be the elementary process of the plastic deformation of polymers. This model is formulated in a framework of crystal plasticity theory for thermoplastic polymers by introducing slip systems defined in molecular chains. This model can simply express various phenomena, e.g., molecular chain orientation, neck propagation, craze evolution, and nonlinear strain recovery in unloading (see the right figure). In this work, the above model is extended to a thermosetting type, and then, an ultraviolet (UV) degradation effect on molecular chains is added. Conducting nonlinear finite element analyses using the present model, some effects of damage and UV degradation behavior on the time-dependent mechanical performance of polymers are predicted for the material design of polymers used in airframes.



Mechanical engineering

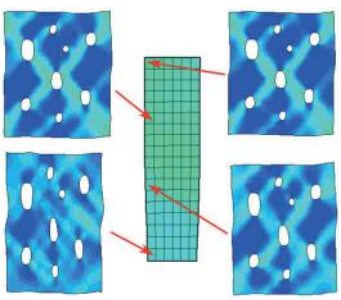
Establishment of a deformation evaluation method for filler-distributed-type thermosetting polymer



MAKOTO UCHIDA Graduate School of Engineering, Osaka City University

Keyword Molecular Chain Network Model, Large Deformation, Homogenization Method, Multiscale

In this research, the deformation behavior of thermosetting polymers from the micro- to macroscopic level is modeled using a molecular chain network model. The model represents the mechanical behavior of polymeric materials based on the kinetics of a molecular chain, and is thus important in considering the relationship between the microscopic deformation mechanism determined using molecular dynamic simulations and the macroscopic mechanical behavior determined from experiments. And the model has already been extended for multiscale simulations as illustrated in the right figure, which depicts the micro- to macroscopic deformation behavior of an amorphous polymer with microscopic voids. In the materials integration project, such a multiscale computational procedure is necessary for the evaluation of the hierarchical deformation behavior of filler-distributed thermosetting polymer matrices and fiber-reinforced thermosetting polymers.



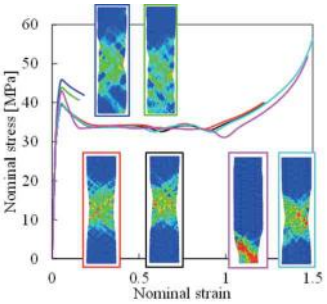
Mechanical engineering

Multiscale simulation of damage and degradation of thermosetting polymers

YOSHITERU AOYAGI Graduate School of Engineering, Tohoku University

Keyword Molecular Chain Plasticity, Damage, Degradation,Multiscale FE Analysis

An analysis code is developed to perform a simulation based on the molecular chain plasticity model by using the material properties of thermosetting polymers estimated from experiments. The right figure depicts the nominal stress–nominal strain curves obtained using simulations considering the microstructures and microscopic deformation processes of polymers. This figure indicates that the mechanical properties of a polymer depend on its microstructure. Multiscale finite element analysis with a homogenization method is performed using the molecular chain plasticity model considering ultraviolet degradation behavior. The effects of microscopic information, such as the density of chemical cross-linking, distance between entanglements, and molecular chain orientation on the mechanical properties of polymers are numerically investigated. Basic data for a numerical system predicting the mechanical performance of polymers are obtained from the present multiscale simulation.



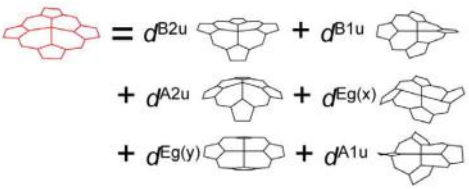
Chemistry

Computational analysis of polymer energetics based on molecular deformation

HIROSHI ISHIKITA Research Center for Advanced Science and Technology, University of Tokyo

Keyword QM/MM, Quantum chemistry, Molecular dynamics simulation

The deformation of molecular structures leads to changes in energies with respect to the most stable conformation. Using theoretical approaches (e.g., quantum mechanical/molecular mechanical approaches, quantum chemistry, and molecular dynamics simulations), we characterize the lowest frequency normal modes, associated atomic coordinates of the conformations, and energetics of the target molecules, including polymers. In doing so, a target molecule can be understood as being composed of a mixture of shapes with characteristic frequency modes, and the energy profile of the target molecule can be presented as the sum of each energy profile of the frequency mode.



Medicine

Development of a material design method based on molecular dynamics

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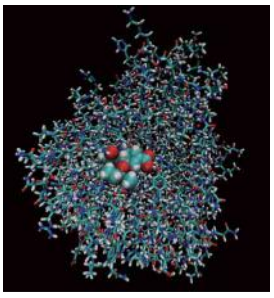
Keyword Molecular dynamics, All-atom model

Because of advances in supercomputers and methodology, molecular dynamics (MD) simulation with the all-atom model (all-atom MD simulation) has become available. In particular, this method has been extensively applied not only to the basic research of biological molecules but also to drug development. The figure shows a medicinal drug bound by an influenza protein. Although the protein is a functional polymer in the cell, the epoxy resin is a synthetic polymer widely used in the manufacturing industry. As it remains challenging to understand the relation between the structure and properties of the epoxy resin, we study this problem by applying the all-atom MD simulation techniques that we have developed. We increase the computational prediction accuracy by improving the model of the epoxy resin, and ultimately, we aim to develop a more rational and accurate material design method.



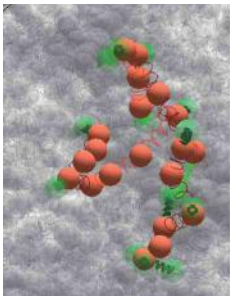
Physics

Development of computer-aided material design technology by using coarse-grained molecular modeling

YUICHI MASUBUCHI National Composite Center, Nagoya University

Keyword Polymer, Dynamics, Coarse-graining, Long-time relaxation

In this project, simulation techniques for polymeric materials are developed based on coarse-grained models. For the design of high-performance functional polymeric materials, the problem is the prediction and control of the non-equilibrium states in which the system is inevitably trapped during the material processing. For the prediction, tracing the dynamics of the system in the time range of processing is necessary. To attain such a long time calculation, we are developing some coarse-grained models on the basis of the primitive chain network model and the multi-chain slip-spring model. We are attempting to realize the simulation having an efficiency of more than 100 times that of conventional coarse-grained simulations using the bead–-spring type model.



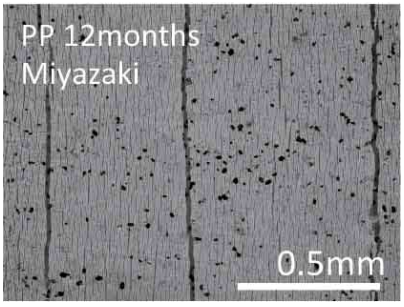
Materials

Development of prediction technology for long time dependence of high-performance polymer materials

TAKASHI KURIYAMA Yamagata University

Keyword Engineering plastics, Long-term characteristics, Degradation behavior

This study investigates the estimation of degradation for high-performance engineering plastics under uses in various environments. Multi-scale analysis of polymers involving the correlation between structural changes due to ultraviolet radiation/moisture and performance has not been previously performed, which has resulted in an insufficient safe-life design of materials and caused a lack of reliability. This study systematically summarizes the experimental results performed to date and evaluates and analyzes the time-dependent characteristics of the degradation behavior. For this purpose, the degradation behavior of plastics in various environments is analyzed from the macro- to microscopic level. The degradation behavior of high performance engineering plastics is classified and simulated, and data that can be used to predict the characteristics after a long period of use from results obtained using computer science and short-term experiments are provided. The provision of these data would demonstrate the utility of materials integration.



Nanometronics

Innovative measurement and analysis for structural materials (IMASM)

MASATAKA OHKUBO AIST Nanometronics Lab

Keyword Nanostructure, Free volume, Fatigue, Quantum probe

The SIP-IMASM team is pursuing two strategic challenges: the acquisition of “manifest information” that is obvious but has never been measured using conventional techniques, and the deduction of “latent information” that is obscure but necessary for controlling the performance and estimating the lifetime of innovative structural materials. An example of the manifest information concerning polymers is the gap in molecular chains, i.e., free volume, with a size of less than 1 nm. The gap size varies with manufacturing conditions and mechanical tests. A sub-nanometer gap cannot be measured using transmission electron microscopy (TEM); instead, an innovative apparatus that uses anti-electrons or positrons at the Tsukuba Innovation Arena (TIA-nano) must be applied. The figure presents an image of a positron–electron pair called a positronium in polymer chains. We determine the guidelines to improve the mechanical properties of polymers by using the positrons and molecular dynamics calculations in coordination with the material integration team.