Fracture phenomena of glassy polymers are both old and new topics, and interesting results on polymer fracture have been reported since the 1960s. Experiments have shown the relationship between molecular motion and fracture strength. Craze criteria were formulated from the theoretical models. Furthermore, simulations have contributed to clarifying the fracture mechanism at the molecular level. However, many unsolved problems remain despite much research on fractures involving experiments, theoretical models, and calculations. For instance, the differences in the fracture modes of different materials have remained unexplained. Specifically, it remained unclear why poly(methyl methacrylate) (PMMA) exhibits brittle fracture while polycarbonate (PC) exhibits ductile fracture.

Recently, large-scale molecular dynamics simulations, which well-mimicked realistic materials, have been performed to resolve the molecular mechanisms of the polymer fracture at the atomistic level.

In Sections 2 and 3, the experimental and theoretical approaches are introduced, followed by a review of insights from simulations in Section 4. Finally, in Section 5, the large-scale simulation results are introduced.

2. MOLECULAR THEORY OF POLYMER FRACTURE PHENOMENA—EXPERIMENTAL STUDIES

Many fracture tests of polymers, such as pulling, Izod, and Charpy tests, have been performed, and physical properties such as extension and fracture energy have been measured. In addition, researchers have attempted to connect the physical properties and molecular motions of the polymer 

Particularly remarkable studies include the research that related the fracture energy to the molecular motion obtained from viscoelasticity measurements. In 1967, Wada et al. found that the Izod impact test strength was correlated with the dynamic shear coefficient in the temperature range of 100 K to 300 K. Moreover, the strength is also correlated with the integral values of the loss tangent. When the loss peak comes from the motion of the polymer main chain, the polymer materials with the loss peak had excellent toughness. However, the loss peak from a side chain did not relate to the toughness. Interestingly, Boyer also found the same results as Heijboer. Subsequently, their results were supported by Vincent, who performed a statistical analysis of 20 thermoplastic polymers. However, he also pointed out that this correlation only accounts for approximately 60% of the variance in impact strength, and the changes in secondary factors, such as additives, bulky side groups, and molecular weight, cause the remaining variance.

Wu attempted to organize the fracture toughness by the physical values representing the polymer structure.
through entanglement density, $\nu$, and characteristic ratio, $C_e$. When $\nu \leq 0.15$ and $C_e > 7.5$, the polymer materials are brittle. In contrast, when $\nu \geq 0.15$ and $C_e < 7.5$, the polymer materials are ductile.

The experiments suggest indices for the polymer fracture, which may provide good guidelines for developing polymer material. However, there are polymer materials whose toughness cannot be predicted from these experiments. That is because it is unclear which specific molecular motions and structures relate to the fracture values, and it is difficult to believe that polymer fracture, which is a large deformation, can be described entirely by the structure and viscoelastic measurements of small deformations.

### 3. THEORETICAL MODEL OF POLYMER FRACTURE

Craze initiation is the critical phenomenon in discussing polymer fracture. Therefore, craze initiation has been studied theoretically, and many craze initiation criteria have been established. Quite recently, a new criterion for craze initiation has been reported. The most well-known criterion is stress bias, advocated by Sternsten et al. However, Oxborough et al. argued against Sternsten et al.’s criterion owing to the unclear physical interpretation of the stress bias, and pointed out that it is unclear how to evaluate stress bias in a triaxial stress state. Therefore, Oxborough et al. formulated a new craze initiation criterion based on the critical strain. Argon et al. developed a craze theory based on the generation of microvoids, and in 2011, reconstructed the theory by incorporating simulation results.

### 4. POLYMER FRACTURE STUDIES BY SIMULATIONS

Molecular dynamics (MD) simulation, a well-known simulation method, is often used to explain the experimental results based on the molecular level and validate and verify the theoretical model. Many simulation studies for polymer fracture have been performed. MD simulations can be divided into two categories: AA-MD simulations, which consider molecularity, and coarse-grained (CG)-MD calculations, which discuss universality.

In 1986, Theodorou et al. performed fracture simulations of atactic polypropylene using the AA-MD simulations. They suggested that the polymer chain topology contributed to the atomic stress, and that microstructure changes contributed most to the elastic modulus. The AA-MD calculations have also been used to study the fracture mechanism of polyethylene (PE). The stress–strain (SS) curve of PE showed three deformations, namely elastic, yield, and plastic at low temperature, and viscoelasticity was found at high temperature. Capaldi et al. found that the SS curve of PE showed strain-hardening in addition to the three deformations, and suggested that the transition of dihedral angles increases with deformation of the PE.

Furthermore, strain-hardening was discussed in detail through the relation with conformational structure. Yashiro et al. found that a transition of the dihedral angles of PE from gauche to trans occurred, and a new network-like structure formed as PE deformed. The fracture simulations of the more complicated polymers of polystyrene (PS) and PC have been studied. It has been shown that the SS curves of PS and PC are different, allowing for studies with different molecules. The AA-MD simulations have clarified the fracture properties of each type of polymer material.

The CG-MD simulations also revealed the polymer fracture of strain-hardening and craze initiation. Hoy and Robbins discussed yielding and craze initiation from the microlevel viewpoint with CG-MD simulations using the beads–spring model. The strain-hardening modulus was proportional to the entanglement density and not related to the stiffness of the polymer chain. The temperature effects of the strain-hardening were very different from the results predicted by the entropy model. The model’s assumptions contradicted the simulation results, and the energy contribution was significant for the increase in the strain-hardening.

Rottler et al. discussed yielding and craze initiation from the microlevel viewpoint with CG-MD simulations. The onset of the share yielding of a glassy polymer is consistent with the prediction of the pressure-modified von Mises criterion. The yield stress and steady-state flow stress decrease as the system temperature increases. The fracture energy was calculated in their simulation, which was consistent with the experimental value. The fracture energy suddenly became large when the chain length was more than two times the entanglement length. In addition, they concluded that the characteristic length of the craze is a third of the entanglement length ($Na$), and the chain scission starts at a length ten times longer than the $Na$.

### 5. AA-MD SIMULATIONS THAT CLOSELY MIMIC ACTUAL MATERIALS

MD simulations contributed to the clarification of the polymer fracture mechanism at the molecular level. However,
the system is too small to mimic the actual materials in the previous AA-MD simulations. Moreover, because the chemical character is neglected in the CG-MD simulations, the material characteristics, such as Poisson’s ratio, must be introduced as a calculation condition.

Fujimoto et al. overcame these problems by using the K-computer and highly paralleled molecular dynamics software MODYLAS, which Andoh et al. developed. As a result, AA-MD simulations that closely mimic actual materials are now possible from both software and hardware aspects. Thereby, Fujimoto et al. succeeded in preparing calculation systems that mimic the actual materials, and performed fracture simulations of PMMA and PC. PMMA showed brittle fracture, and PC showed ductility from the molecular level viewpoints (Figs. 1 and 2). Tang et al. found that the difference in the fracture type between PMMA and PC came from the flexibility of the dihedral angles, the entanglement density, and inhomogeneity. Furthermore, from the stress decomposition analysis, the stress from bond, bond–angle, and van der Waals interactions significantly contributed to the elastic stress. After yielding, strain-softening occurred owing to the lowering or remaining constant of these stresses.

The author recently started to study the toughness produced by the molding process of the polymer material and solvent cracks using our developed calculation method. The brittle material PMMA becomes ductile when subjected to the press orientation molding method. The calculated SS curve of the processed PMMA showed a ductile-like shape. It is found that the chemical character of PMMA does not change, but the polymer chain more easily elongates owing to the planar alignment. This result causes the processed PMMA to behave in a ductile manner. Our AA-MD simulation also suggested that the yielding stress of the PMMA with solvent becomes lower than without solvent.

Advanced computational and simulation methods reveal previously unknown chemical properties of the polymer fracture. In addition, the results of simulations will contribute to the construction of fracture theories.

6. FUTURE CHALLENGES

As shown here, polymer fracture has been studied from experiments, theoretical models, and MD simulations. In particular, the MD simulations have contributed significantly to clarifying polymer fracture at the molecular level.

With the recent development of computers such as K and Fugaku, AA-MD calculations that closely mimic the actual polymer materials are now possible. So, the problem of spatial scale of the AA-MD system is being solved, and this will allow for the fracture study of heterogeneous polymer materials. However, there remains the problem of the time scale. A computer dedicated to MD calculations, such as Anton, can perform AA-MD calculations on the order of seconds, but a general-purpose computer can barely perform calculations on the order of microseconds. Namely, phenomena on the order of microseconds or longer cannot be studied with AA-MD calculations. Historically, many MD calculation algorithms have been developed to overcome the time-scale order in the biological field. Unfortunately, according to the experience of the author it is difficult to apply these algorithms to polymer studies at this time. However, an
algorithm will be developed that can be applied to the slow-motion behavior of a polymer. This may allow AA-MD calculations to be applied to various phenomena in addition to the fracture of polymers and may provide knowledge at the molecular level. These molecular insights will surely advance not only the development of polymer materials but also polymer science.

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