Evaluation of Interfacial Properties of Polymeric Materials with Reversible Cross-linking

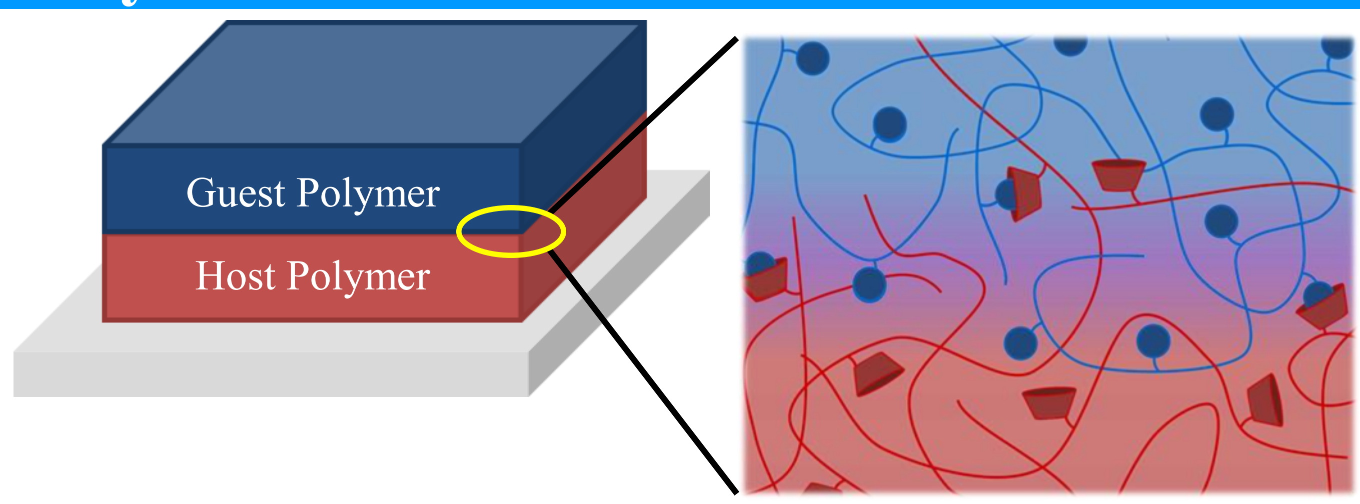
Takeru KOMYO[*1], Chao LUO[*1], Kenji YAMAOKA[*2], Yoshinori TAKASHIMA[*2], Yasutomo UETSUJI[*1]
*1 Osaka Institute of Technology, *2 Osaka University

Abstract

In recent years, disposing of large amounts of polymers has posed a serious environmental issue, driving the need for more durable materials. In particular, polymer materials incorporating reversible cross-linking formed between β-cyclodextrin (β-CD) as a ring-shaped host and adamantane (Ad) as a cage-shaped guest have demonstrated excellent toughness, owing to efficient energy dissipation through reversible complex dissociation under stress. Furthermore, the reversibility of the crosslinks has attracted attention for self-healing applications, with experimental studies underway.

In this study, all-atom molecular dynamics (MD) simulations were used to investigate polymers with β-CD/Ad reversible crosslinks. First, a local host–guest model confirmed that the complex formation is stable and matching experimental data. Next, PMMA-based polymers incorporating the crosslinks were analyzed to study interfacial diffusion and layer thickness at temperatures above the glass transition temperature (Tg). The results successfully explained experimental trends without contradiction. Finally, tensile tests in MD revealed that β-CD/Ad complexation contributes significantly to the enhancement of mechanical properties, particularly toughness.

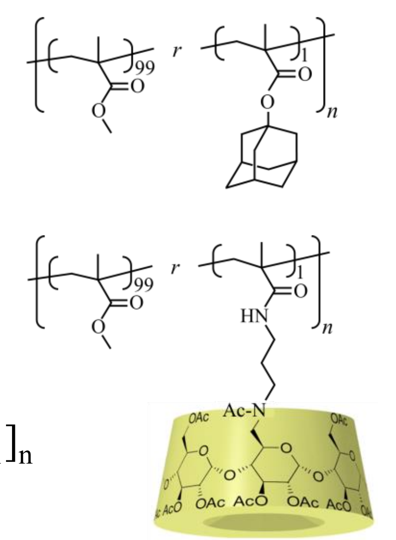
Polymeric Materials with Reversible Cross-linking



Self-healing interface via reversible cross-linking

Guest Polymer $[(MMA)_{98}\text{-}(Ad)_2]_n$

Host Polymer $[(MMA)_{99}\text{-}(\beta\text{-CD})_1]_n$



Simulation Tools

Modeling software : Materials Studio

Solver : All-atom molecular dynamics simulations performed using LAMMPS

Analysis conditions

Force field : Consistent Valence Force Field (CVFF)

Boundary conditions : periodic in all directions

Timestep : 1.0 fs

Ensemble : NPT (constant number of particle, pressure, and Temperature)

Interfacial Phenomena at Polymer Bilayers

Stability of Host-Guest Complex

Auletta T et al. ACS, 126, (2004), 1577

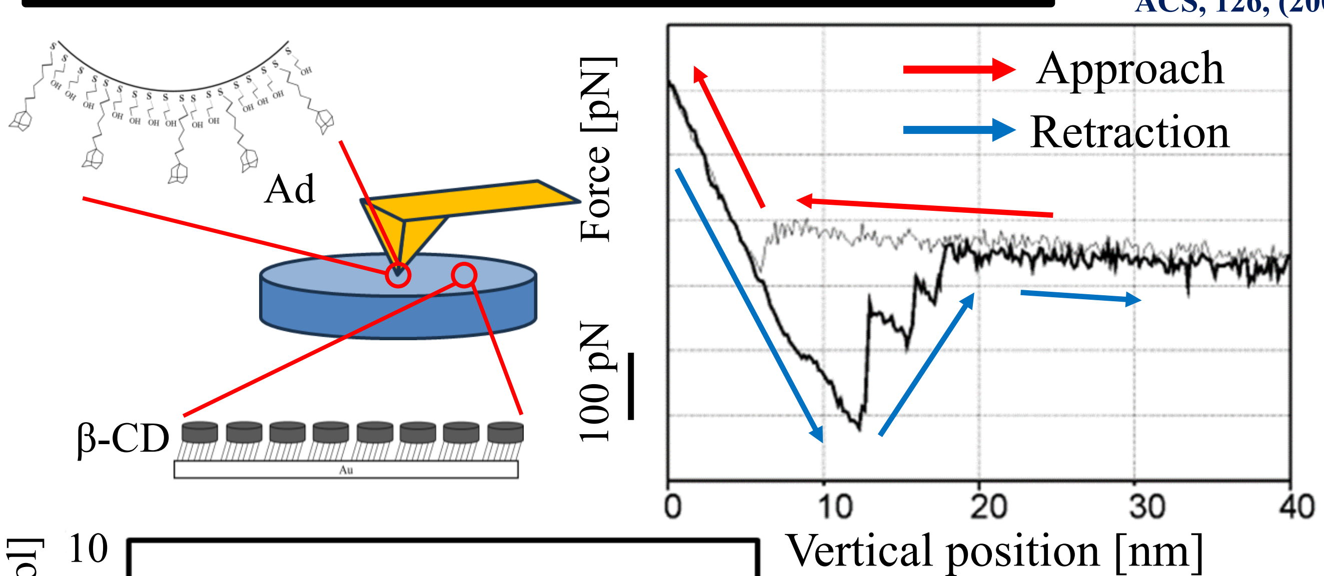


Fig. AFM prove test

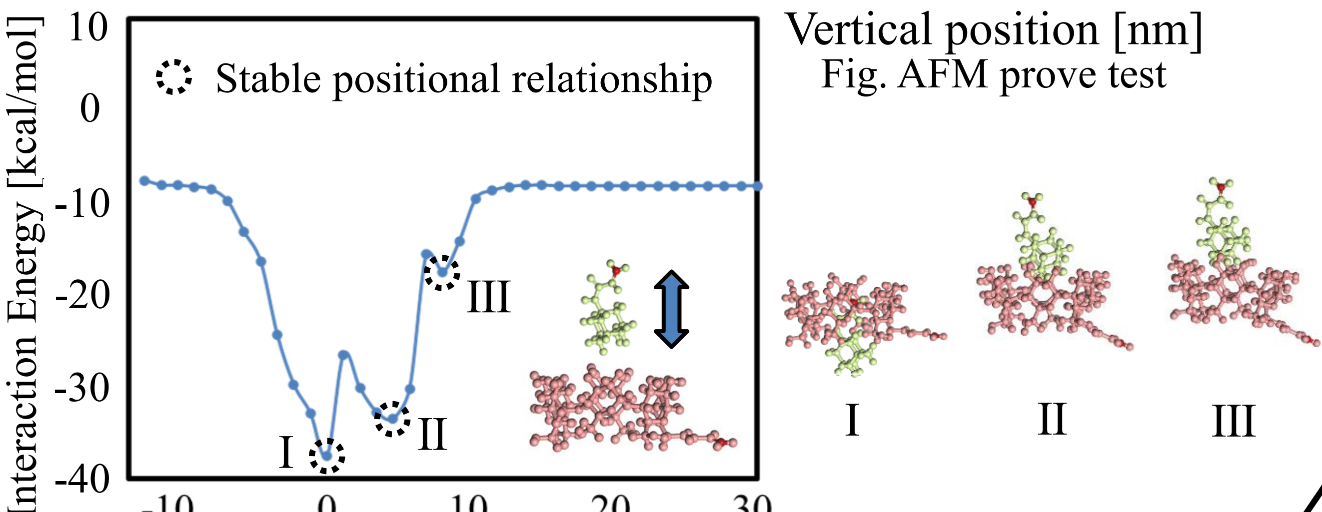
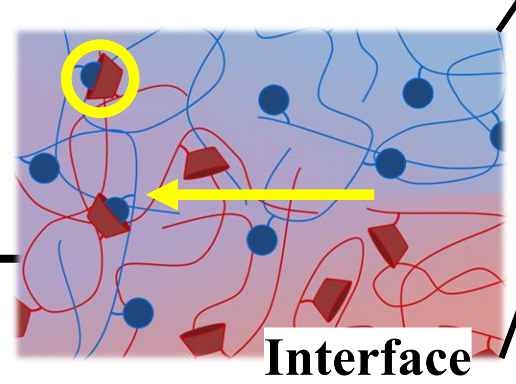
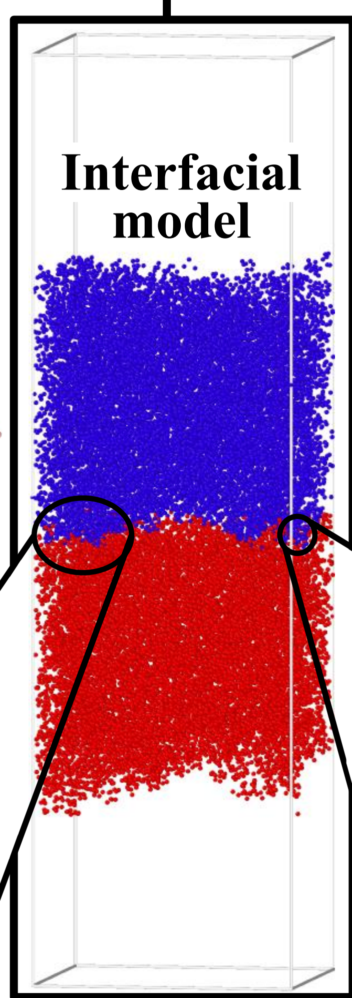
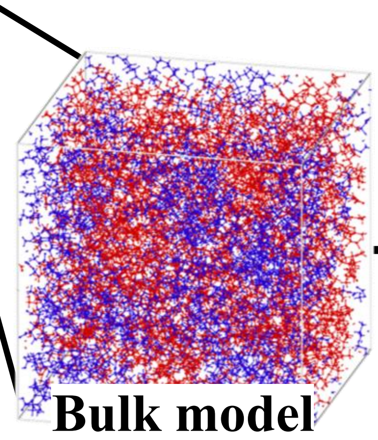


Fig. Host-Guest position and stability

Clarification of the stepwise force pattern observed in AFM







Interfacial Thickness

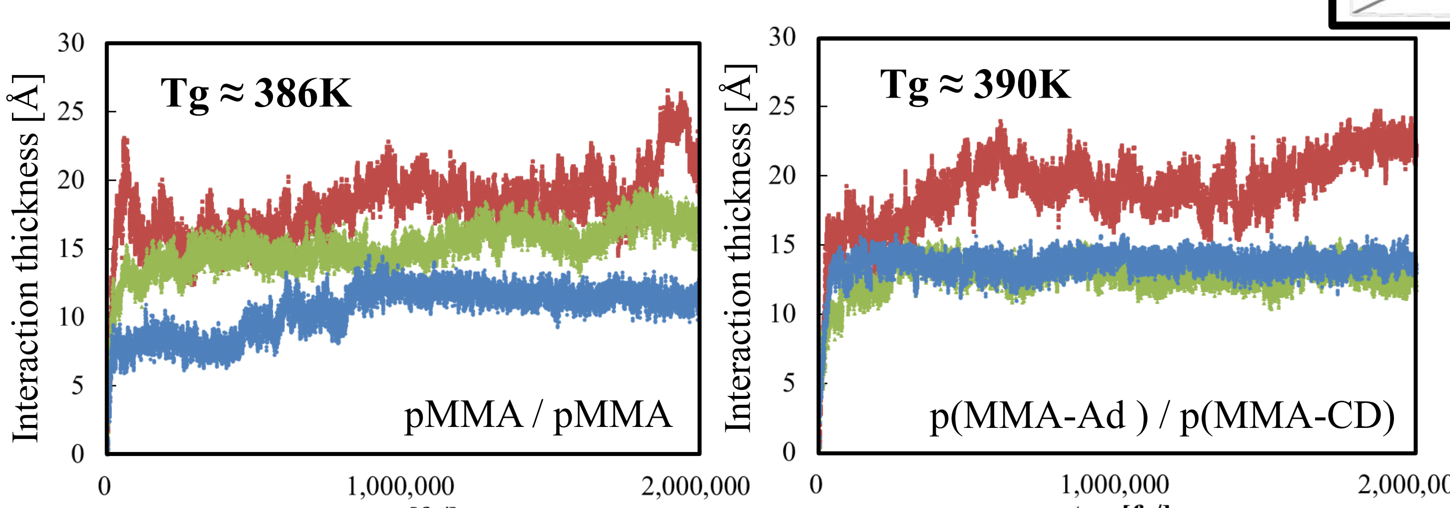


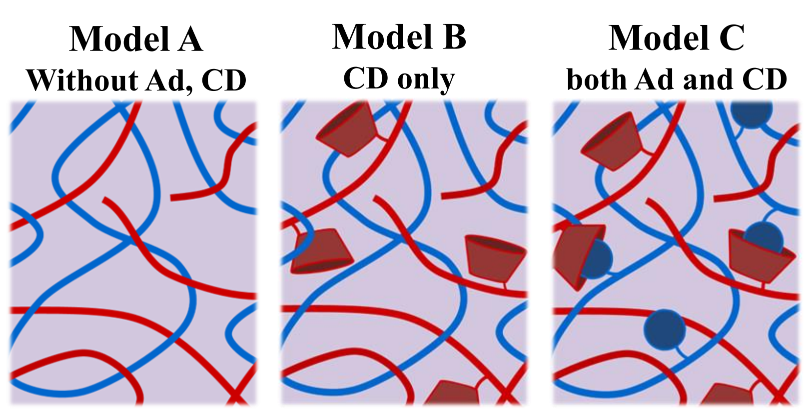
Fig. Interfacial broadening as a function of temperature at 300K, 400K, and 500K

Active interfacial diffusion was observed above the *Tg*.

No clear difference between models were observed within 2ns (2,000,000fs).

Analysis of Bulk Mixed Polymer Structure

Influence of Host-Guest on Atomic Diffusion



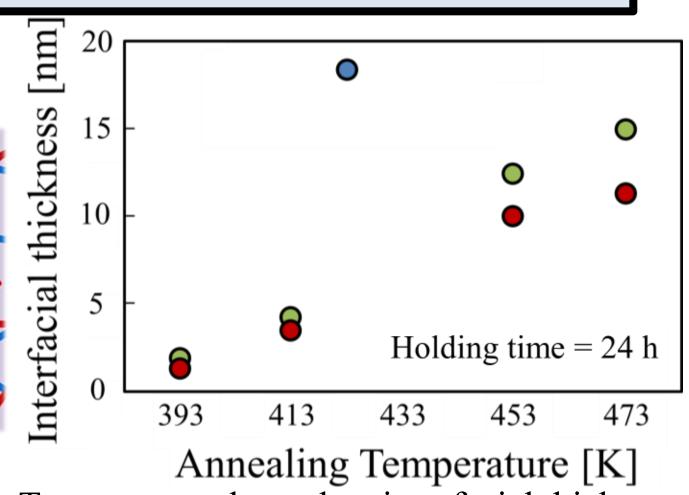


Fig. Temperature-dependent interfacial thickness

Diffusion coefficient (D)

$$D = \frac{1}{6}\frac{dMSD}{dt}$$

$$MSD(t) = \frac{1}{N}\sum_{i}^{N}|r_i(t) - r_i(0)|^2$$

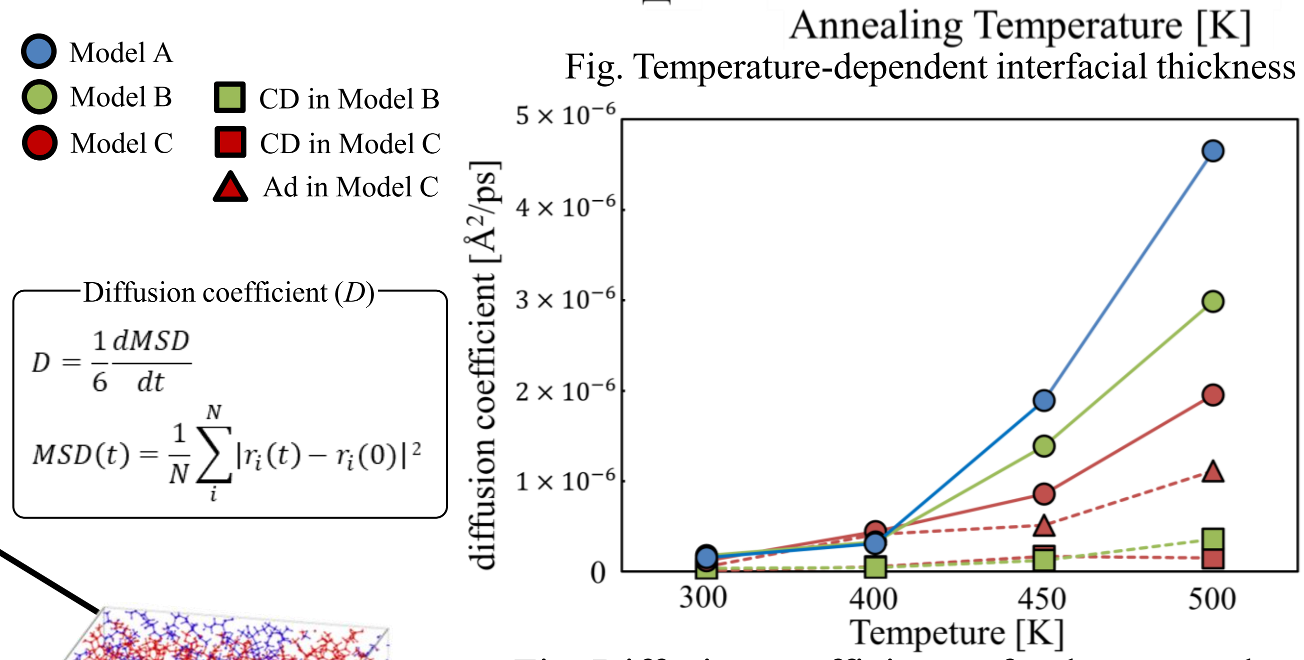


Fig. Diffusion coefficients of polymers and Host-Guest molecules

Ad and CD restrict the diffusion of chain

Mechanical Properties

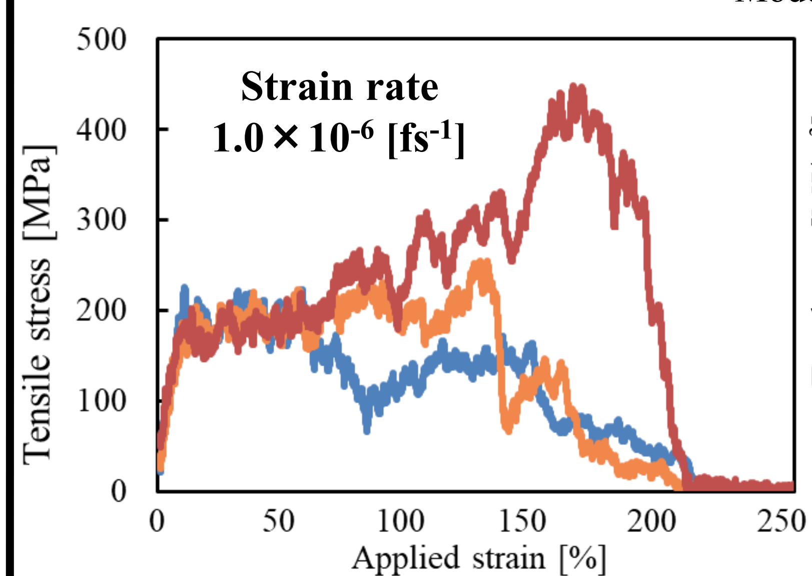


Fig. Stress-strain curve of the bulk

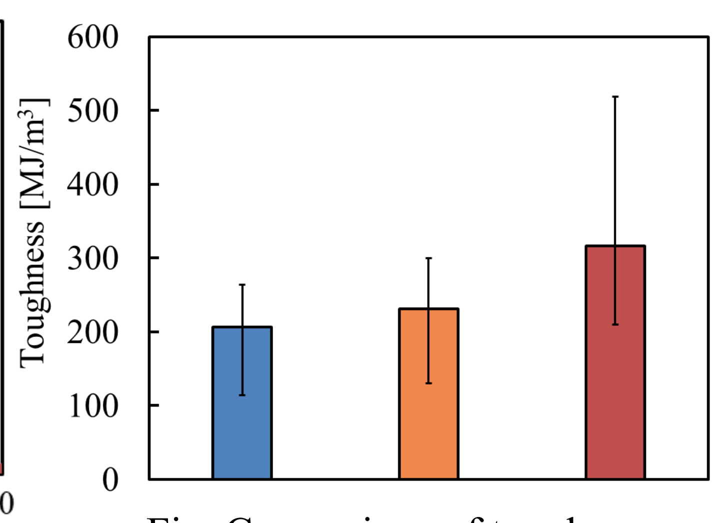


Fig. Comparison of toughness

Toughness were enhanced by crosslinking