

Molecular origin of asymmetric yield surface of crosslinked epoxy polymers

Jinyoung Kim^{a,1}, Kyeongmin Hong^b, Yong-Seok Choi^b, Dayoung Jang^c, Jang-Woo Han^c,
Hyungbum Park^{a,*}

^a Department of Mechanical Engineering, Incheon National University, (Songdo-dong) 119 Academy-ro, Yeonsu-gu, Incheon, 22012, Republic of Korea

^b Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do, 55324, Republic of Korea

^c Department of Mechanical Design Engineering, Kumoh National Institute of Technology, 61, Daehak-ro, Gumi-si, Gyeongsangbuk-do, 39177, Republic of Korea

ABSTRACT

In this study, we investigate the multiaxial mechanical behavior of thermosetting epoxy polymers and explore the asymmetry between tension and compression in their yield surfaces at the molecular level using molecular dynamics simulations, complemented by experimental validation through polymer synthesis. After constructing an atomistic-scale amorphous epoxy system based on molecular dynamics simulations, we derived equivalent stress–strain curves and yield surfaces as functions of the degree of crosslinking through biaxial deformation analysis. The results show that increasing the degree of crosslinking leads to an increase in equivalent stress in all loading directions, resulting in an expansion of the yield surface. Notably, a more accelerated expansion of the yield surface in the biaxial compression direction was observed at higher degrees of crosslinking, which is attributed to a deformation mechanism that more effectively accommodates stress in this loading direction. This unique deformation behavior is attributed to high non-bonded stress arising from reduced polymer chain mobility by crosslinking effect. To experimentally validate the deformation mechanisms, epoxy polymer samples were synthesized, and uniaxial tensile and plane-strain compression (PSC) tests were conducted to obtain stress–strain profiles and yield surfaces according to different degrees of cure. These results provide fundamental insights into the distinct mechanical properties of polymer materials, such as the asymmetry of the yield surface, by revealing their behavior at the molecular level.

1. Introduction

Epoxy polymers are widely used as multifunctional matrices in fiber-reinforced and nanocomposite materials, playing a critical role in structural components within the aerospace, aviation, and defense industries. Depending on various service environmental conditions, different types of epoxy monomers and crosslinking agents with distinct molecular structures are employed. These diverse combinations alter the polymer's structural network characteristics, highlighting the importance of understanding the structure–physical property relationships. Consequently, this has become a long-standing and significant topic of research in the field of polymer composites.

A wide range of experimental [1–5] and theoretical [6–21] studies have been conducted to investigate the correlation between the structural characteristics and properties of epoxy polymers. In particular, studies have focused on the relationship between crosslinking characteristics and the mechanical behavior under elastic and plastic deformation [9–16,19]. These studies have primarily explored how the packing of polymer chains, influenced by crosslink structure, affects density and, consequently, changes in mechanical properties. Most

research has been limited to mechanical behavior under uniaxial tensile or compressive loads, as these tests are relatively straightforward to perform [4,9,11,13–16].

Generally, when low molecular weight monomers undergo chemical bonding and crosslinking progresses, the density tends to increase [5,6,8–16,19]. This is because the movement of freely moving monomers is restricted, leading to the continuous growth of the polymer network structure and resulting in the packing of polymer chains. The extent of this density change varies depending on the molecular weight and molecular structure of the monomers, sometimes exhibiting nonlinear characteristics [10,15]. For instance, previous study [19] has demonstrated through computational methods that once the degree of crosslinking reaches a certain value, the density may actually decrease due to the molecular size of the monomers themselves.

These structural changes naturally lead to variations in mechanical properties. Generally, as the degree of crosslinking increases, the mechanical properties in the elastic region are observed to improve. Some studies report a linear increase in properties [1,5,9,10,13,18], while others indicate a sharp rise near a specific crosslinking threshold after the gelation point [11,12,14,15,19]. As far as the yield and plastic

* Corresponding author.

E-mail addresses: wlsdud1208@inu.ac.kr (J. Kim), gamamle@inu.ac.kr (H. Park).

¹ First author: Jinyoung Kim, +82-32-835-4535.

deformation regions are concerned, yield strength typically increases with higher crosslinking density [11,12,14,15,19], while yield strain shows no clear trend [9,13]. Regarding fracture properties, as crosslinking progresses, the dominant failure mechanism shifts from non-covalent interactions between polymer chains to chain scission within the network, leading to increased brittleness. As a result, unlike the yield properties [4,9,20,21], the failure properties exhibit a decreasing trend [4,20]. The elongation at break and toughness decrease nonlinearly with increasing crosslink density and may converge beyond a certain level of crosslinking [4].

As discussed above, numerous studies have investigated the uniaxial mechanical behavior and properties of epoxy polymers, and efforts to establish structure-property relationships are ongoing. However, considering that most polymers or polymer composites in practical applications experience multiaxial stress states at the microscale within the matrix even under simple loadings, there is a clear need for research into the mechanical behavior and properties under multiaxial loading. To understand such complex multiaxial stress behaviors, finite element analysis (FEA) is indispensably used in the structural design of composite materials. Accurate 3D mechanical properties are, therefore, essential for highly precise structural analysis. In particular, establishing the shape of the yield surface, which is used as a 3D yield criterion in constitutive equations, is of primary importance, as it governs the onset and evolution of plastic deformations under multiaxial stress conditions and must be determined with highly precise dataset.

Unlike traditional metallic materials, polymers exhibit unique deformation behavior that is highly sensitive to testing pressure conditions [22,23]. This makes it challenging to represent multiaxial yielding with simplified yield surface models [24,25]. This difficulty arises from the load path dependence on multiaxial hardening behavior, which is governed by the unique structural characteristics of polymers [24–27]. Under multiaxial deformation, polymers, therefore, typically exhibit asymmetric yield surfaces under plane stress condition between tension- and compression-related loading paths, unlike the symmetric yield functions described by classical criteria such as von Mises or Tresca [24–28]. Continuous efforts have been made to describe the unique three-dimensional plastic deformation behaviors of polymers using various types of asymmetric yield functions, such as pressure-modified von Mises [29], pressure-modified Tresca [29,30], conical [28], paraboloidal [31], and other modified models [25,28]. However, the choice of yield function is often made without thorough characterization of the yield stress states across a broad range of load paths leaving the validity of these models for describing asymmetry in question.

Accurate measurement of multiaxial yield stresses has not been easily achieved due to the absence of standardized testing protocols for three-dimensional stress states. Experimental characterizations using tubular specimens [32,33], cylindrical specimens [33], Arcan specimens [34,35], and cruciform specimens [27,36] have all been used to evaluate multiaxial stress states. However, these methods cannot comprehensively measure yield responses, even under plane stress conditions [33]. For instance, tubular specimen can capture tension-torsion, tension-internal pressure, and torsional responses, while cylindrical specimens capture uniaxial and shear responses. Arcan fixtures enable tension, shear, and partial biaxial compression testing but fail to characterize equibiaxial compression, a critical path for assessing yield asymmetry. Cruciform testing provides access to biaxial compression but is prone to buckling, complicating subsequent yielding characterization [27]. Recent advancements in customized equipment for biaxial and triaxial deformation testing [37] offer promise but have yet to achieve standardization.

Consequently, there have been relatively few attempts to accurately measure and establish a three-dimensional yield criterion for polymeric materials. Although multiaxial deformation tests have been conducted under specific testable loading paths, even within these few paths, it has been confirmed that yield surfaces vary among different polymeric structures [24,25]. For example, Quinson [24] found that thermoplastic

polymers exhibit asymmetrical yield surfaces, with the optimal shape (elliptical or angular) depending on the testing temperature and polymer structure. Ghorbel [25] demonstrated that existing yield functions fail to accurately represent the yield surfaces of polymers especially for biaxial compressive loading. These findings underscore the need for detailed characterization of yield surfaces based on the molecular structures of polymers and their physical conditions. Moreover, they highlight the potential variability in biaxial stress states (asymmetry) depending on these factors. However, the fundamental mechanisms driving this variability in asymmetry remain poorly understood. Recently, computational approaches, such as molecular dynamics (MD), have been used to investigate multiaxial deformation behaviors, providing abundant yield data across broad multiaxial loading paths and addressing some limitations of experimental testing methods [26].

The goal of this study is to understand the mechanisms behind the yield surface characteristics of crosslinked epoxy structures under multiaxial stress at the molecular level and to predict changes in the yield surface shape as a function of crosslinking density. The focus is on elucidating the fundamental correlation between the unique tensile-compressive asymmetry of the yield surface in polymer materials and the crosslinking structure. This will provide foundational data for establishing yield functions for epoxy materials based on crosslinking density. To achieve this, we will utilize molecular dynamics simulations to directly observe the material's molecular structure and deformation characteristics and evaluate the behavior of loading paths that are difficult to experimentally investigate. Furthermore, polymer synthesis and multiaxial stress tests under plane stress conditions will be conducted simultaneously to validate the simulation data.

2. Methodology

2.1. Simulations

2.1.1. MD model preparation for TGAP/DETDA epoxy system

Epoxy polymer systems were constructed using the commercial molecular dynamics simulation software package, Materials Studio 2023, based on the molecular structures and crosslinking mechanisms depicted in Fig. 1. Tri-glycidyl para-amino phenol (TGAP, Araldite MY 0510) was selected as the epoxy resin in the epoxy polymer system, and diethyl toluene diamine (DETDA) was chosen as the curing agent, as shown in Fig. 1(a). 481 TGAP epoxy monomers and 361 DETDA curing agent monomers were used to build a highly crosslinked epoxy polymer system satisfying the stoichiometric ratio of 4:3 between the two monomers. Subsequently, three-dimensional unit cells with periodic boundary conditions were created using the Amorphous Cell module. This process resulted in the formation of epoxy polymer unit cells composed of approximately 30,000 atoms.

To prepare the energetically relaxed structures before crosslinking, energy minimization procedure was carried out using the conjugate-gradient method, with convergence criteria set for energy, force, and displacement at 6.0×10^{-8} kcal/mol, 1.0×10^{-5} kcal/mol/Å, and 6.0×10^{-8} Å, respectively. Following this, canonical (NVT) isothermal ensemble dynamics simulations were conducted for 200 ps at a temperature of 500 K to simulate the crosslinking reaction environment of epoxy system by applying sufficient thermal energy. Covalent bonds between chains were formed based on distance criteria using the dynamic crosslinking methodology [7,41], completing the three-dimensional crosslinked network structure. The methodology and specific procedures for dynamic crosslinking used in this study are described in detail in Section 2.1.2.

To construct a stabilized molecular structure of the epoxy under ambient conditions, we first conducted canonical (NVT) isothermal ensemble dynamics simulations at 300 K for 3 ns, followed by isothermal isobaric (NPT) ensemble dynamics simulations for an additional 3 ns to fully equilibrate the epoxy unit cell. The ensemble simulations were performed using a Nose-Hoover thermostat and barostat to

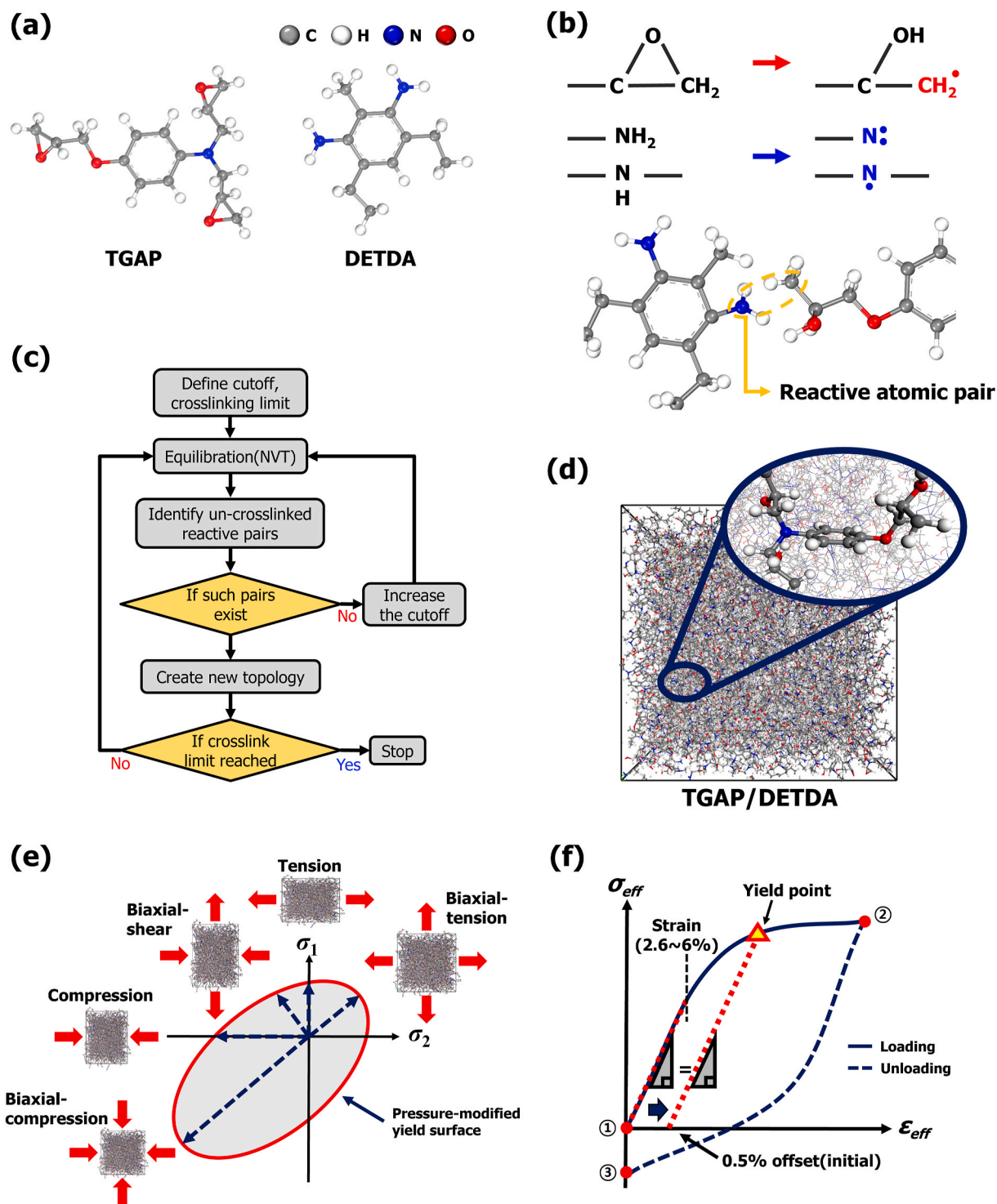


Fig. 1. Schematic representation of the MD simulation model construction and deformation simulation method for epoxy polymers: (a) Molecular structures of TGAP epoxy resin monomer and DETDA hardener monomer. The symbols C, H, N, and O in the figure represent carbon, hydrogen, nitrogen, and oxygen atoms, respectively. (b) Crosslinking reaction mechanism of epoxy groups and amine groups, and the reaction scheme for the considered monomer structures. (c) Simplified algorithm of the dynamic crosslinking methodology. (d) Visualization of the TGAP/DETDA unit cell after complete crosslinking. (e) Example of the equivalent stress-strain profile from a loading-unloading simulation under multiaxial loading, and a schematic of the yield criterion (① initial state, ② deformed state, ③ unloaded state). (f) Method for deriving the yield surface under plane stress conditions using multiaxial deformation simulations.

appropriately satisfy the given temperature and pressure conditions. The temperature damping parameter was set to 100 timesteps (fs) while the pressure damping parameter was set to 1000 timesteps (fs), both with an oscillation of 0.01, determining the relaxation rates. Throughout this equilibration process, the potential energy and density of the system

were monitored, and the convergence was confirmed as both parameters stabilized over the 6 ns period, indicating that the system had reached equilibrium, as shown in Supplementary Fig. S1.

In this study, MD simulations were performed using the PCFF (Polymer Consistent Force Field) [38,39] potential function, which is

one of the widely used force fields for modeling interatomic interactions of polymers. PCFF aims to accurately predict the interactions of various polymer chains and also other organic molecular behaviors, and its accuracy has been validated through previous literature [6,39]. Consequently, the PCFF potential function was chosen for this study, and it can be expressed as shown in Eq. (1).

$$\begin{aligned}
 E_{\text{total}} = & \sum_b [k_2(b - b_0)^2 + k_3(b - b_0)^3 + k_4(b - b_0)^4] \\
 & + \sum_{\theta} [H_2(\theta - \theta_0)^2 + H_3(\theta - \theta_0)^3 + H_4(\theta - \theta_0)^4] \\
 & + \sum_{\phi} [V_1(1 - \cos \phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)] \\
 & + \sum_{\chi} K_{\chi} \chi^2 + \sum_{b,b'} F_{bb'}(b - b_0)(b' - b'_0) \\
 & + \sum_{b,\theta} F_{b\theta}(b - b_0)(\theta - \theta_0) + \sum_{\theta,\theta'} F_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta'_0) \\
 & + \sum_{b,\phi} (b - b_0)(V \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) \\
 & + \sum_{\theta,\phi} (\theta - \theta_0)(V \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) \\
 & + \sum_{b,\theta,\phi} F_{b\theta\phi}(b - b_0)(\theta - \theta_0)\cos \phi \\
 & + \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \varepsilon_{ij} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \right].
 \end{aligned} \quad (1)$$

Eq. (1) can be broadly divided into bonded and non-bonded interaction terms. The bonded interaction terms include bond(b), angle(θ), dihedral angle(ϕ), and improper(χ) interactions, while the non-bonded interaction terms comprise van der Waals (vdW) and Coulomb interactions. The vdW interactions, which is part of the non-bonded terms, were calculated using the Lennard-Jones 9-6 (LJ-9-6) potential function with a cut-off distance of 18.5 Å, and the Coulomb interactions were calculated using the Particle-Particle Particle-Mesh (PPPM) [40] summation method with an accuracy of 1×10^{-5} to accurately capture long-range interactions.

2.1.2. Dynamic cross-linking procedure

The dynamic crosslinking methodology [7,41], as illustrated in Fig. 1(b) and (c), is briefly outlined as follows. The dynamic crosslinking scheme considers the actual crosslinking mechanism, in which a carbon atom with two hydrogen bonds from the epoxide group reacts with a nitrogen atom from the curing agent to form a covalent bond. Reactive atom pairs (C-N) are selected accordingly (Fig. 1(b)). Subsequently, using a distance-based criterion, reactive atom pairs satisfying the cutoff distance are connected through covalent bonds. During this process, the O-CH₂ bond within the epoxy ring of the participating epoxy monomer is broken as shown in Fig. 1(b). It iteratively searches reaction candidates and assigns the covalent bonding between them and performs short relaxation steps (500 K canonical (NVT) isothermal ensemble dynamics for 40ps) until the crosslinking conversion ratio reaches the target value. The cut-off distance is initially set to 3 Å and incrementally increased by 0.5–1 Å up to a maximum of 10 Å. Once the desired crosslinking ratio is reached, the crosslinking process is terminated. The specific flow is shown in Fig. 1(c) and the constructed unit cell is depicted in Fig. 1(d). To create TGAP/DETDA epoxy polymer models with varying crosslinking densities, target crosslinking limits of 0 %, 15 %, 35 %, 55 %, 65 %, 75 %, and 85 % were utilized. The detailed information on constructed structures is provided in Table 1 and Supplementary Fig. S2.

2.1.3. Multiaxial deformation (loading-unloading) simulations considering plane stress condition

To investigate the elasto-plastic deformation behavior and yield surface of epoxy polymer materials under multiaxial deformation, MD simulation models, which have undertaken crosslinking and structural relaxation, were adopted. Simulations under plane stress conditions ($\sigma_3 = 0$) for biaxial deformation were conducted using the widely utilized MD simulator, *Large-scale Atomic/Molecular Massively Parallel*

Table 1

Detailed information on the epoxy polymer model under room temperature and atmospheric pressure conditions.

Material	Number of Atoms	Crosslinking Ratio	Density(g/cc)	Cell Legnth (Å)
TGAP/DETDA	29950	0 %	1.0119	68.7191
		15 %	1.0356	68.1916
		35 %	1.0659	67.5376
		55 %	1.0797	67.2490
		65 %	1.0893	67.0516
		75 %	1.0819	67.2039
		85 %	1.0799	67.2450

Simulator (LAMMPS), as shown in Fig. 1(e) and (f). In these simulations, the consistent equivalent strain rate definition (with a value of $10^9/s$) was exploited to apply displacements in two axial directions while performing NPT ensemble dynamics under ambient conditions (300 K, 1 atm) in the direction without deformation, allowing for the natural structural relaxation of polymer network within the unit cell. Consequently, multiaxial deformation simulations considering various loading paths under $\sigma_3 = 0$, from uniaxial to biaxial deformation, can be carried out under consistent strain rate. Note that the all deformation simulations were carried out by imposing a strain of 15 % in each direction. This study aimed to evaluate uniform testing in all directions, including biaxial tension, biaxial shear, and biaxial compression, under plane stress conditions (Fig. 1(e)). Additionally, loading-unloading analyses were also performed to investigate the multiaxial elasto-plastic behavior and deformation mechanisms. After the loading is completed, the deformation was reversed in the opposite direction to the initial loading state as shown in Fig. 1(f).

To consistently define stress and strain across various loading conditions, the equivalent stress (σ_{eff}) and strain (ε_{eff}) described below were used to derive the equivalent stress-strain profile, as illustrated in Fig. 1(f) [29].

$$\begin{aligned}
 \sigma_{\text{eff}} &= \frac{1}{3} \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2}, \\
 \varepsilon_{\text{eff}} &= \frac{1}{\sqrt{2(1+\nu)}} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_3 - \varepsilon_1)^2}
 \end{aligned} \quad (2)$$

$\sigma_1, \sigma_2, \sigma_3$ represent the principal stresses along each axis, while $\varepsilon_1, \varepsilon_2, \varepsilon_3$ denote the corresponding strains. The parameter ν represents Poisson's ratio. Consequently, the equivalent stress-strain curve can be plotted as shown in Fig. 1(f). In this study, since the epoxy polymer system is isotropic, the average equivalent stress and strain curves were derived using identical deformation conditions across three different deformation directions. Additionally, the consistent equivalent strain rate ($\dot{\varepsilon}_{\text{eff}}$) can also be defined [42] as:

$$\dot{\varepsilon}_{\text{eff}} = \sqrt{\frac{1}{2} \sqrt{(\dot{\varepsilon}_1 - \dot{\varepsilon}_2)^2 + (\dot{\varepsilon}_2 - \dot{\varepsilon}_3)^2 + (\dot{\varepsilon}_3 - \dot{\varepsilon}_1)^2}}, \quad (3)$$

where $\dot{\varepsilon}_1, \dot{\varepsilon}_2, \dot{\varepsilon}_3$ represent the principle strain rates for each axis.

The virial stress obtained from deformation simulations can be decomposed into contributions from each detailed molecular interaction and thermal energy component of the PCFF potential function, as follows:

$$\sigma_{\text{total}} = \sigma_{\text{ke}} + \sigma_{\text{bonded}} + \sigma_{\text{non-bonded}}, \quad (4)$$

$$\begin{aligned}
 \sigma_{\text{bonded}} &= \sigma_{\text{bond}} + \sigma_{\text{angle}} + \sigma_{\text{dihed}} + \sigma_{\text{imp}}, \\
 \sigma_{\text{non-bonded}} &= \sigma_{\text{vdW}} + \sigma_{\text{coulomb}}.
 \end{aligned} \quad (5)$$

The total stress, as expressed in Eq. (4), consists of contributions from kinetic energy, bonded interactions, and non-bonded interactions. Specifically, the bonded contributions include bond stress, angle stress, dihedral angle stress, and improper stress, while the non-bonded contributions are derived from van der Waals and Coulombic interactions.

Consideration of each of these stress components will be extensively utilized throughout this study to explain the mechanisms by which external forces are accommodated.

The yield criteria selected for the epoxy polymer in this study are illustrated in Fig. 1(f). Considering the difficulty in identifying a distinct yield point for polymer materials, the offset method proposed in previous studies [28] was employed to determine the yield point. To account for the overestimation of stress arising from the strain rate discrepancy and nonlinearity in the elastic region observed in MD calculations, a larger offset range ($\epsilon_{\text{eff}}^{\text{offset}} = 2 - 3\%$) was utilized compared to the conventional method used for metallic materials. Additionally, a specific strain range ($\epsilon_{\text{eff}}^{\text{slope}} = 1 - 8\%$) was selected to determine the slope for defining the yield stress. For the initial yield criterion, an offset of 0.5 % was chosen, with a strain range of 2.6–6 % to calculate the slope. To determine the yield stress for the subsequent yield surface, equivalent plastic strains of 3 % and 6 % were further considered from the initial yield point to establish the subsequent yield surfaces.

2.2. Experiments

2.2.1. Sample preparation

For the synthesis of the epoxy polymer, TGAP supplied by Angene Chemical (UK) was selected as the epoxy resin monomer, and a mixture of DETDA containing 75 % 2,4-isomer and 25 % 2,6-isomer, provided by BLDpharmatech (China), was chosen as the curing agent monomer.

To prepare the specimens for the deformation tests, TGAP epoxy resin (277.32 g/mol, 92.44 g/equivalent) and DETDA curing agent (178.28 g/mol, 44.57 g/equivalent) were mixed at an equivalent ratio of 1:0.4822 (Fig. 2(a)). The mixture was stirred at 2000 rpm for 5 min and then degassed for 30 min to remove microbubbles and air pockets before being poured into molds (as presented by Fig. 2(b–c)). The molds were placed in a forced convection oven, where the lowly crosslinked (LC) samples were cured for 1 h at 100 °C and then for an additional hour at 130 °C. The highly crosslinked (HC) samples were cured for 1 h at 100 °C, followed by 1.5 h at 130 °C. After curing, the samples were removed from the oven, allowed to cool to room temperature, and the LC and HC samples were obtained as shown in Fig. 2(d). In the present study, specimens were fabricated using teflon-coated molds specifically designed for uniaxial tensile test (Fig. 2(b)) and plane-strain

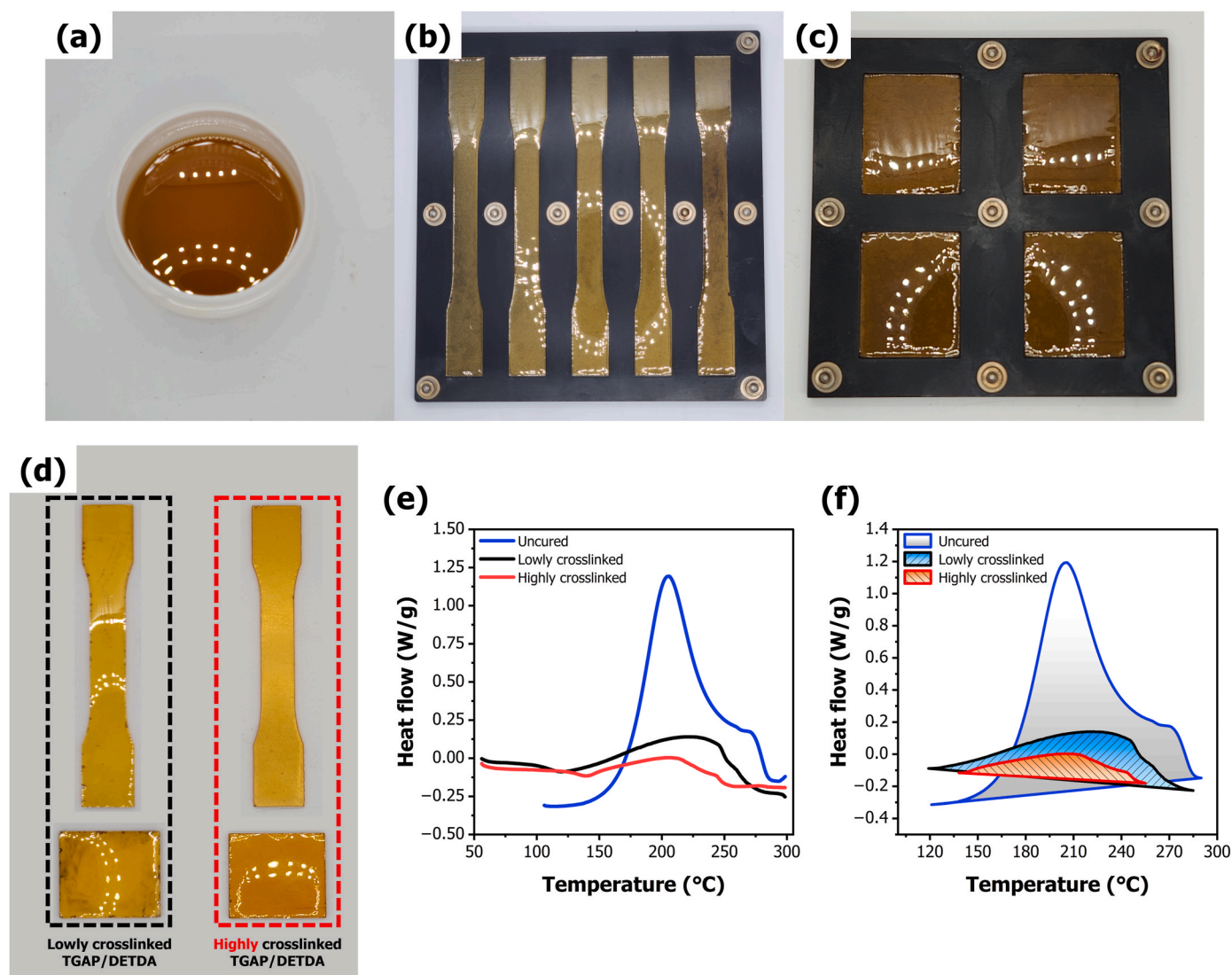


Fig. 2. Epoxy polymer synthesis, specimen preparation, and degree of cure calculation using differential scanning calorimetry (DSC) analysis. (a) Mixture of the epoxy resin and curing agent. The mixture is then poured into molds for (b) uniaxial tensile tests and (c) PSC tests. After curing, (d) the final samples produced through the epoxy synthesis process. (e) DSC measurement results for different crosslinking degrees to assess the degree of cure and (f) area calculations for the heat of absorption.

compression (PSC) test (Fig. 2(c)), respectively.

To compare the degree of cure (DOC) of the fabricated specimens, differential scanning calorimetry (DSC) analysis was performed, and the heat flow curves were plotted as shown in Fig. 2(e). First, to calculate the total curing heat, the uncured mixture was heated from 100 °C to 300 °C at a rate of 10 °C/min to obtain the DSC profile. Next, to evaluate the difference in the degree of cure between the LC and HC samples, the residual curing heat was measured for both samples after specimen preparation. The LC and HC samples were heated from 50 °C to 300 °C at a rate of 10 °C/min, as illustrated in Fig. 2(e). The reaction heat of all samples was then determined by calculating the area under the heat flow profiles over time [43–46] (Fig. 2(f)). Consequently, the DOC for each sample was calculated as the ratio of the reaction heat of each sample to the total reaction heat, as shown in Eq. (6) [46].

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \quad (6)$$

Here, α represents the degree of cure, ΔH_t denotes the reaction heat at time t , and ΔH_{total} is the total heat of reaction. Accordingly, based on Eq. (6), the LC sample has a degree of cure of 66.52 %, while the HC sample has a degree of cure of 86.95 %.

2.2.2. Mechanical testing

For the uniaxial tensile deformation test, ASTM D-638 standards

were followed, and the test was conducted at a quasi-static displacement rate of 5.0 mm/min to obtain the stress-strain profile. The equipment used for this test included an Instron 5567A machine with a 30 kN load cell (Fig. 3(a)). For the multiaxial deformation test, since there is no ASTM standard specifically for PSC tests of polymer materials, the experiment was conducted based on existing PSC test methods for thermoplastic polymers [47–49]. The equipment chosen for this test was a tensile and compression testing machine (TO-F-HS) with a 5-ton capacity, manufactured by TEST ONE (Fig. 3(b)).

Unlike the uniaxial tensile test, the PSC test utilized custom-made compression tools consisting of a plunger and a deep channel-die, as depicted in Fig. 3(c). The first compression tool is the plunger, a plate with dimensions 50 mm and a thickness of 4 mm, which applies pressure to the epoxy polymer sample from above. The second compression tool is the deep channel-die, which has dimensions 50 mm and a channel width of 4.05 mm, designed to ensure proper assembly with the specimen. The deep channel-die constrains the epoxy sample to prevent expansion in the constraint direction (CD) while allowing expansion in the flow direction (FD) under plane-strain conditions, applying biaxial compression in both the loading direction (LD) and CD when the plunger compresses the sample. For all PSC tests, the loading was applied at a displacement rate of 5.0 mm/min. Detailed 3D modeling of the plunger and deep channel-die tools is provided in Supplementary Fig. S3.

Furthermore, during biaxial compression deformation, to quantita-

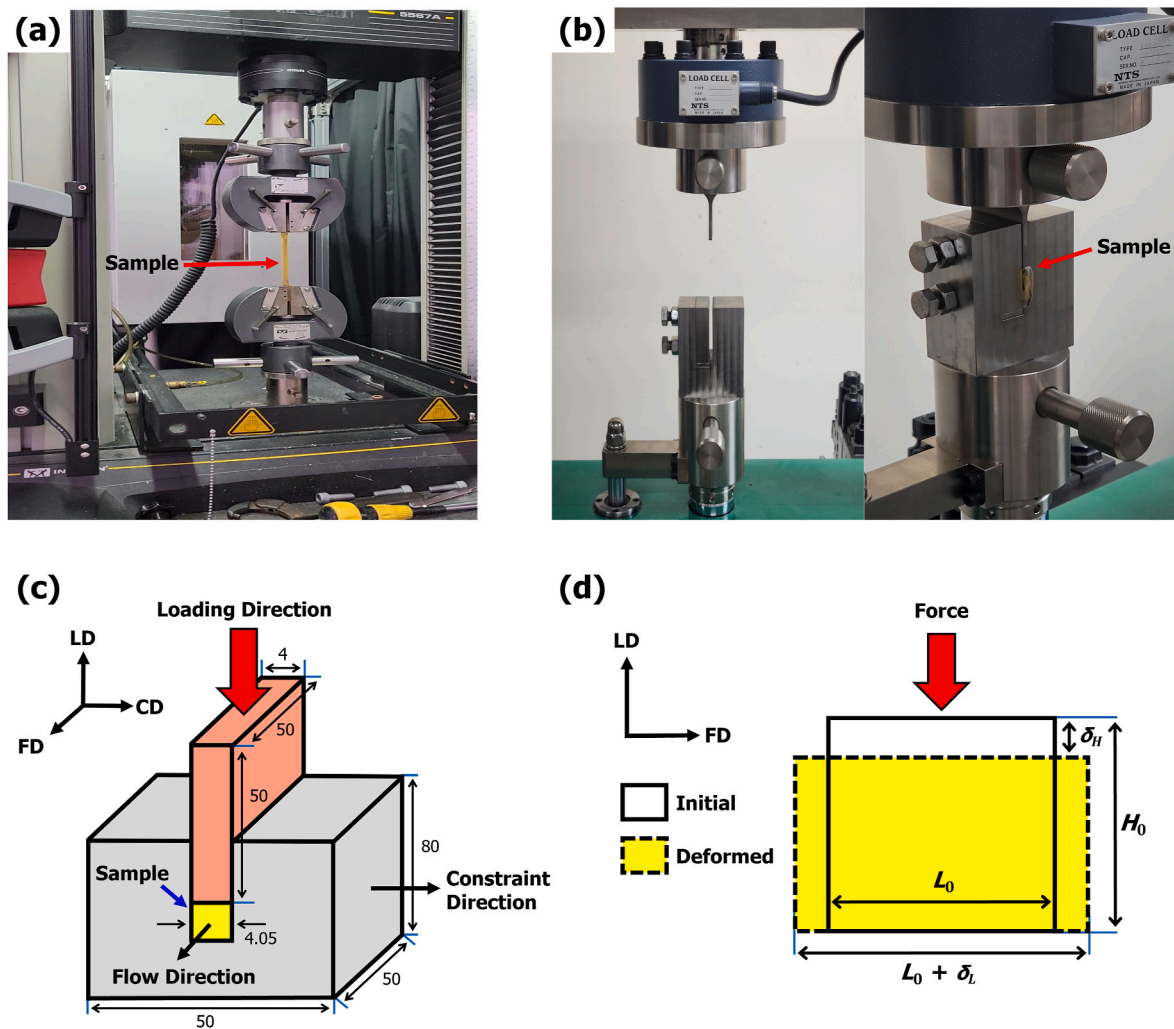


Fig. 3. (a) Uniaxial tensile test equipment with a specimen. (b) Testing setup with PSC-specific jig and specimen. (c) Schematic of the PSC test method and jig configuration. All units in the (c) are in millimeters (mm). (d) Schematic showing the displacement and strain measurement before and after deformation of the specimen in the PSC test.

tively observe the differences in expansion into the flow direction (FD) compared to the loading direction (LD) of TGAP/DETDA polymer models and samples with varying degrees of crosslinking, we measured the strains in both LD(ϵ_{LD}) and FD(ϵ_{FD}), as shown in Fig. 3(d), and calculated the strain ratio ($|\epsilon_{FD}/\epsilon_{LD}|$). Here, δ_H represents the displacement relative to the initial height (H_0), and δ_L represents the displacement relative to the initial width (L_0), allowing us to calculate the strain in each axial direction. The overall procedures for the uniaxial tensile test and the PSC test can be found in Supplementary Fig. S4.

In this experiment, the yield criterion applied was identical to that in Section 2.1.3, utilizing the offset method on the stress–strain curves obtained from experimental data. Accordingly, a 0.5 % offset was employed as the yield criterion, consistent with the initial yield criterion selected in the previous MD simulations. And, to calculate the slope for determining the yield stress, we established a strain range of 0.2–0.5 % in the uniaxial tensile tests and a strain range of 5–7% in the PSC tests.

3. Effect of degree of crosslinking on static mechanical property

To understand the structural characteristics according to the degree of crosslinking, the radial distribution function (RDF) was derived based on the following definition:

$$g_{\alpha\beta}(r) = \frac{n_{\alpha\beta}(r)}{4\pi r^2 (N_\alpha N_\beta / V)}, \quad (7)$$

where $n_{\alpha\beta}(r)$ represents the number of atomic pairs of type α and type β

within a spherical shell at a distance range of $(r - \frac{\Delta r}{2}, r + \frac{\Delta r}{2})$. N_α and N_β represent the number of atoms of type α and type β , respectively, while V represents the total volume of the model.

As a result of deriving the RDF according to the crosslinking structure of the epoxy polymer, it was found that the models with 85 % and 55 % crosslinking, excluding the 0 % crosslinking model, exhibit a prominent peak at approximately 1.5 Å as shown in Fig. 4(a). This peak originates from the formation of C–N covalent bonds within the crosslinked epoxy polymer structure, corresponding to a bond length of about 1.5 Å. Naturally, as the degree of crosslinking increases, the intensity of this peak becomes more pronounced. A similar trend is observed for non-covalent interactions between carbon and nitrogen atoms. As the distance r increases, the inset in Fig. 4(a) reveals that the smaller peaks corresponding to non-bonded C–N atomic pairs also increase in magnitude at higher crosslinking levels, indicating a more substantial development of the three-dimensional crosslinked network.

The densities of all models, after equilibration, were determined to observe the changes in the density of the epoxy unit cell according to the degree of crosslinking, as shown in Fig. 4(b). As the crosslinking conversion ratio of the TGAP/DETDA polymer system increases, the overall density of the unit cell increases in a relatively linear manner, which can be seen in Fig. 4(b). This is attributed to the restricted mobility of the monomers and the increased packing efficiency due to crosslinking, as expected. However, beyond a crosslinking ratio of 65 %, a decrease in density is observed, showing a trend consistent with previous literature

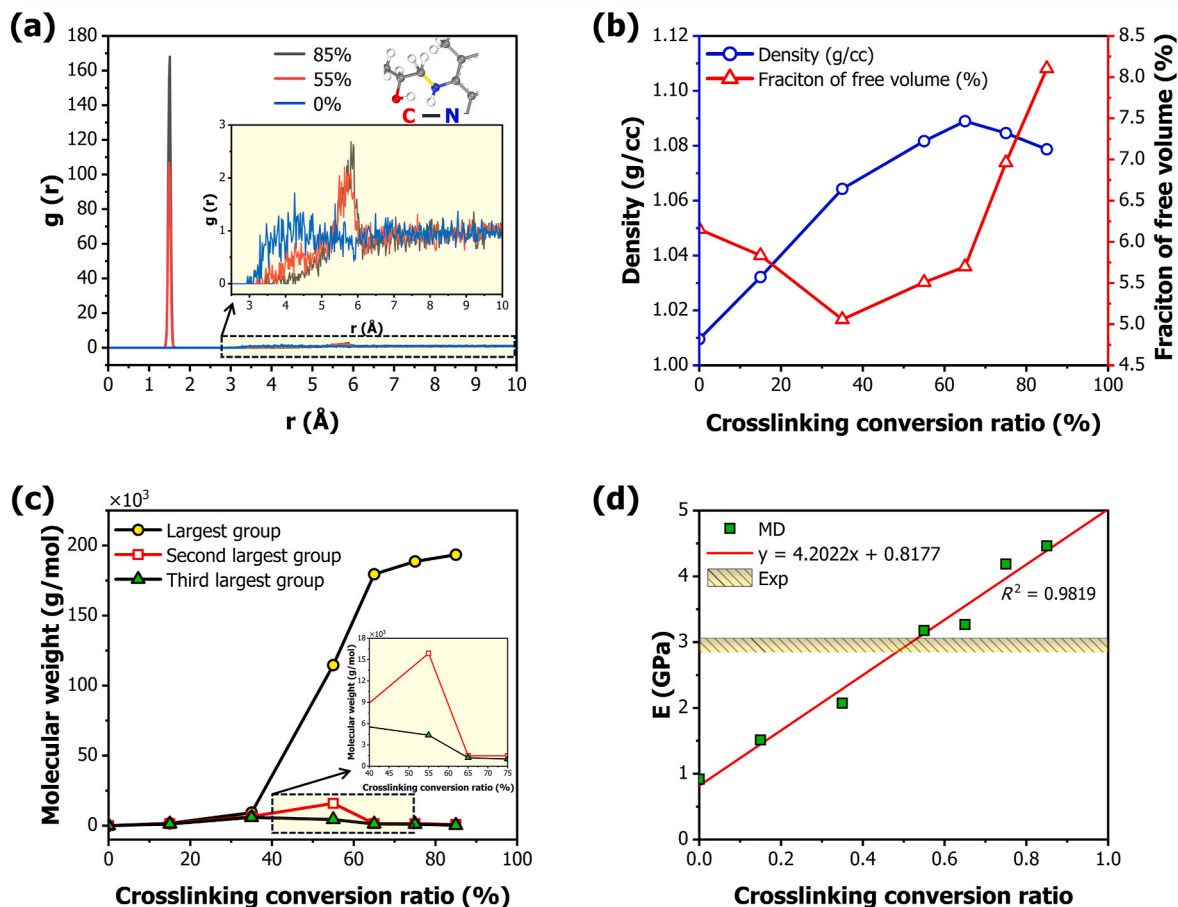


Fig. 4. Changes in physical properties according to the degree of crosslinking: (a) radial distribution function of reactive atomic pairs, (b) density and fraction of free volume, (c) molecular weight variation, and (d) changes in elastic modulus with crosslinking degree. The inset in (a) illustrates the RDF curve highlighting the small peak point corresponding to different degrees of crosslinking. In (b), the left y-axis represents density, while the right y-axis indicates the fraction of free volume. The fraction of free volume was calculated by dividing the free volume by the volume of each unit cell, corresponding to different crosslinking densities of the epoxy unit cells. The inset in (c) compares the second and third largest molecular weight groups.

[19]. The decrease in density in epoxy polymer systems with a crosslinking ratio above 65 % is related to an increase in the ratio of free volume after the crosslinked structure has formed to a certain extent [50–52]. As the crosslinking ratio increases, larger voids [50] and free volume [51,52] between chains are formed, and the covalent bonding between reactive atoms causes the structure to become more rigid, hindering efficient packing [51], and thereby reducing the density owing to the size of the monomer itself. Indeed, it can be observed in Fig. 4(b) that the fraction of free volume begins to rise steeply from the 65 % crosslinking model onward.

To observe the changes in molecular weight with varying crosslinking ratios, we classified the molecular weights into the largest group, second largest group, and third largest group, as shown in Fig. 4(c). Consistent with the previously observed result of density increase with increasing crosslinking ratio, the molecular weight of the largest group monotonically increased. Notably, in the 35–65 % crosslinking ratio range where the density significantly rises, the molecular weight sharply increased. During this process, the molecular weights of the second and third largest groups markedly decreased around the 55 % crosslinking ratio, due to crosslinking with the largest group. This trend aligns with previous studies [15,50].

To investigate the changes in elastic properties according to the degree of crosslinking, the variation in Young's modulus is illustrated in Fig. 4(d). To determine Young's modulus through MD simulations and experimental testing, the elastic modulus for each crosslinking model

was obtained by performing a linear regression on the stress-strain curves derived from uniaxial tensile deformation simulations (strain rate of $10^9/s$) and uniaxial tensile tests (strain rate of 5.0 mm/min) at 1 % strain. The elastic modulus increased linearly with the degree of crosslinking, showing a stiffness increase of 42.02 MPa for each 1 % increase in crosslinking degree. The stiffness in the range typically considered to represent complete crosslinking (80–100 %) was found to be approximately 4.18–5.02 GPa.

4. Relationship between degree of crosslinking and dynamic mechanical response

4.1. Elasto-plastic deformation behaviors

Using the previously described Eq. (2), the equivalent stress-strain profiles for various crosslinking degrees based on MD simulations are shown in Fig. 5(a–b), while the experimental stress-strain profiles obtained through synthesis and testing are presented in Fig. 5(c–d). The results from the MD simulations indicate that, except for the yield strain, the mechanical properties such as elastic modulus, equivalent stress, and yield stress improved overall with increasing crosslinking degree. For the yield strain, there is minimal change with varying crosslinking degrees across all loading directions.

In uniaxial deformation comparisons (Fig. 5(a)), the elastic modulus and initial yield point are higher in the uniaxial compression direction

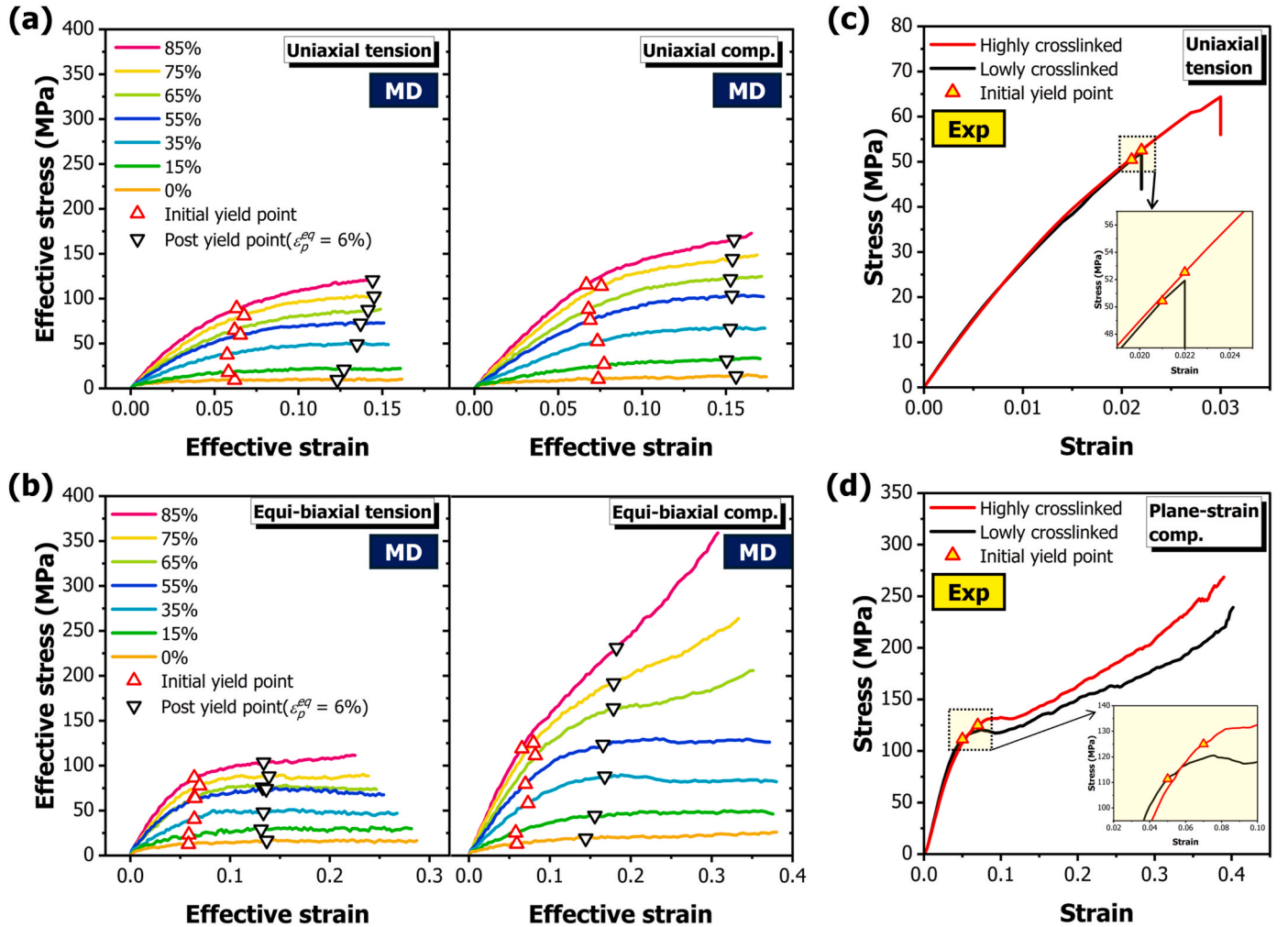


Fig. 5. Equivalent stress-strain profiles for various loading paths: (a) uniaxial tension and compression (MD), (b) equibiaxial tension and compression (MD), (c) uniaxial tension (experiment), and (d) biaxial compression (experimental PSC test). The red triangles indicate the initial yield points based on the yield criterion, while the black inverted triangles represent the post-yield points at 6 % equivalent plastic strain.

compared to the uniaxial tension direction. Notably, after initial yielding, the post-yield stress increases more significantly in the uniaxial compression direction. This suggests that the material can accommodate stress more effectively in the compression direction compared to tension, which is associated with differences in microscopic deformation mechanisms.

This trend is even more pronounced in equibiaxial deformation (Fig. 5(b)). As the crosslinking degree increases, both the elastic modulus and initial yield stress in the equibiaxial compression direction are higher compared to the equibiaxial tension direction. A notable point is that stress in the equibiaxial compression direction increases non-linearly with increasing crosslinking degree. This stress behavior is indicative of the formation of an asymmetric shape of the yield surface and is consistent with the physics of pressure-dependent yield functions commonly used in polymer constitutive modeling [28,29,31].

To experimentally investigate these trends, uniaxial tensile and plane-strain compression (PSC) tests were also conducted, and the resulting stress-strain profiles are presented in Fig. 5(c) and (d). In the uniaxial tensile tests, it was observed that higher degrees of crosslinking led to a slight increase in yield stress, accompanied by significant enhancements in both fracture stress and strain. In contrast, the PSC tests revealed that higher degree of crosslinking resulted in a more substantial increase in yield stress compared to the uniaxial tension. Moreover, the rate of stress rise beyond the initial yield point was accelerated with higher crosslinking degrees, particularly above 55 %, which nearly

corresponds to the gelation point. This indicates that, an increase in crosslinking degree leads to a rise in plastic stress with the involvement of multiaxial compression, as identified by both simulations and experiments. Broken specimens from all deformation experiments are shown in Supplementary Fig. S5.

To more closely examine the relationship between crosslinking degree and yield stress depicted in Fig. 5, the initial and post-yield stresses for various crosslinking degrees are shown in Fig. 6. The initial yield stress in all loading directions exhibits a linear relationship with the crosslinking degree. In contrast, the post-yield stress increases non-linearly with increasing crosslinking degree in all deformation directions except for the equibiaxial tensile yield stress (Fig. 6(c)). Notably, as shown in Fig. 6(d), the post-yield stress under equibiaxial compression load has the most distinct non-linear relationship with the crosslinking degree, with an accelerated rate of increase in post-yield stress. While the post-yield stress under uniaxial tension and uniaxial compression also exhibits non-linearity with respect to the crosslinking degree, it remains within a range that does not deviate significantly from a linear relationship (Fig. 6(a) and (b)). This sudden non-linearity in stress increase behavior within the equibiaxial compression suggests the possibility of different deformation mechanisms at play.

4.2. Yield surface evolution

The yield surfaces of the TGAP/DETDA epoxy material under plane

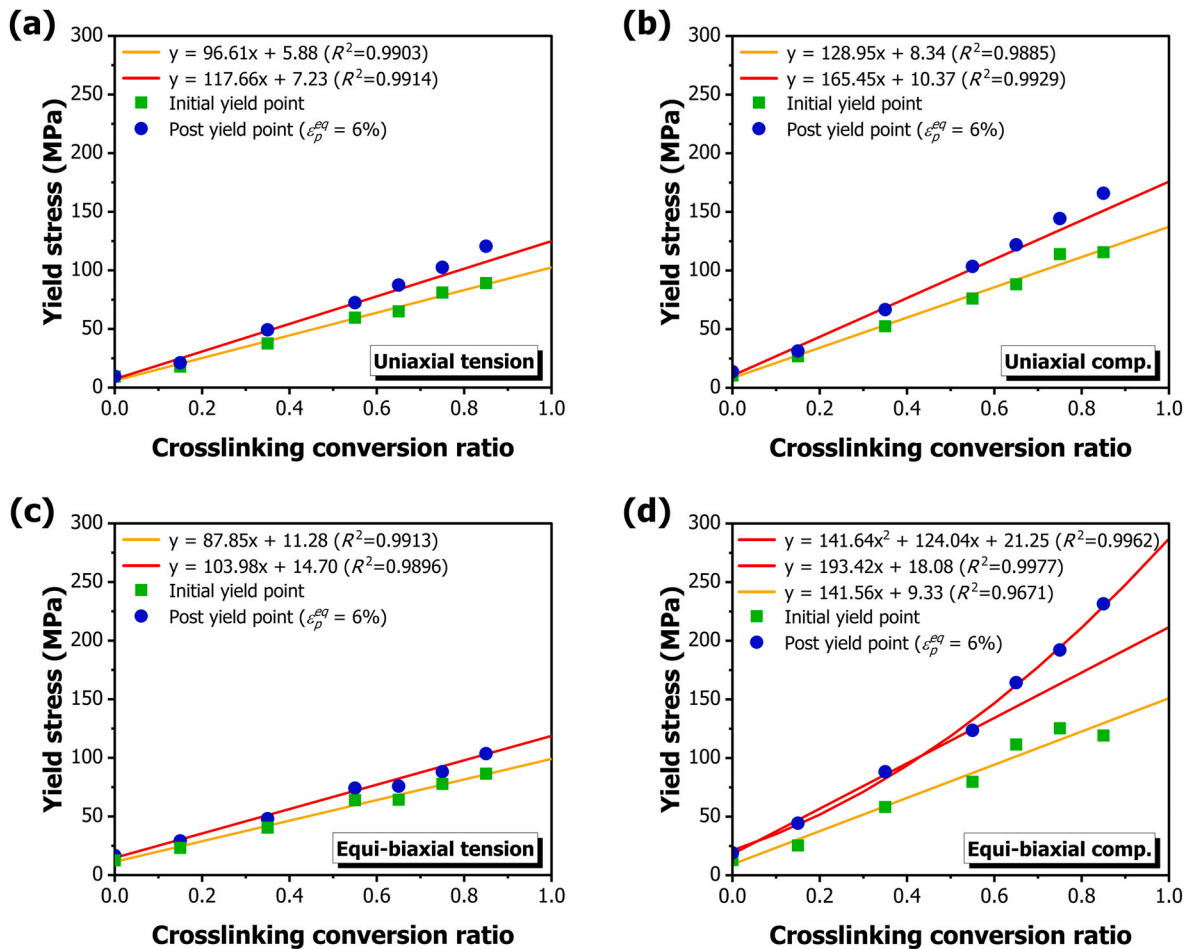


Fig. 6. Relationship between crosslinking degree and yield stress under various loading directions: (a) uniaxial tension, (b) uniaxial compression, (c) equibiaxial tension, (d) equibiaxial compression. The light green squares represent the initial yield points, with the regression curve shown as an orange solid line. The blue circles indicate the post-yield points at an equivalent plastic strain of 6 %, with the regression curve depicted as a red solid line. For the two regression analysis curves in (d), the polynomial curve fitting adopted yield stresses across the entire range of crosslinking ratios, while the linear regression used yield stresses within the crosslinking ratio range of 0 to 0.55.

stress conditions are presented in Fig. 7(a) and (b) as a function of the crosslinking degree and equivalent plastic strain. Additionally, to quantify the degree of asymmetry of each surface, the yield stress ratio of biaxial compression to uniaxial tension ($|\sigma_{cc}/\sigma_t|$) based on MD simulations and the yield stress ratio of plane-strain compression to uniaxial tension ($|\sigma_{PSC}/\sigma_t|$) based on experiments are introduced and shown in Fig. 7(c). Here, σ_t , σ_{cc} , and σ_{PSC} represent the distances from the origin of the yield surface to the surface in the directions of uniaxial tension and biaxial compression ($\sigma_t = \sigma_{t1} = \sigma_{t2}$, $\sigma_{cc} = \sqrt{\sigma_{c1}^2 + \sigma_{c2}^2}$, $\sigma_{PSC} = \sqrt{\sigma_{c1}^2 + (\nu\sigma_{c1})^2}$ (ν = Poisson's ratio)), respectively. In the case of the PSC test, since only the stress in the LD direction (σ_{c1}) could be measured using the equipment, the stress state in the CD direction was determined using the relationship of based on the assumptions of three-dimensional Hooke's law, $\sigma_{c2} = \nu\sigma_{c1}$. The Poisson's ratio for each degree of curing was measured and applied (the LC sample had a Poisson's ratio of 0.445, while the HC sample had a Poisson's ratio of 0.41, as shown in Supplementary Fig. S6).

Examining the changes in the yield surface with respect to the crosslinking conversion ratio, it is observed that, as the crosslinking ratio increases, the yield surface expands in all loading directions due to improved load transferability resulting from the formation of a cross-linked network. The extent of this expansion varies by direction, with more rapid expansion observed in the direction of biaxial compressive loading (Fig. 7(a)). As the plastic strain progresses, the yield surface

continues to expand due to the strength increase associated with plastic hardening. Similar to the effect of crosslinking ratio, the expansion accelerates more prominently in the biaxial compressive loading region as the plastic strain advances.

When examining the asymmetry ratio in Fig. 7(c), it can be seen that the increase in crosslinking degree and the progression of plastic deformation intensify the asymmetry. Compared to the uncrosslinked state, a 100 % crosslinking completion results in an increase in the indicator by approximately 0.74, while an equivalent plastic strain progression of 3 % results in an increase of about 0.7–0.83.

To perform a comparative validation with the yield surface data based on MD analysis, the experimental yield surface of the TGAP/DETDA epoxy system was derived as shown in Fig. 7(b), based on the yield stresses previously investigated through uniaxial tension and PSC tests (Fig. 5(c) and (d)).

The results indicate that, consistent with the previously observed MD results, the yield surface expanded in both the uniaxial tension and biaxial compression directions as the degree of curing increased from the LC sample to the HC sample, with a more pronounced expansion in the biaxial compression direction. As a result, it was observed that $|\sigma_{PSC}/\sigma_t|$ increased with the degree of curing, and the intensification of asymmetry was found to be in relatively good agreement with the MD analysis results (Fig. 7(c)). In conclusion, the yield surface of the epoxy polymer forms asymmetrically due to its dependency on the loading direction, and this dependency becomes more pronounced as the degree

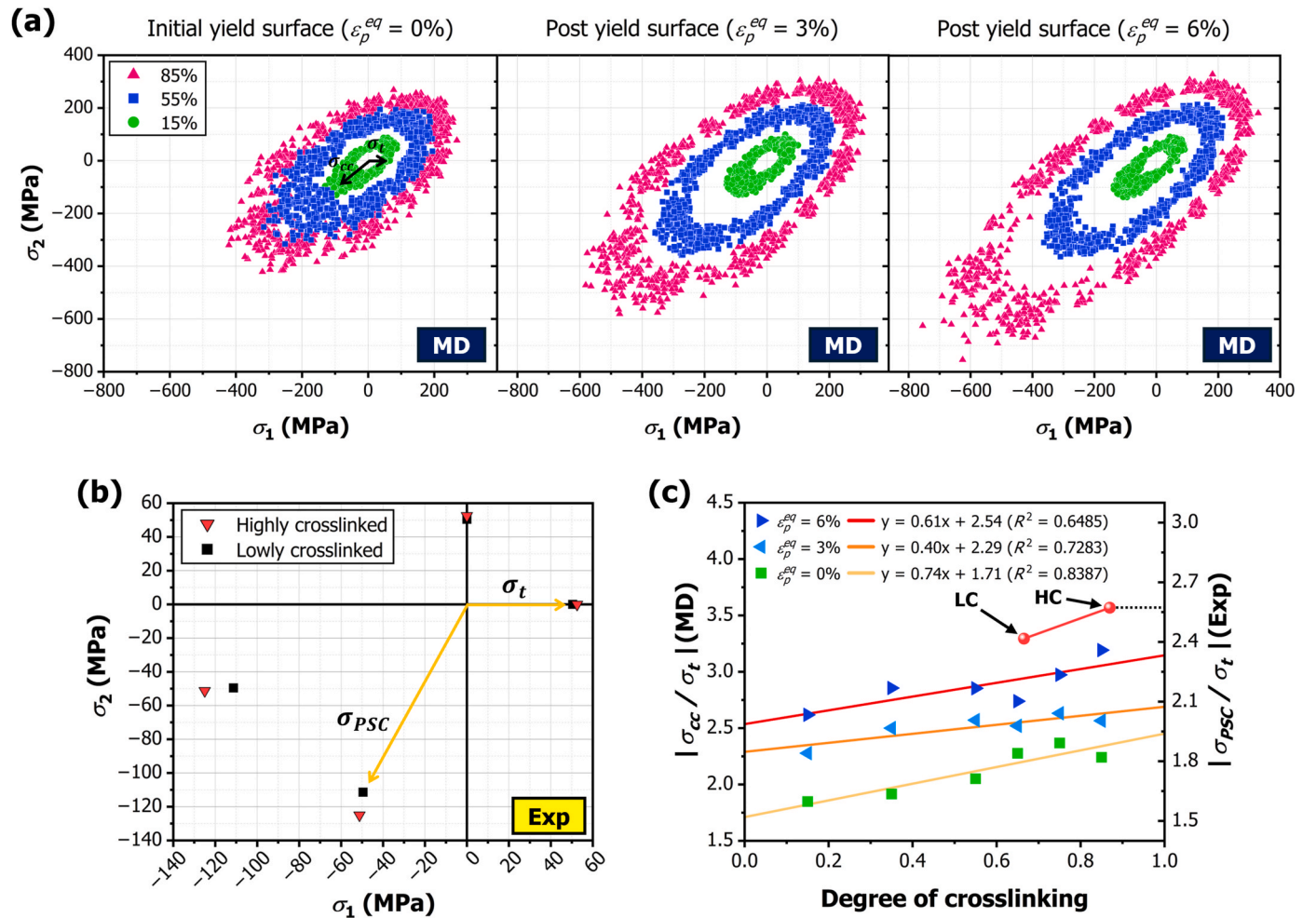


Fig. 7. (a) Yield surfaces based on MD deformation tests according to crosslinking degree and equivalent plastic strain. (b) Initial yield surfaces under LC and HC conditions obtained from uniaxial tensile and PSC tests. (c) Intensification of asymmetry in yield surfaces with respect to crosslinking degree and equivalent plastic strain. The left y-axis in (c) represents the absolute value of the ratio $|\sigma_{cc}/\sigma_t|$ obtained from MD simulations, while the right y-axis represents the absolute value of the ratio obtained from PSC tests.

of cure increases. It is worth noting that these trends have also been quantitatively confirmed through simulations conducted at a lower strain rate ($10^8/s$) and by fitting the results to pressure-dependent yield functions, as shown in Figs. S7 and S8 and summarized in Table S1.

To analyze in greater depth the phenomenon of the intensified asymmetry in the yield surface, changes in the hardening coefficient in the directions of uniaxial tension (σ_t) and biaxial compression (σ_{cc}) are

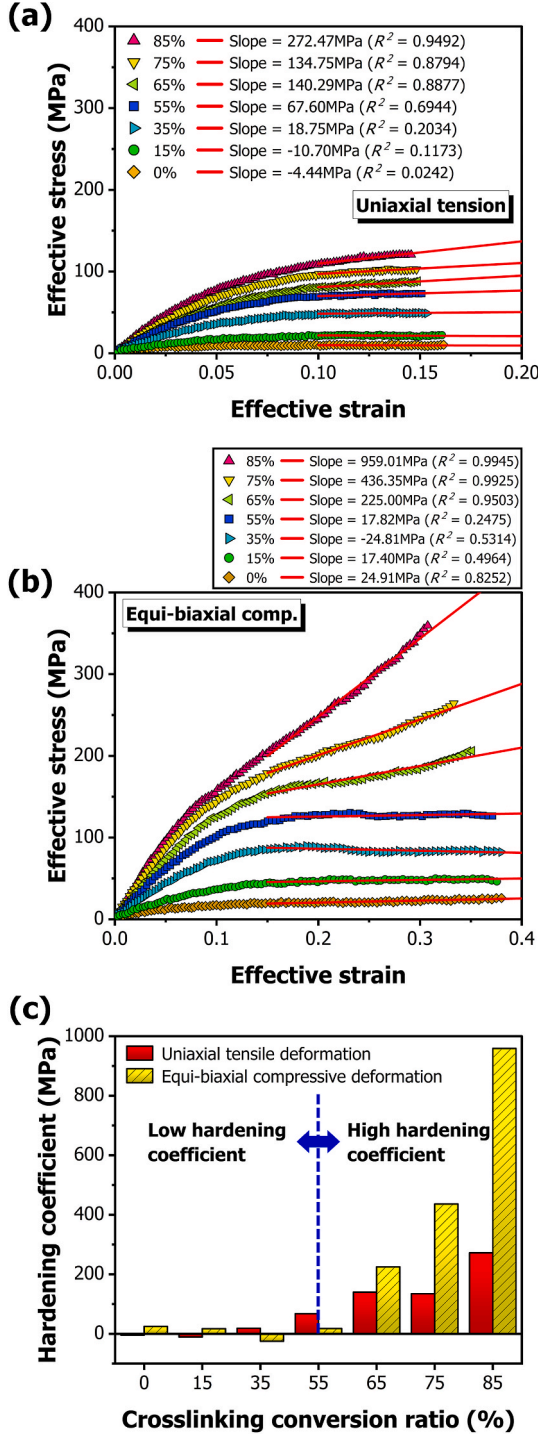


Fig. 8. Equivalent stress-equivalent strain profiles and regression plots for determining the hardening coefficient according to the crosslinking conversion ratio for (a) uniaxial tension and (b) biaxial compression loading paths. To derive the linear regression curve, the starting points for the regression line were set at an effective strain of 10 % for (a) and 15 % for (b). (c) Changes in the hardening coefficient with crosslinking ratio.

presented in Fig. 8. In both loading directions, the increase in the hardening coefficient is not significant in the crosslinking conversion ratio range below 55 %. However, from a crosslinking ratio around 55 %, where gelation typically begins, the increase in the hardening coefficient starts in earnest.

As the crosslinking network forms beyond the 55 % crosslinking ratio, Fig. 8(c) shows that the increase rate of the hardening coefficient is faster in the biaxial compression loading direction (Fig. 8(b)) than in the uniaxial tension loading direction (Fig. 8(a)). Notably, for crosslinking densities above 55 %, this corresponds with the point at which the second and third largest molecular groups in the system, based on molecular weight (as shown in Fig. 4(c)), are rapidly absorbed into the largest molecular group, causing a sharp increase in the molecular weight of the largest group. This suggests that changes in the behavior characteristics of a sufficiently large crosslinked structure induce changes in the deformation mechanisms under multiaxial deformation.

5. Multiaxial deformation mechanisms

5.1. Stress components analysis

As crosslinking progresses, the change in the deformation mechanism ultimately leads to the dependency of the hardening coefficients on the loading path. This results in the expansion of the yield surface due to improved load transfer capability, which simultaneously intensifies the asymmetry, as confirmed in Sections 3 and 4.

Therefore, it is crucial to investigate how the microscopic deformation mechanism changes as the crosslinking degree varies and how this relates to the dependency on the loading path, in order to establish the multiaxial mechanical behavior characteristics of epoxy materials. In this study, we aim to discuss this through stress components analysis introduced in Eqs. (4) and (5). Based on previous investigations (Fig. 8), models with a 55 % crosslinking degree, where the hardening coefficient increases rapidly with crosslinking conversion ratio in the biaxial compression loading path, and the highest crosslinking ratio of 85 % were selected for stress component analysis (Fig. 9).

In the behavior under uniaxial tensile deformation (Fig. 9(a) and (b)), most of the overall stress is accommodated through bonded stress. At a low crosslinking degree of 55 %, there is almost no contribution from non-bonded stress, and its impact becomes even more negligible during plastic deformation. At a high crosslinking degree of 85 %, the contribution of bonded stress remains significant, but there is a noticeable increase in the contribution of non-bonded stress compared to the 55 % case.

This shift in the contributions of bonded and non-bonded stresses is similarly observed in uniaxial compression deformation (Fig. 9(c) and (d)). At a 55 % crosslinking degree, bonded stress accounts for the majority of the total stress, with non-bonded stress contributing very little. Although the contribution of non-bonded stress increases somewhat at an 85 % crosslinking degree, the bonded stress contribution remains dominant.

In the behavior under equibiaxial compression deformation (Fig. 9 (e) and (f)), the mechanism changes due to the influence of the loading path. In the case of a 55 % crosslinking degree, the influence of bonded stress is still higher, similar to the trend observed in uniaxial deformation (Fig. 9(a) and (c)). However, this trend reverses at an 85 % crosslinking degree. The increase in crosslinking degree under equibiaxial compression leads not only an increase in bonded stress but also to a significant increase in non-bonded stress. This indicates that the contribution of non-bonded stress to the overall stress becomes dominant. In other words, the high stress increase in plastic range observed in the biaxial compression region in Fig. 8 reveals that the increase in non-bonded stress plays a crucial role in driving the steep rise in stress, rather than the mere increase in bonded stress with a higher crosslinking ratio.

The effect of crosslinking degree on stress increase can be understood by expressing the increase in stress in terms of the contributions of

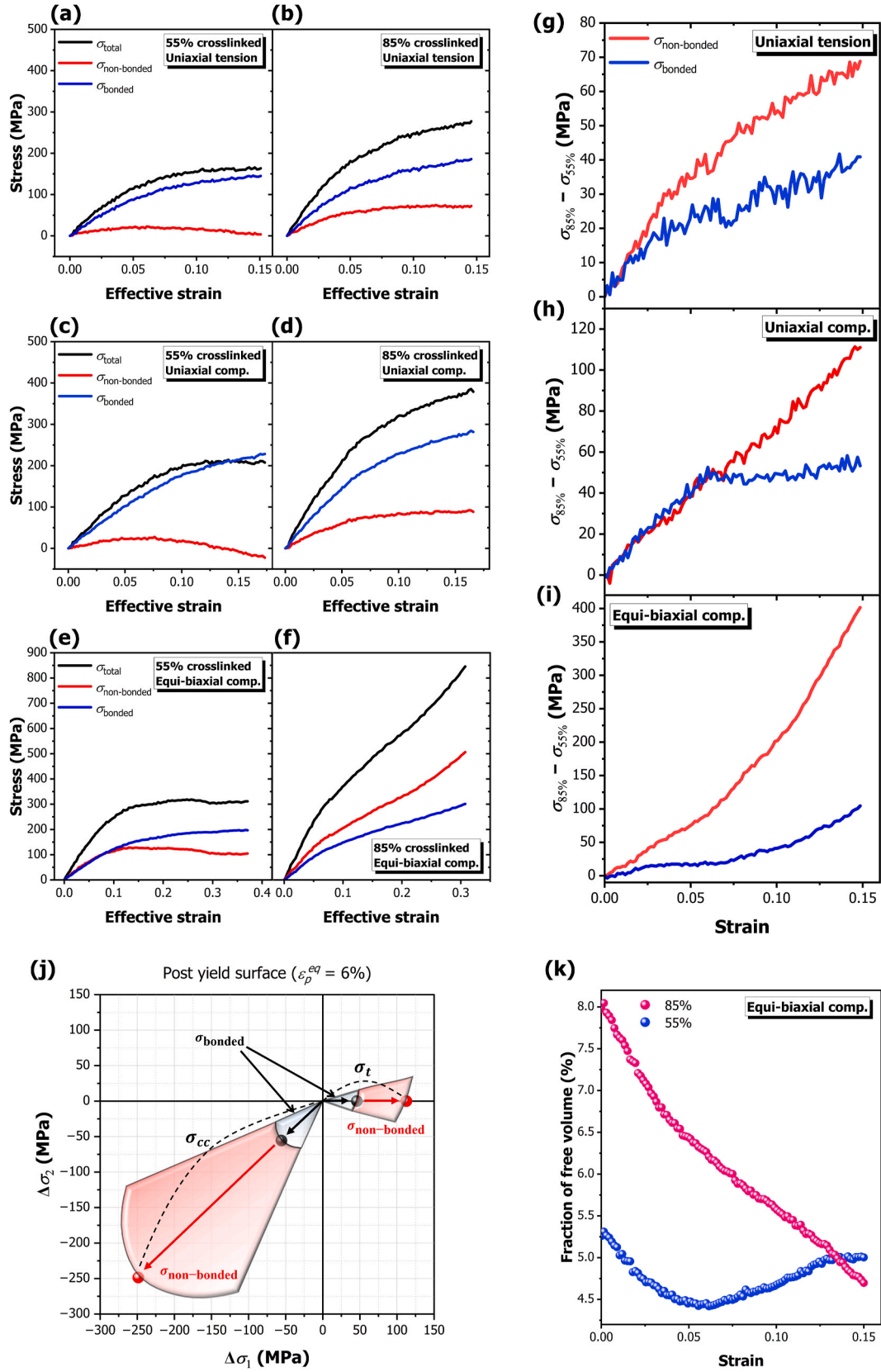


Fig. 9. Comparison of contributions between non-bonded stress and bonded stress in stress behavior and the progression of free volume. (a–f) Comparison of stress components according to the crosslinking degree under (a–b) uniaxial tensile loading, (c–d) uniaxial compression loading and (e–f) equibiaxial compression loading. (a), (c), and (e) represent the 55 % crosslinking ratio, and (b), (d), and (f) represent the 85 % crosslinking ratio. Net stress increase between the 55 % and 85 % crosslinking models: (g) under uniaxial tensile loading, (h) uniaxial compression loading, and (i) equibiaxial compression loading. The x-axis in (g), (h), and (i) represents the axial strain. (j) The contribution of stress components that constitute the total stress on the yield surface expansion ($\epsilon_p^{eq} = 6\%$). (k) Change in the fraction of free volume for equibiaxial compression loading.

bonded and non-bonded stresses. As shown in Fig. 9(g-i), the increase in stress is largely dominated by non-bonded stress as it enters the plastic region. This difference becomes more pronounced as plastic deformation progresses under biaxial compression loading paths (Fig. 9(i)). The contribution of bonded and non-bonded stresses to the expansion of the yield surface in multiaxial stress space is illustrated in Fig. 9(j). This highlights the importance of polymer non-bonded interactions in the expansion and intensification of asymmetry in the yield surface of epoxy polymers. In other words, the asymmetric expansion of the yield surface with increasing crosslinking degree is predominantly influenced by the non-bonded interactions resulting from the crosslinked network effect. Note that the same conclusion has been derived under a lower strain rate condition (Supplementary Fig. S9).

5.2. Free volume evolution

To explain the high contribution of non-bonded stress to the formation of the yield surface under high crosslinking conditions, the fraction of free volume, a structural factor that is directly related to the non-bonded chain interaction, is shown in Fig. 9(k). The method for calculating the free volume fraction was referenced from previous studies [50,53]. As discussed in Fig. 4(b), the free volume fraction is higher at 85 % than at 55 % due to reduced packing caused by the inherent size effect of the epoxy monomers. This fraction sharply decreases during the initial deformation phase due to compression effects. After 0.05 strain, the 55 % crosslinked system maintains its value due to active chain rearrangement facilitated by high chain mobility, eventually showing a slight increase. In contrast, the 85 % crosslinked system displays a monotonous decrease. This indicates that at strains beyond 0.05, the relative atomic distances within the epoxy system continue to decrease (becoming smaller than the equilibrium distance between atoms) in the 85 % crosslinked case, whereas in the 55 % system, the chain rearrangement allows for maintaining a certain distance. This opposing trend is naturally attributed to the load transfer characteristics caused by the fully formed crosslinked network at 85 %.

Free volume analysis provides insight into the loading direction dependency of the yield surface. As shown earlier in Fig. 9, the increase in non-bonded stress occurs more sharply under biaxial compression than under uniaxial tension or uniaxial compression. This phenomenon can be explained by the relaxation of polymer chain structures and changes in free volume under multiaxial loading, as depicted in Fig. 9 and S10.

Firstly, in the uniaxial tensile loading path, the polymer chains can relax in two transverse directions. Supplementary Fig. S10 confirms that the free volume fraction increases as the interatomic distances expand. This effect becomes more pronounced with higher crosslinking ratio. In contrast, during uniaxial compression which also has two transverse directions the interatomic distances decrease due to axial compression. At a 55 % crosslinking ratio, the free volume fraction slightly decreased but then increased after a strain of 0.05 because of the high mobility of the chains. However, in the highly crosslinked 85 % model, the reduced chain mobility led to a continuous decrease in the free volume fraction.

This indicates that when the loading direction is compressive, maintaining free volume becomes disadvantageous. Particularly in biaxial compression, there is only one direction for the polymer chains to relax, significantly reducing chain mobility. This is evidenced by the more rapid reduction in free volume in the biaxial compression direction (Fig. 9(k)) compared to the uniaxial case (Supplementary Fig. S10), which causes the most fastest expansion of yield surface toward the biaxial compression loading paths.

5.3. Loading-unloading behavior

Loading-unloading simulations were conducted in the biaxial compression loading direction to investigate the influence of internal stress components on the plastic strain in each direction according to the crosslinking degree of the TGAP/DETD epoxy as shown in Fig. 10.

First, examining the impact of stress components in the LD, it aligns with the results from Fig. 9, indicating that as the crosslinking degree increases, stress accommodation increases across all components except for the dihedral angle stress. As expected, it is reaffirmed that non-bonded interactions have the most significant contribution to stress determination.

This loading-unloading test provides insight into the factors that determine the progression of plastic strain according to the structural characteristics of epoxy [54]. After plotting the stress difference profiles between the total stress and each stress component, as shown in Supplementary Fig. S11, the plastic strain during unloading (corresponding to stress-free strain) was calculated for each stress component, and these points are also shown in Table 2. In the case of the 55 % crosslinking degree model, when compared to the plastic strain of the total stress ($\epsilon^p = 0.2519$), the plastic strain of the non-bonded stress component is 0.1041, exhibiting the largest decrease (-0.1478). This effect is due to the active rearrangement of free volume, as previously mentioned, leading to greater plastic deformation at a 55 % crosslinking degree, thereby increasing the plastic strain of the total stress. On the other hand, the plastic strains of bond, angle, and dihedral angle components are 0.2605(+0.0086), 0.2525(+0.0006), and 0.2964(+0.0445), respectively, thereby contributing to the reduction of plastic strain of total stress.

In the case of the 85 % crosslinking degree model, the internal stress components that increase the plastic strain of the total stress ($\epsilon^p = 0.1214$) are the non-bonded ($\epsilon^p = 0.0895$) and bond ($\epsilon^p = 0.1200$) stress components, possessing increments of 0.0319 and 0.0014, respectively. While the internal stress component that decreases it is the angle ($\epsilon^p = 0.1274$) and dihedral angle ($\epsilon^p = 0.1292$) stress components. An interesting observation is that the bond stress component, due to the formation of the crosslinked network, transitions to contribute to an increase in the plastic strain. This implies that load transfer within the polymer chains becomes more active owing to the construction of a three-dimensional crosslinked network, thereby increasing the contribution of the bond stress component to the plastic strain of the total stress during unloading.

Therefore, when considering the observed changes in plastic strain of each component with varying crosslinking ratios, the decrease in the plastic strain of the total stress as the crosslinking ratio increases can be attributed to the reduction in the plastic strain of all stress components, with non-bonded stress having a predominant influence. Consequently, as the crosslinking ratio increases, the yield surface at the same plastic strain inevitably expands further. Additionally, since the hardening coefficient of the biaxial yield stress is large, the asymmetry of the yield surface inevitably becomes more pronounced with plastic strain, as shown in Fig. 7(c).

The mechanical response of each stress component in the stress-free FD direction was investigated and presented along with the behavior in the LD direction in Fig. 10. During biaxial compression loading, non-bonded stress accommodates compressive stress (Fig. 10(b)) and shows increased compressive stress with higher crosslinking degrees (Fig. 10(g)). Overall, non-bonded stress accommodates compressive load in all directions, regardless of the axis (LD or FD). This is because, despite the lack of external load in the FD direction, the load applied in the LD direction induces polymer chain rearrangement in the FD direction. However, due to the crosslinked network, the rearrangement is impeded, resulting in compressive non-bonded stress in the FD direction as well. To counterbalance this compressive stress, other bonded stress components exhibit tensile stress in the polymer chains' FD direction (Fig. 10(c-j)). Thus, the stress-free state in the FD direction is determined by the balance between the tensile stress caused by the bonded stress in the LD direction loading and the compressive stress due to the cross-linked network.

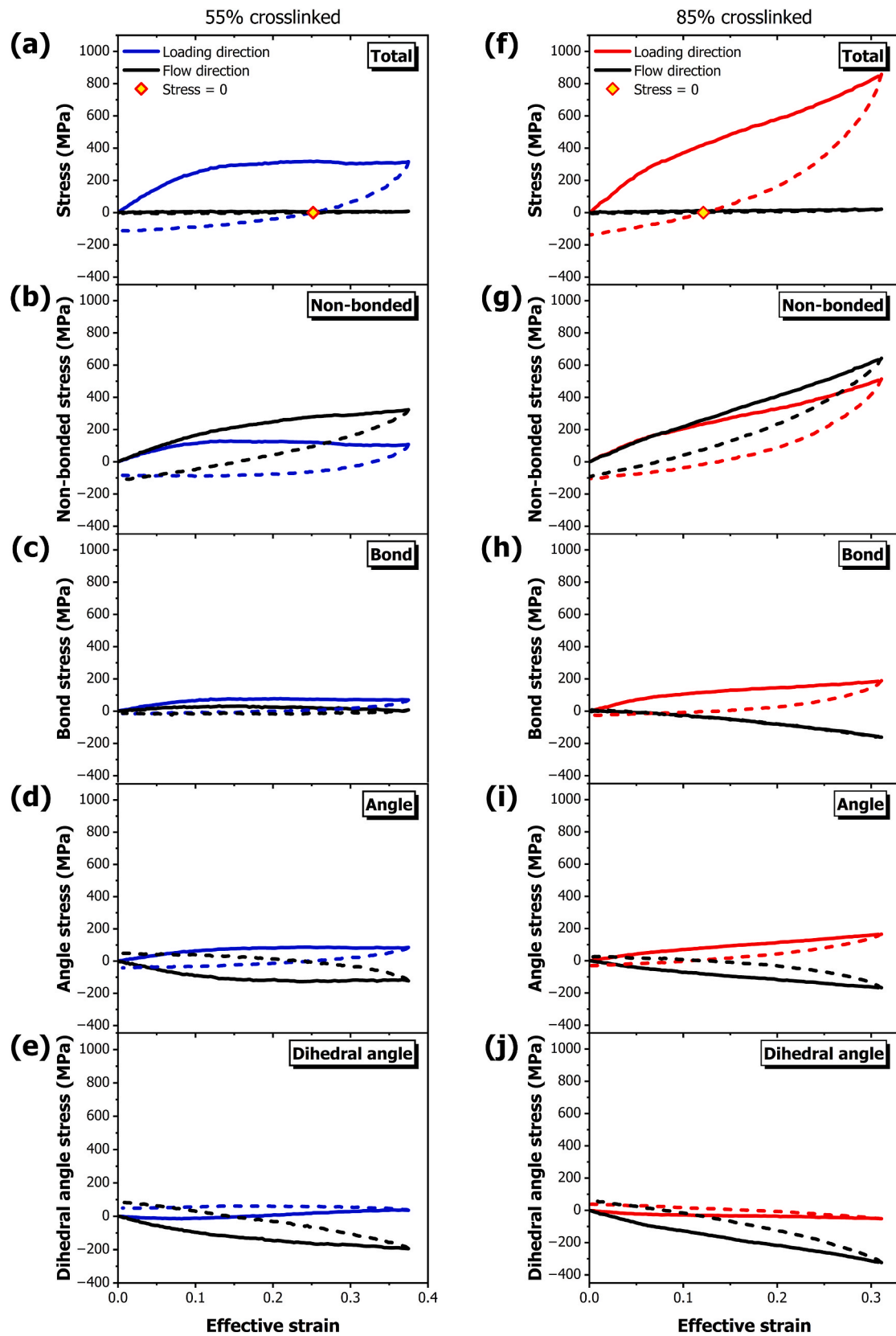


Fig. 10. Stress components responses of biaxial compression loading with different crosslinking degree during loading-unloading simulations: (a-e) represent the low crosslinking (55 %) epoxy model, and (f-j) represent the high crosslinking (85 %) model. (a) and (f) show total stress, (b) and (g) show non-bonded stress, (c) and (h) show bond stress, (d) and (i) show angle stress, and (e) and (j) show dihedral angle stress. The blue (55 %) and red (85 %) solid lines represent stress in the LD direction, while the black solid line represents stress in the FD direction where no load is applied. Each short dashed line indicates unloading behavior. Red diamond markers denote the stress-free state during unloading.

Table 2

Plastic strain (ϵ^p) for total stress – stress components ($\sigma_{\text{total}} - \sigma_{\text{components}}$) for according to crosslinking conversion ratio.

Stress components	55 % crosslinked epoxy		85 % crosslinked epoxy	
	ϵ^p	Deviation	ϵ^p	Deviation
Total	0.2519	0	0.1214	0
Non-bonded	0.1041	−0.1478	0.0895	−0.0319
Bond	0.2605	+0.0086	0.1200	−0.0014
Angle	0.2525	+0.0006	0.1274	+0.0060
Dihedral angle	0.2964	+0.0445	0.1292	+0.0078

5.4. Crosslinked network confinement effects

As discussed in Section 5.3, the confinement effect due to the crosslinking structure in the FD direction inevitably intensifies as the degree of crosslinking increases. As observed in Fig. 9(k), this results in a sharp reduction in free volume at higher crosslinking densities as deformation progresses, leading to higher non-bonded stress. Ultimately, this contributes to the increase in yield stress in the biaxial compression direction, which exacerbates the asymmetry of the yield surface. In other words, the origin of the asymmetric yield surface is the reduced mobility of polymer chains due to crosslinked network confining effects, and this effect is particularly amplified in the direction of biaxial compression loading.

To validate the so-called "crosslinked network confinement effects," we compared strain ratios and stress components under biaxial compression loading (both equibiaxial compression direction and PSC direction). To analyze the extent of chain rearrangement in the FD direction, strain ratios $|\epsilon_{FD}/\epsilon_{LD}|$ as a function of crosslinking degree are illustrated in Fig. 11(a) and (b). MD simulations show that the strain ratio under uniaxial tension and compression decreases slightly as the crosslinking conversion ratio increases (Fig. 11(a)). Furthermore, the strain ratio under equibiaxial compression significantly decreases with increasing crosslinking ratio. This indicates that the strain in the FD direction under biaxial compression loading is highly dependent on crosslinking degree, which is also confirmed by PSC experiments (Fig. 11(a) and (b)). The significant reduction in strain ratio ($|\epsilon_{FD}/\epsilon_{LD}|$) for biaxial compression loading with increased crosslinking degree is attributed to the reduced mobility of polymer chains due to the confinement effects of the crosslinked network.

The involvement of these network confinement effects is better understood through the analysis of stress components in the FD direction (Fig. 11(c)). As observed in Section 5.3, with increasing crosslinking conversion ratio, the contribution of each component to the bonded stress increases. Notably, the bond stress component shows a substantial increase in stress capacity (Fig. 11(c)). This phenomenon occurs because as the crosslinked network becomes denser, the stress generated is due to the increased length of covalent bonds resulting from the direct load transfer between polymer chains, rather than the natural chain

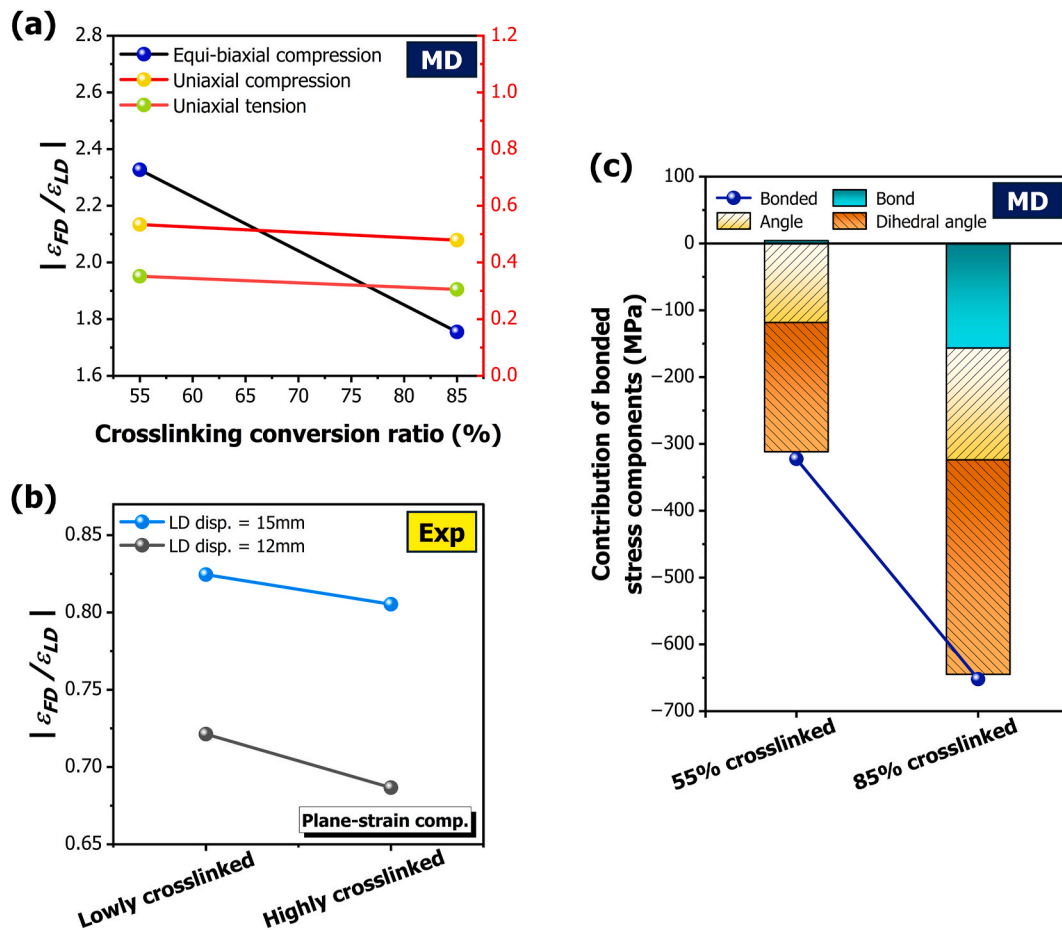


Fig. 11. Comparison of the strain ratio ($|\epsilon_{FD}/\epsilon_{LD}|$) of TGAP/DETDA epoxy according to loading direction and degree of crosslinking, and changes in bonded stress components. (a) Comparison of strain ratio based on loading direction from MD analysis. In (a), the left y-axis represents under equibiaxial compression conditions. The right y-axis, represented by a red solid line, indicates under uniaxial tension and compression conditions. (b) Strain ratio measured through PSC tests. In the PSC test, was derived at two specific displacements of 12 mm and 15 mm in the loading direction. (c) Changes in the contribution of bonded stress components according to crosslinking degree in the flow direction after equibiaxial compression deformation. The contribution of each stress component is represented by the stress at the final effective strain.

alignment and slip behavior in the FD direction.

The deformation mechanisms are illustrated in Fig. 12. For epoxies with low crosslinking degree, the crosslinking network is relatively sparse allowing for freer molecular movement, which results in flexible chain motion and high free volume fluidity. Consequently, such network

structure cannot accommodate high biaxial compression stresses and exhibits significant deformation in the FD direction. In contrast, epoxy materials with high crosslinking degree develop a highly crosslinked network structure that restricts the mobility of polymer chains, reducing deformation in the FD direction and leading to a direct decrease in free

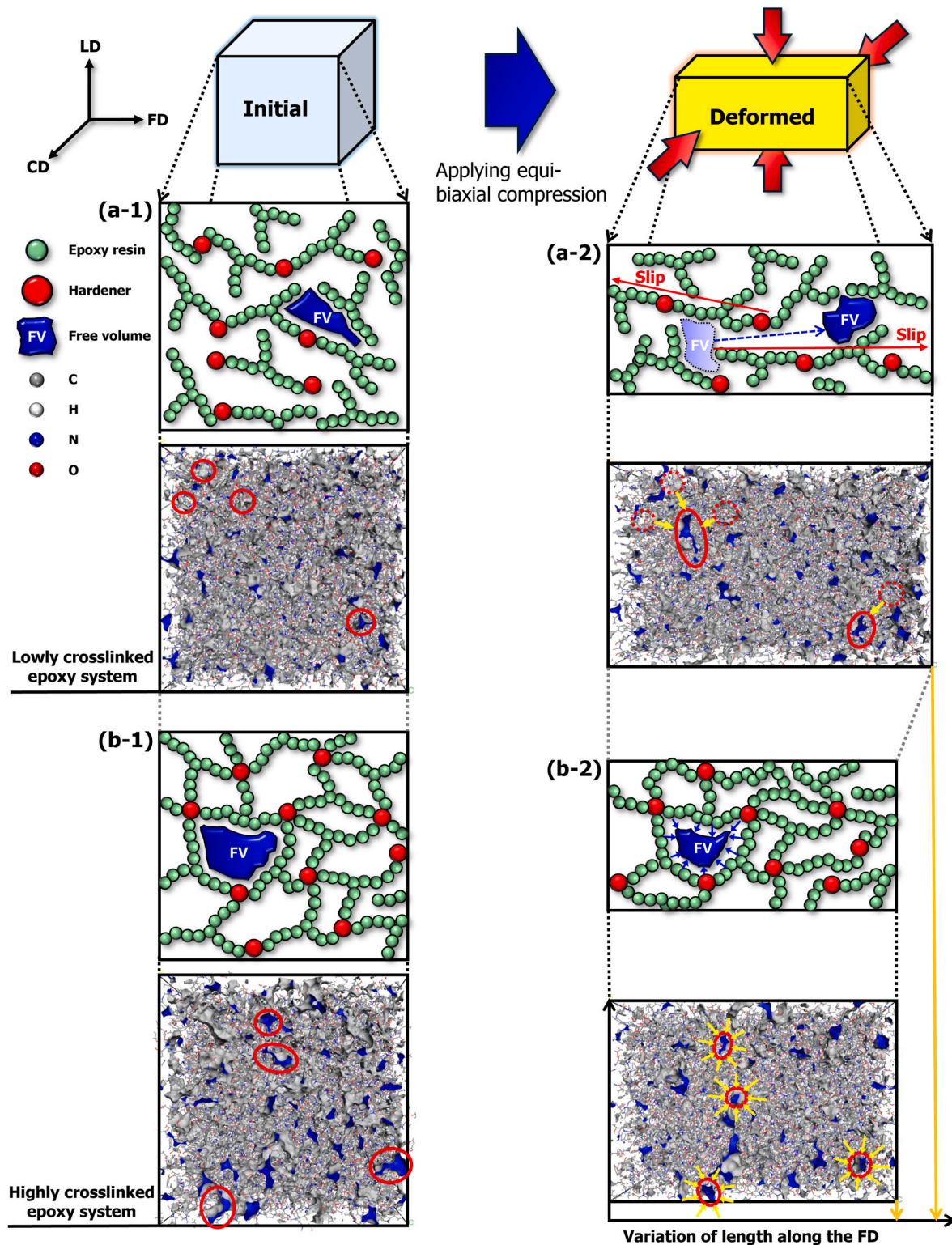


Fig. 12. Schematic and MD model snapshots of the different deformation mechanisms of TGAP/DETDA epoxy polymer material according to degree of crosslinking under equibiaxial compression loading: (a-1) an initial epoxy system with relatively low crosslinking degree, (b-1) an initial epoxy system with comparatively high crosslinking degree, (a-2), and (b-2) molecular structural changes in the epoxy depending on the degree of crosslinking after deformation. It can be observed that the length changes in the flow direction due to the structural changes (crosslinking degree) of the epoxy polymer material differ from each other.

volume. From a mechanical perspective, this reduction in chain mobility and free volume significantly strengthen the capacity to accommodate non-bonded stress, which fundamentally contributes to the asymmetric yield stress.

6. Conclusion

This study elucidates the molecular-scale origins of yield surface asymmetry in crosslinked polymer materials through a combination of MD simulations, polymer synthesis, and mechanical testing. We found that increasing the degree of crosslinking leads to an expansion of the asymmetric yield surface, which is directly linked to the load-direction dependence of deformation mechanisms. The asymmetry of the yield surface is predominantly driven by a sharp increase in stress in the biaxial compression direction, a phenomenon that intensifies with higher degrees of crosslinking and advancing plastic strain. The underlying molecular mechanism for this asymmetric expansion was identified as the rapid evolution of non-bonded stress resulting from the network confinement effect of the three-dimensional crosslinked structure. This influence on yield surface asymmetry is further evidenced by the degree of chain rearrangement in the flow direction during biaxial compression. Our research provides fundamental insights into the relationship between the microstructure of epoxy polymers and their multiaxial mechanical properties, which has importance for constructing accurate yield functions for polymers and polymer composites. This work holds significant implications for the future integration of data-driven constitutive modeling in the design and analysis of polymeric materials.

Future research should focus on continuous efforts to characterize the multiaxial yield responses of polymers and establish yield functions. Considering the limitations of the current study, two important issues of focus emerge. One is the in-depth understanding of multiaxial yielding in polymers, with a systematic investigation of the effects of time and temperature. Since polymers exhibit viscoelasto-plastic deformation behaviors, their yield surfaces are largely influenced by the deformation environment. Generalizing multiaxial yielding under varying time and temperature conditions is essential to account for diverse deformation scenarios. Another crucial issue is the development of advanced techniques for multiaxial stress measurements to bridge the gap between MD simulations and experimental results. This includes the need for improved MD methods capable of effectively evaluating stress behaviors under quasi-static conditions, as well as comprehensive experimental characterizations, particularly for biaxial compression loading paths. Such efforts are vital for a more accurate and complete understanding of multiaxial yield responses in polymers.

CRediT authorship contribution statement

Jinyoung Kim: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Kyeongmin Hong:** Methodology. **Yong-Seok Choi:** Methodology. **Dayoung Jang:** Methodology. **Jang-Woo Han:** Methodology. **Hyunbum Park:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No.

2022R1F1A1073774). Additionally, this work was supported by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIT) (CRC23012-000)

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2025.108710>.

Data availability

Data will be made available on request.

References

- [1] E. Morel, V. Bellenger, M. Bocquet, J. Verdu, Structure-properties relationships for densely cross-linked epoxide-amine systems based on epoxide or amine mixtures: Part 3 Elastic properties, *J. Mater. Sci.* 24 (1989) 69–75.
- [2] B. Ellis, M.S. Found, J.R. Bell, Influence of cure treatment on extent of reaction and glassy modulus for BADGE-DDM epoxy resin, *J. Appl. Polym. Sci.* 82 (2001) 1265–1276.
- [3] M.J. Marks, R.V. Snelgrove, Effect of conversion on the Structure–Property relationships of amine-cured epoxy thermosets, *ACS Appl. Mater. Interfaces* 1 (2009) 921–926.
- [4] J. Huang, P. Fu, W. Li, L. Xiao, J. Chen, X. Nie, Influence of crosslinking density on the mechanical and thermal properties of plant oil-based epoxy resin, *RSC Adv.* 12 (2022) 23048–23056.
- [5] Y. Zhao, G. Kikugawa, Y. Kawagoe, K. Shirasu, T. Okabe, Molecular-scale investigation on relationship between thermal conductivity and the structure of crosslinked epoxy resin, *Int. J. Heat Mass Tran.* 198 (2022) 123429.
- [6] H.B. Fan, M.M. Yuen, Material properties of the cross-linked epoxy resin compound predicted by molecular dynamics simulation, *Polymer* 48 (2007) 2174–2178.
- [7] V. Varshney, S.S. Patnaik, A.K. Roy, B.L. Farmer, A molecular dynamics study of epoxy-based networks: cross-linking procedure and prediction of molecular and material properties, *Macromolecules* 41 (2008) 6837–6842.
- [8] C. Li, A. Strachan, Molecular simulations of crosslinking process of thermosetting polymers, *Polymer* 51 (2010) 6058–6070.
- [9] C. Li, A. Strachan, Molecular dynamics predictions of thermal and mechanical properties of thermoset polymer EPON862/DETDA, *Polymer* 52 (2011) 2920–2928.
- [10] N.B. Shenogina, M. Tsige, S.S. Patnaik, S.M. Mukhopadhyay, Molecular modeling approach to prediction of thermo-mechanical behavior of thermoset polymer networks, *Macromolecules* 45 (2012) 5307–5315.
- [11] S. Yang, J. Qu, Computing thermomechanical properties of crosslinked epoxy by molecular dynamic simulations, *Polymer* 53 (2012) 4806–4817.
- [12] B. Kim, J. Choi, S. Yang, S. Yu, M. Cho, Influence of crosslink density on the interfacial characteristics of epoxy nanocomposites, *Polymer* 60 (2015) 186–197.
- [13] C. Li, A. Strachan, Molecular scale simulations on thermoset polymers: a review, *J. Polym. Sci. B Polym. Phys.* 53 (2015) 103–122.
- [14] Y. Fu, J.G. Michopoulos, J.-H. Song, On investigating the thermomechanical properties of cross-linked epoxy via molecular dynamics analysis, *Nanoscale Microscale Thermophys. Eng.* 21 (2017) 8–25.
- [15] J. Fan, A. Anastassiou, C.W. Macosko, E.B. Tadmor, Molecular dynamics predictions of thermomechanical properties of an epoxy thermosetting polymer, *Polymer* 196 (2020) 122477.
- [16] X. Wu, A. Aramoon, J.A. El-Awady, Hierarchical multiscale approach for modeling the deformation and failure of epoxy-based polymer matrix composites, *J. Phys. Chem. B* 124 (2020) 11928–11938.
- [17] A. Shokuhfar, B. Arab, The effect of cross linking density on the mechanical properties and structure of the epoxy polymers: molecular dynamics simulation, *J. Mol. Model.* 19 (2013) 3719–3731.
- [18] S. Masoumi, B. Arab, H. Valipour, A study of thermo-mechanical properties of the cross-linked epoxy: an atomistic simulation, *Polymer* 70 (2015) 351–360.
- [19] A. Bandyopadhyay, P.K. Valavala, T.C. Clancy, K.E. Wise, G.M. Odegard, Molecular modeling of crosslinked epoxy polymers: the effect of crosslink density on thermomechanical properties, *Polymer* 52 (2011) 2445–2452.
- [20] Y. Liu, Z. Tang, J. Chen, J. Xiong, D. Wang, S. Wang, et al., Tuning the mechanical and dynamic properties of imine bond crosslinked elastomeric vitrimers by manipulating the crosslinking degree, *Polym. Chem.* 11 (2020) 1348–1355.
- [21] X. Wan, B. Demir, M. An, T.R. Walsh, N. Yang, Thermal conductivities and mechanical properties of epoxy resin as a function of the degree of cross-linking, *Int. J. Heat Mass Tran.* 180 (2021) 121821.
- [22] D. Mears, K. Pae, J. Sauer, Effects of hydrostatic pressure on the mechanical behavior of polyethylene and polypropylene, *J. Appl. Phys.* 40 (1969) 4229–4237.
- [23] I.M. Ward, The yield behaviour of polymers, *J. Mater. Sci.* 6 (1971) 1397–1417.
- [24] R. Quinson, J. Perez, M. Rink, A. Pavan, Yield criteria for amorphous glassy polymers, *J. Mater. Sci.* 32 (1997) 1371–1379.
- [25] E. Ghorbel, A viscoplastic constitutive model for polymeric materials, *Int. J. Plast.* 24 (2008) 2032–2058.
- [26] H. Park, M. Cho, A multiscale framework for the elasto-plastic constitutive equations of crosslinked epoxy polymers considering the effects of temperature,

- strain rate, hydrostatic pressure, and crosslinking density, *J. Mech. Phys. Solid.* 142 (2020) 103962.
- [27] H. Park, J.-W. Han, W. Na, J. Yu, Characterizing the biaxial compressive deformation behavior of epoxy polymer through cruciform experiment and finite element analysis, *Compos. Struct.* 305 (2023) 116488.
- [28] H. Park, M. Cho, Multiscale constitutive model using data-driven yield function, *Compos. B Eng.* 216 (2021) 108831.
- [29] J. Rottler, M.O. Robbins, Yield conditions for deformation of amorphous polymer glasses, *Phys. Rev.* 64 (2001) 051801.
- [30] K. Hachour, F. Zaïri, M. Nait-Abdelaziz, J.-M. Gloaguen, M. Aberkane, J.-M. Lefebvre, Experiments and modeling of high-crystalline polyethylene yielding under different stress states, *Int. J. Plast.* 54 (2014) 1–18.
- [31] N. Tschoegl, Failure surfaces in principal stress space, in: *Journal of Polymer Science Part C: Polymer Symposia*, Wiley Online Library, 1971, pp. 239–267, 32.
- [32] S. Kubo, T. Kuwabara, T. Sumiyama, T. Kobayashi, K. Furuichi, C. Nonomura, Measurement and analysis of deformation behavior of thermoplastic elastomer tube subjected to biaxial tensile stress under loading and unloading, *Int. J. Material Form.* 16 (2023) 27.
- [33] V. Bonnard, J. Chaboche, P. Gomez, P. Kanouté, D. Pacou, Investigation of multiaxial fatigue in the context of turboengine disc applications, *Int. J. Fatig.* 33 (2011) 1006–1016.
- [34] L. Alfonso, C. Badulescu, N. Carrère, Use of the modified Arcan fixture to study the strength of bonded assemblies for automotive applications, *Int. J. Adhesion Adhes.* 80 (2018) 104–114.
- [35] M. Arcan, Z.a. Hashin, A. Voloshin, A method to produce uniform plane-stress states with applications to fiber-reinforced materials: a specially designed specimen yields material properties under pure shear or uniform plane-stress conditions, *Exp. Mech.* 18 (1978) 141–146.
- [36] M. Upadhyay, T. Panzner, S. Van Petegem, H. Van Swygenhoven, Stresses and strains in cruciform samples deformed in tension, *Exp. Mech.* 57 (2017) 905–920.
- [37] M. Shafiq, R.S. Ayyagari, M. Ehaab, M. Vural, Multiaxial yield surface of transversely isotropic foams: Part II—experimental, *J. Mech. Phys. Solid.* 76 (2015) 224–236.
- [38] H. Sun, Force field for computation of conformational energies, structures, and vibrational frequencies of aromatic polyesters, *J. Comput. Chem.* 15 (1994) 752–768.
- [39] H. Sun, S.J. Mumby, J.R. Maple, A.T. Hagler, An ab initio CFF93 all-atom force field for polycarbonates, *J. Am. Chem. Soc.* 116 (1994) 2978–2987.
- [40] R.W. Hockney, J.W. Eastwood, *Computer Simulation Using Particles*, crc Press, 2021.
- [41] D.R. Heine, G.S. Grest, C.D. Lorenz, M. Tsige, M.J. Stevens, Atomistic simulations of end-linked poly (dimethylsiloxane) networks: structure and relaxation, *Macromolecules* 37 (2004) 3857–3864.
- [42] N. Vu-Bac, P. Areias, T. Rabczuk, A multiscale multisurface constitutive model for the thermo-plastic behavior of polyethylene, *Polymer* 105 (2016) 327–338.
- [43] M. Dusi, R. Galeos, M. Maximovich, Physiorheological characterization of a carbon/epoxy prepreg system, *J. Appl. Polym. Sci.* 30 (1985) 1847–1857.
- [44] J. Moranco, J. Salla, Relaxation in partially cured samples of an epoxy resin and of the same resin modified with a carboxyl-terminated rubber, *Polymer* 40 (1999) 2821–2828.
- [45] C.L. Lee, K.H. Wei, Curing kinetics and viscosity change of a two-part epoxy resin during mold filling in resin-transfer molding process, *J. Appl. Polym. Sci.* 77 (2000) 2139–2148.
- [46] S. Li, E. Vuorimaa, H. Lemmetyinen, Application of isothermal and model-free isoconversional modes in DSC measurement for the curing process of the PU system, *J. Appl. Polym. Sci.* 81 (2001) 1474–1480.
- [47] Z. Bartczak, Influence of molecular parameters on high-strain deformation of polyethylene in the plane-strain compression. Part II. Strain recovery, *Polymer* 46 (2005) 10339–10354.
- [48] D. Samios, S. Tokumoto, E.L. Denardin, Investigation of the large plastic deformation of iPP induced by plane strain compression: stress-strain behavior and thermo-mechanical properties, *Int. J. Plast.* 22 (2006) 1924–1942.
- [49] E. Abreu, H. Ngo, A. Bellare, Characterization of network parameters for UHMWPE by plane strain compression, *J. Mech. Behav. Biomed. Mater.* 32 (2014) 1–7.
- [50] C. Li, A. Strachan, Free volume evolution in the process of epoxy curing and its effect on mechanical properties, *Polymer* 97 (2016) 456–464.
- [51] V. Gupta, C. Brahatheeswaran, Molecular packing and free volume in crosslinked epoxy networks, *Polymer* 32 (1991) 1875–1884.
- [52] A. Shundo, S. Yamamoto, K. Tanaka, Network formation and physical properties of epoxy resins for future practical applications, *Jacs Au* 2 (2022) 1522–1542.
- [53] S. Yu, S. Yang, M. Cho, Analysis of thermal conductivity of polymeric nanocomposites under mechanical loading, *J. Appl. Phys.* 114 (2013).
- [54] H. Park, I. Chung, M. Cho, Effect of molecular structure of curing agents on cyclic creep in highly cross-linked epoxy polymers, *J. Polym. Sci.* 58 (2020) 1617–1631.