Electronic Supporting Information (ESI†) for

Effect of epoxy monomer structure on the curing process and thermo-mechanical characteristics of tri-functional epoxy/amine systems: A methodology combined atomistic molecular simulation with experimental analyses

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1. Simulation details

1.1 Cross-linking simulation method

The flow chart of the cross-linking simulation procedure is shown in **Figure S1**.

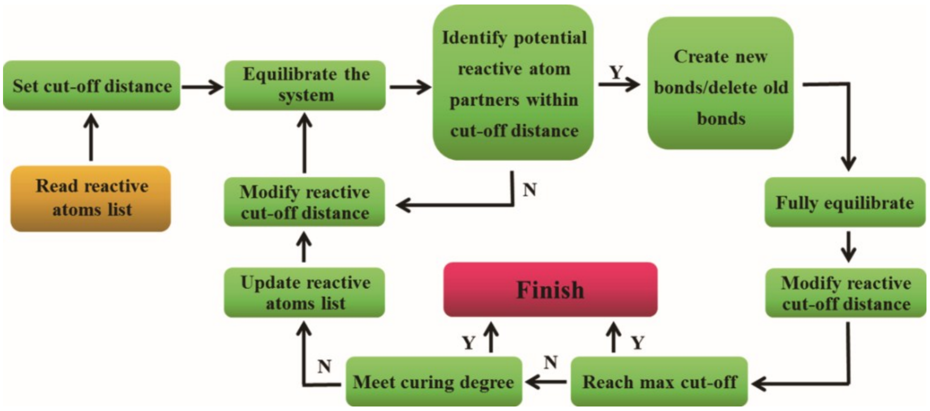


Fig. S1 Schematic of the multi-step cross-linking procedure in atomistic MD simulation.

1.2 Mulliken population analysis

Mulliken population analysis was one of the most common types of charge and bond order analysis by means of the density functional theory (DFT) electronic structure program DMol^3 calculation. It provided a means of estimating partial atomic charges by using the methods of computational chemistry. First, a density matrix must be defined, or as it sometimes was called, a charge-density bond-order matrix. If Φ was a molecular orbital, $and\ C_{i\mu}$ were the self-consistent field (SCF) expansion coefficients, then **(Eq. S1)**:

$$P_{\mu v} = \sum C_{i\mu} C_{iv} \tag{S1}$$

The matrix $P_{\mu v}$ and a set of atomic orbitals completely can specify the charge density. The trace of matrix P and the overlap S were equal to the total number of electrons in the molecule **(Eq. S2)**:

$$N = Tr\ PS = \sum_{\mu} (PS)_{\mu} \tag{S2}$$

summing $(PS)_{\mu v}$ contribution over all μ∈A, v∈B, where A and B were centers, P_{AB} can be obtained, which can be interpreted as the number of electrons associated with the bond A-B. This was the so called Mulliken population analysis. The net charge associated with the atom was then given by **Eq. S3**:

$$q_A = Z_A - \sum_{\mu A} (PS)_{\mu\mu} \tag{S3}$$

where Z_A was the charge on the atomic nucleus A. The quality was set to medium, the functional to GGA (generalized gradient approximation) and BLYP. In the electronic tab, we set the basis set to DNP (double numerical plus polarization).

1.3 Local structure analysis and cohesive energy density

The torsional angles of chemical bonds were investigated by the grid scan method. When a specific torsional angle was changed over a grid, the potential energy was calculated.

Radial distribution function (RDF) analysis reflected the local structure evolution and stacking mode of the cross-linked network. RDF was used to describe the probability of finding species α and β separated by a distance r in the local structure during the curing process, which was calculated as **Eq.S4**:

$$g_{\alpha\beta}(r) = \frac{n_{\alpha\beta}(r)}{4\pi r^2 dr\left(N_\alpha N_\beta / V\right)} \tag{S4}$$

where N_α and N_β were the number of species of type α and β, V was the system volume. $n_{\alpha\beta}$ (r) represented the number of α-β pairs within the range of (r $-\Delta$r/2, r $+\Delta$r/2).

The accessible free volume of the cross-linked systems was obtained utilizing the "Atom Volume & Surfaces" tool. First, the theoretical van der Waals volume (V_w) was calculated to obtain the occupied volume. Meanwhile, the specific volume (V_s) could be estimated through dividing the molecular weight of the repeat unit by the bulk density of the membrane, which was measured using the buoyancy method.

The cohesive energy density (CED) was equal to the square of the solubility parameter, which reflected the interactions between mixture systems. The cohesive energy (E_{coh}) was defined as the increment in energy per mole of the system if all intermolecular forces were removed. And the cohesive energy can be calculated by the follow **Eq. S5**:

$$E_{coh} = \langle E_{inter} \rangle = \langle E_{total} \rangle - \langle E_{intra} \rangle \qquad \text{(S5)}$$

where E_{total} represented the total number of the system, E_{inter} represented the total energy between all molecules, E_{intra} represented the intramolecular energy, and the bracket represented an average over a NVT or NPT ensemble.

1.4 The glass transition temperature

The glass transition was a unique dynamic phenomenon for amorphous polymers and it was demonstrated with strongly heterogeneous character in experiments and simulations. In the simulation part, the glass transition temperature (T_g) was obtained from the specific volume-temperature relationship during the cooling process and each value was averaged from three independent models.

2. Simulation setting of curing degree

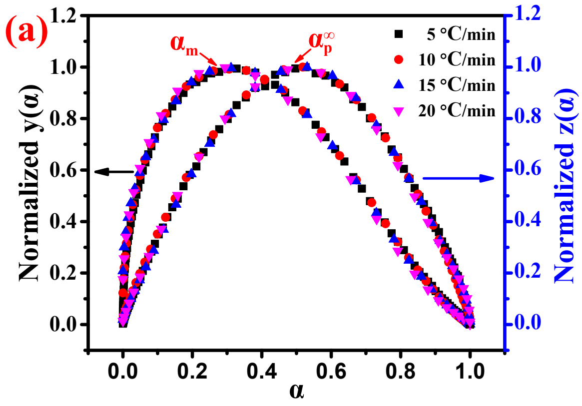
Table S1 The curing degree setting details of the two simulation models (TDE-85/DDS system and AFG-90/DDS system)

System	Component	Number	Number of unreactive epoxy groups	Curing degree (%)
TDE-85/DDS	TDE-85 DDS	128 96	27	93.0

AFG-90/DDS	AFG-90	128	30	92.2
	DDS	96		

In our simulation setting, the curing degree of epoxy/amine systems was manually controlled around 90 %, and the value was calculated according to the number of unreactive epoxy groups (**Table S1**). Therefore, it was credible and convincing to compare the obtained simulation value with the experiment one. The similar curing degree ruled out its disturbance to the comparison of the final performance between Diglycidyl ester of aliphatic cyclo (TDE-85) / 4, 4'-diamino diphenyl sulfone (DDS) system and N, N-diglycidyl-4-Glycidyloxyaniline (AFG-90) /DDS system.

3. Málek method analysis



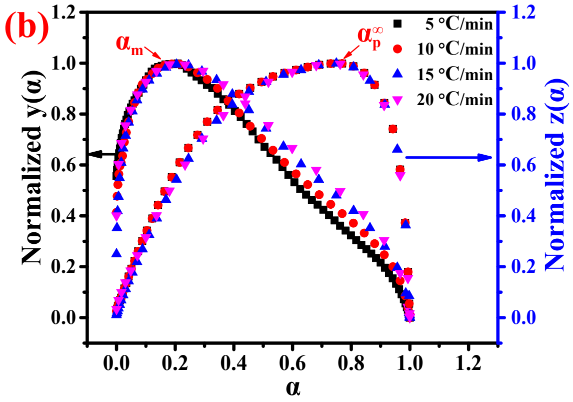


Fig. S2 Plots of normalized y (α) and z (α) against α of (a) TDE-85/DDS system and (b) AFG-90/DDS system.

The function curves of y (α), z (α), which were normalized in order to simplify, could be constructed as shown in **Figure S2**.

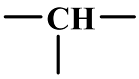
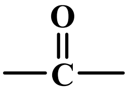
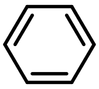
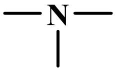
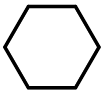
Table S2 Kinetic parameters for non-isothermal DSC analysis of TDE-85/DDS system and AFG-90/DDS system with multiple heating rates of 5, 10, 15 and 20 °C /min

The constant kinetic parameters n, m, and lnA were determined, and their average values were listed in **Table S2**.

System	β (°C/min)	α_p	α_m	α_p^∞	p	m	n	lnA
TDE-85/DDS	5	0.482	0.292	0.521	0.412	0.544	1.321	11.37
	10	0.491	0.299	0.525	0.427	0.584	1.370	11.35
	15	0.484	0.293	0.529	0.414	0.555	1.343	11.39
	20	0.487	0.297	0.523	0.422	0.591	1.404	11.31
	mean	0.486	0.295	0.524	0.419	0.569	1.362	11.35
AFG-90/DDS	5	0.680	0.190	0.750	0.235	0.173	0.737	10.44
	10	0.671	0.188	0.754	0.232	0.171	0.735	10.34
	15	0.673	0.192	0.758	0.238	0.177	0.742	10.43
	20	0.677	0.182	0.753	0.222	0.164	0.740	10.48
	mean	0.675	0.188	0.754	0.232	0.171	0.739	10.42

4. Cohesive energy density calculated by group contribution

Table S3 Calculated cohesive energy density (CED) of selected chemical groups. The values were obtained through group contribution calculations using data presented by Van Krevelen[1]

Structure	CED calculated using the cohesive energy values of Fedors (J/mol)
$-CH_2-$	4940
 $-\underset{\vert}{CH}-$	3430
$-NH-$	8370
$-OH$	29800
 $-\overset{O}{\overset{\Vert}{C}}-$	17370
	31940
 $-\underset{\vert}{N}-$	4190
$-O-$	3350
	1050

Cohesive energy density (CED) values of selected chemical groups, which can be used to measure the specific group contribution, were presented by Van Krevelen[1] in **Table S3**.

References

1. Krevelen, D. W. V.; Nijenhuis, K. T. Cohesive Properties and Solubility - Properties of Polymers (Fourth Edition) - Chapter 7. *Properties of Polymers* **2009,** (1), 189–227.

Figure captions

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Table captions

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