Electronic Supplementary Information

Molecular Picture of Curing and Incomplete Cross-Linking of Epoxy at a Solid Interface

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1. Density profile of epoxy and amine compounds

Fig. S1(a) shows the density profiles of DGEBA and DDM as a function of distance from the substrate. Similar to the overall density trend in Fig. 2(b), both densities increased near 0.8 nm at the outermost interface on the substrate side and then leveled off in the bulk region. A slight increase in DDM density and a corresponding decrease in DGEBA density were also observed around 9 nm in the surface region.

Fig. S1(b) shows the molar ratio of DGEBA to DDM versus distance from the substrate. In the bulk region, the molar ratio matched the stoichiometric ratio of 2. However, within 1 nm of the interface, it was lower than 2, indicating a local excess of DDM. This amine segregation, driven by their smaller molecular size, is consistent with previous simulations and in experiments. Beyond 9 nm, the molar ratio was again slightly below 2, reflecting higher mobility of the smaller amine molecules.
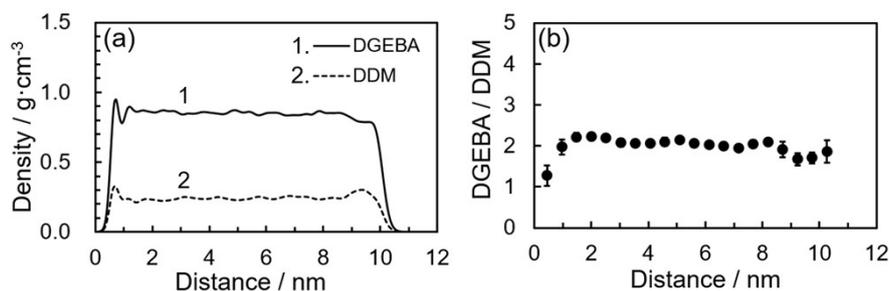

Fig. S1. (a) Density profiles of DGEBA and DDM, and (b) molar ratio of DGEBA to DDM, as a function of distance from the substrate.

2. Relationship between reaction time and initial molecular orientation

2.1 Outermost interface on the substrate side.

Table S1 summarizes the average reaction time, with the initial vectors $\mathbf{v}_1$-$\mathbf{v}_3$ classified into 10° intervals. Regions with fewer than two data points were excluded from the analysis. For DGEBA, no remarkable dependence of reaction rate on orientation angle was observed. In contrast, for DDM, the reaction time was delayed when $\mathbf{v}_1$ was 50–60° and $\mathbf{v}_2$ was 30–40°, corresponding to cases where the molecular principal axis and the phenyl groups were not

strongly oriented parallel to the substrate.

Table S1. Relationship between the reaction time and the initial molecular orientation at the outermost interface on the substrate side.

Angle / deg.	Time / ns					
	DGEBA			DDM		
	v_1	v_2	v_3	v_1	v_2	v_3
0 – 10			0.36 ± 0.43			0.73 ± 0.39
10 – 20			0.86 ± 0.89			0.82 ± 0.30
20 – 30			0.14 ± 0.27			0.38 ± 0.10
30 – 40			0.36 ± 0.57		2.70 ± 1.24	0.54 ± 0.14
40 – 50	0.30 ± 0.28		0.64 ± 0.45		0.24 ± 0.14	0.74 ± 0.20
50 – 60	0.19 ± 0.17	0.35 ± 0.22	0.61 ± 0.45	2.11 ± 0.55	0.87 ± 0.38	1.49 ± 0.60
60 – 70	0.58 ± 0.37	0.28 ± 0.11		0.64 ± 0.32	0.84 ± 0.21	0.43 ± 0.18
70 – 80	0.21 ± 0.13	0.55 ± 0.20		0.63 ± 0.29	0.71 ± 0.21	0.82 ± 0.73
80 – 90	0.49 ± 0.09	0.46 ± 0.10		0.65 ± 0.10	0.42 ± 0.09	

2.2 Bulk region.

Fig. S2 shows the relationship between reaction time and the initial orientation angles of v_1, v_2 and v_3 in the bulk region, approximately 5 nm from the substrate. For all vectors, the orientation angles exhibited a broader distribution than those at the outermost interface on the substrate side.
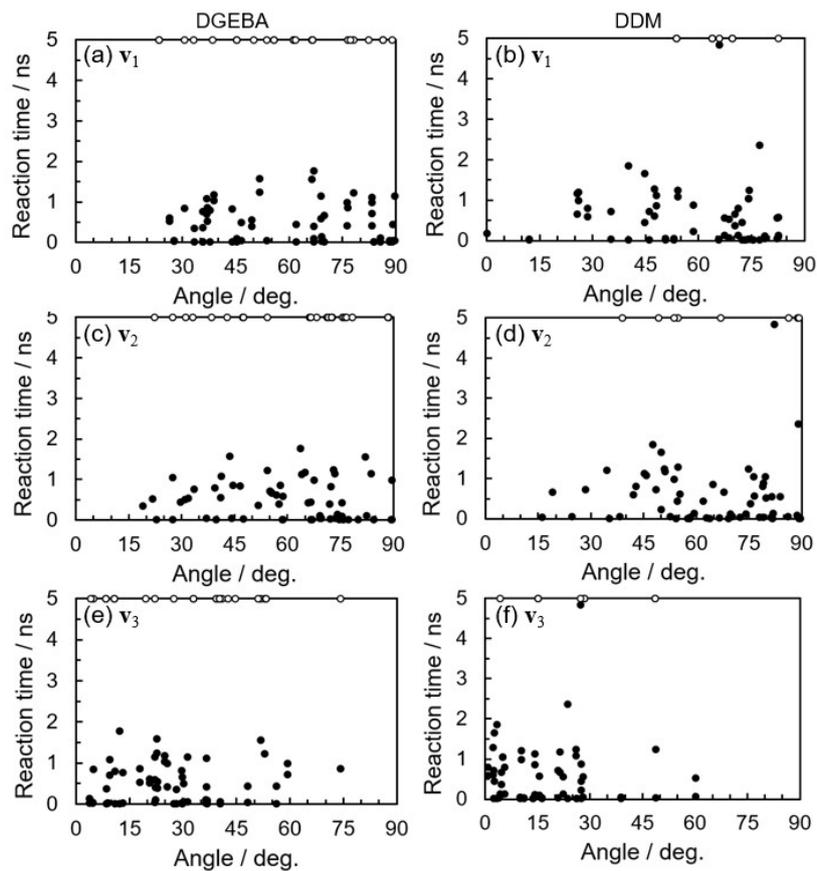
Fig. S2. Relationship between reaction time and initial orientation angle for molecules in the bulk region, approximately 5 nm from the interface: (a, b) $\mathbf{v}_1$, (c, d) $\mathbf{v}_2$, and (e, f) $\mathbf{v}_3$ for DGEBA and DDM, respectively. White symbols at 5 ns represent molecules that did not react.