Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A ReaxFF Molecular Dynamics Study of Molecular-Level Interactions During Binder Jetting 3D-Printing

Supplementary Information

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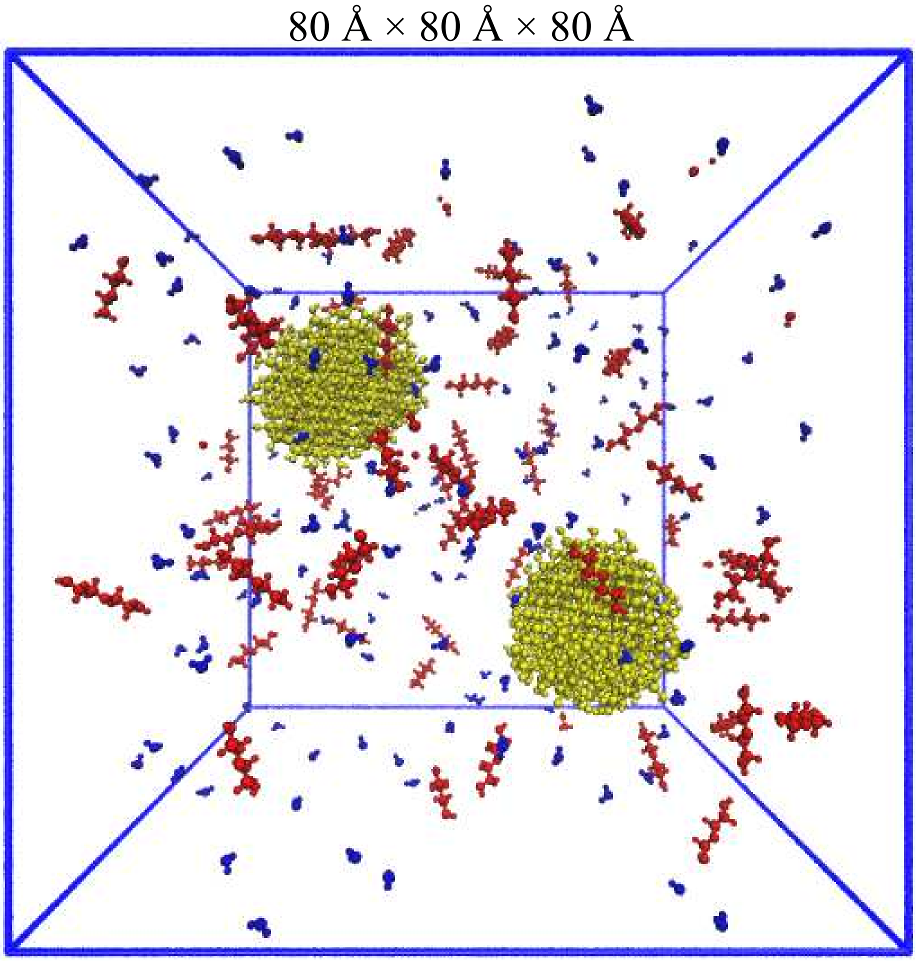


Fig. S1: The random distribution of water, DEG, and Cr-oxide nanoparticles before MD simulations. The Cr-oxide, water, and DEG molecules are shown in yellow, blue, and red, respectively. None of the molecules inside the simulation cell is fixed. If the free boundary condition is applied in this system, molecules that fly outside the simulation cell are removed. In this scenario, the number of water and DEG molecules cannot be controlled. In contrast, the periodic boundary translates back the molecules that cross the boundary back into the cell, which prevents the system from losing any molecules at the print stage.

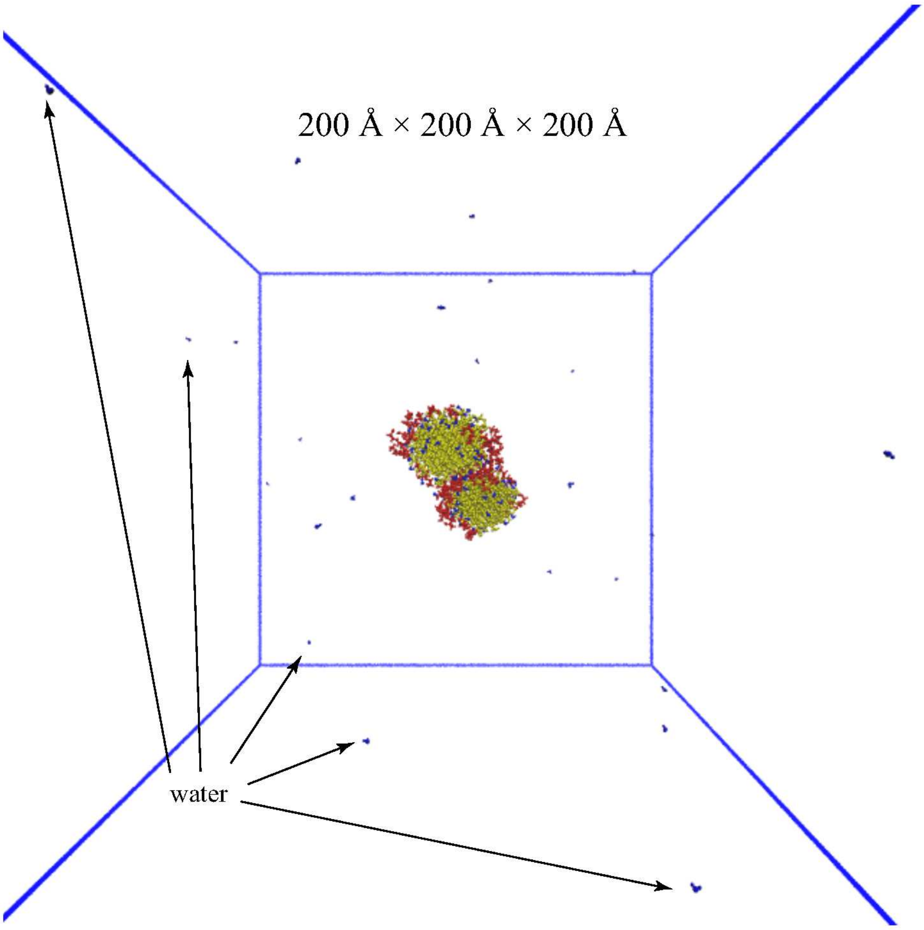
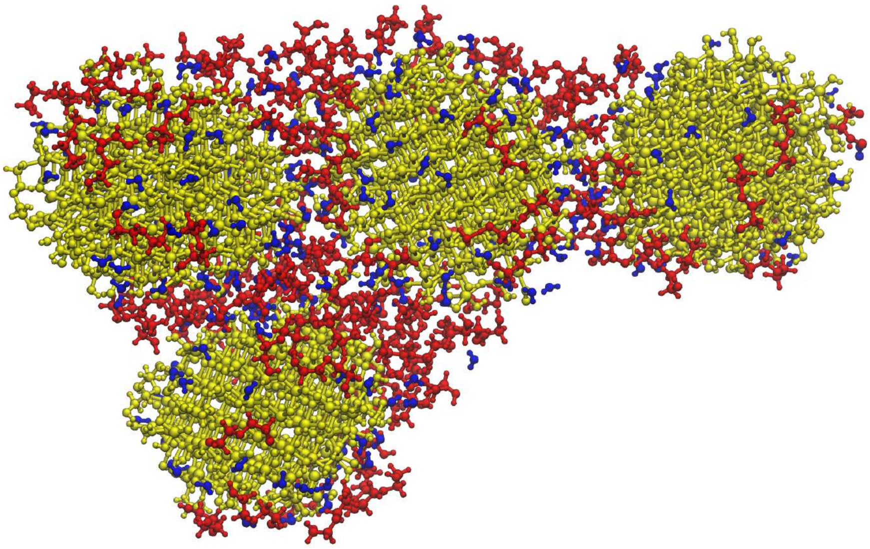
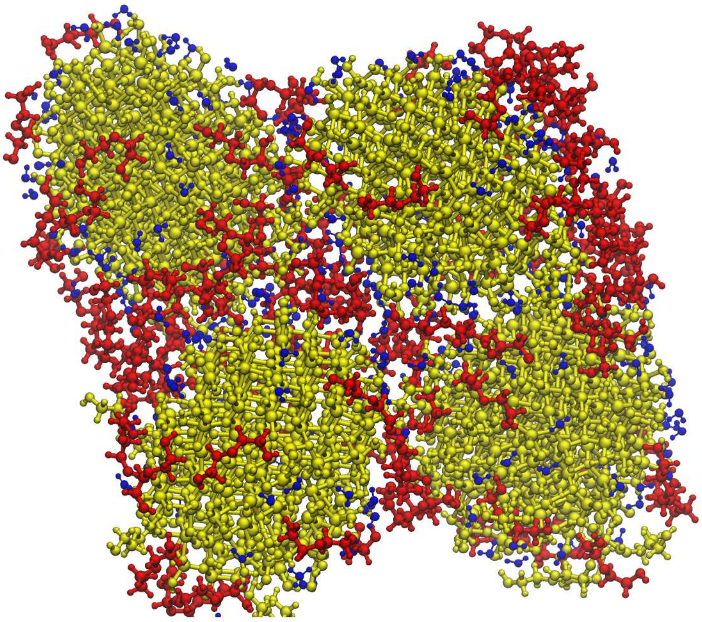


Fig. S2: A snapshot of the 200 Å × 200 Å × 200 Å simulation system during curing. The Cr-oxide, water, and DEG molecules are shown in yellow, blue, and red, respectively. The evaporated water during curing dissociate from the Cr-oxide nanoparticles or the network and fly away. Our in-house ReaxFF solver in principle treats every system as periodic. It simulates a non-periodic cell by setting a very large cell parameter. In our present work, a 200 Å × 200 Å × 200 Å cell was used. Although the cell is large, the periodic boundary keeps evaporated water molecules inside the cell. Therefore, we artificially remove the evaporated water molecules after curing.

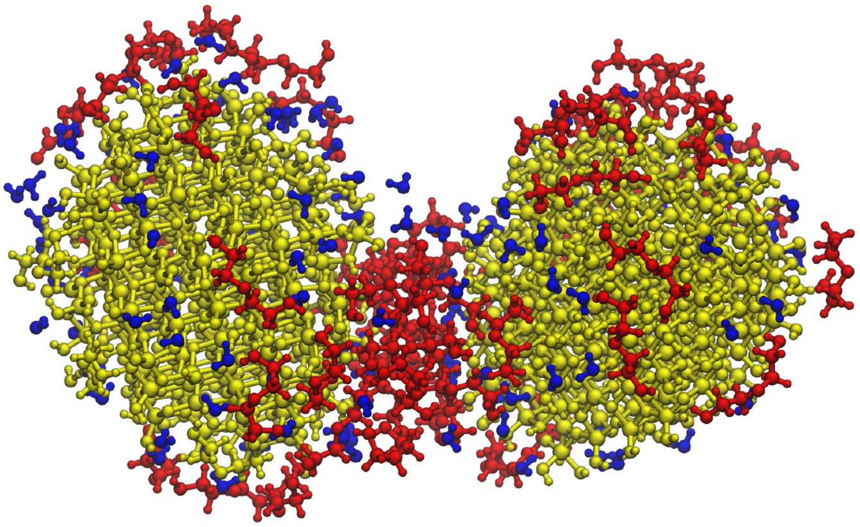


(a) Chain configuration

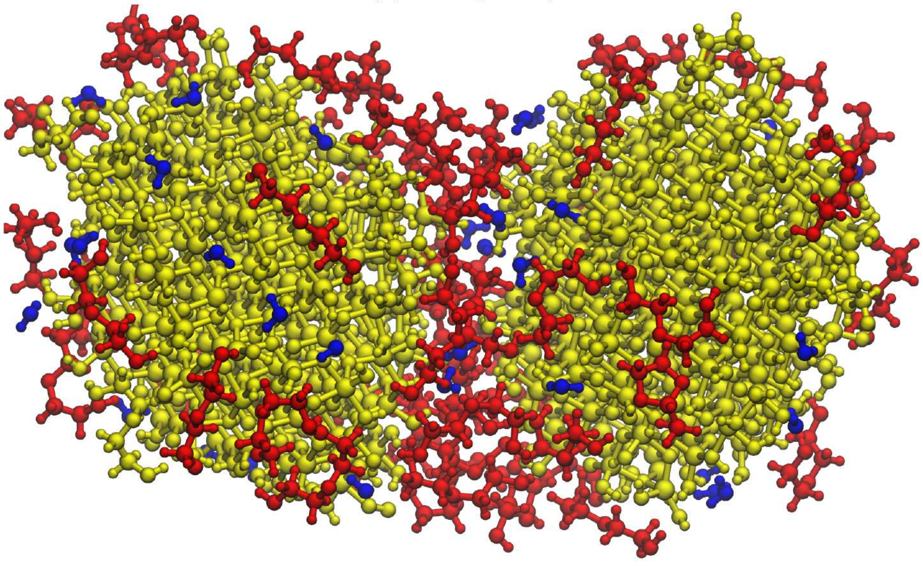


(b) Cluster configuration

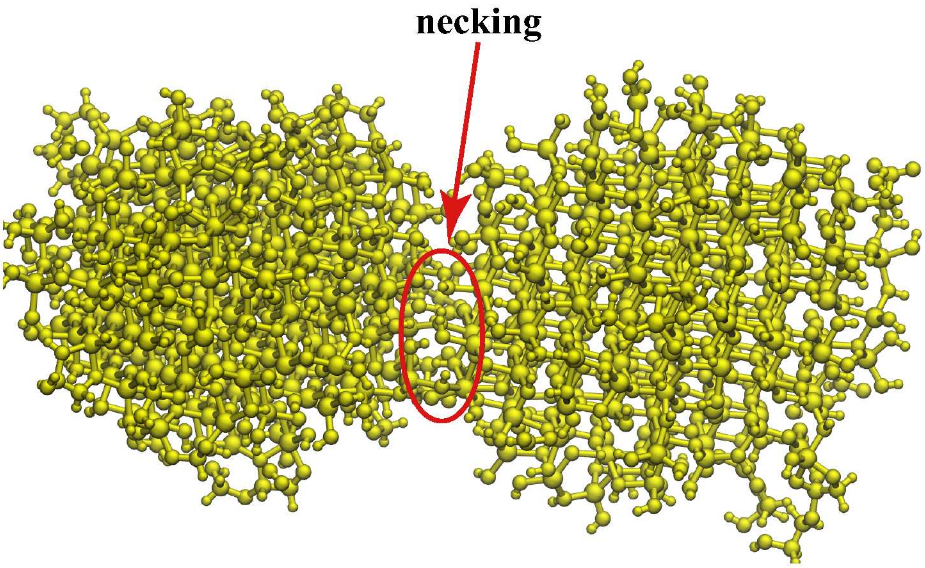
Fig. S3: Snapshots of two connecting configurations. The Cr-oxide particles, DEG and water molecules are illustrated in yellow, red and blue, respectively. The 4 Cr-oxide particles of (a) align almost in a chain, while the 4 Cr-oxide particles of (b) are arranged more compactly. The configuration in (b) generally features a significantly higher breaking strength than its counterpart in (a), especially after sintering.



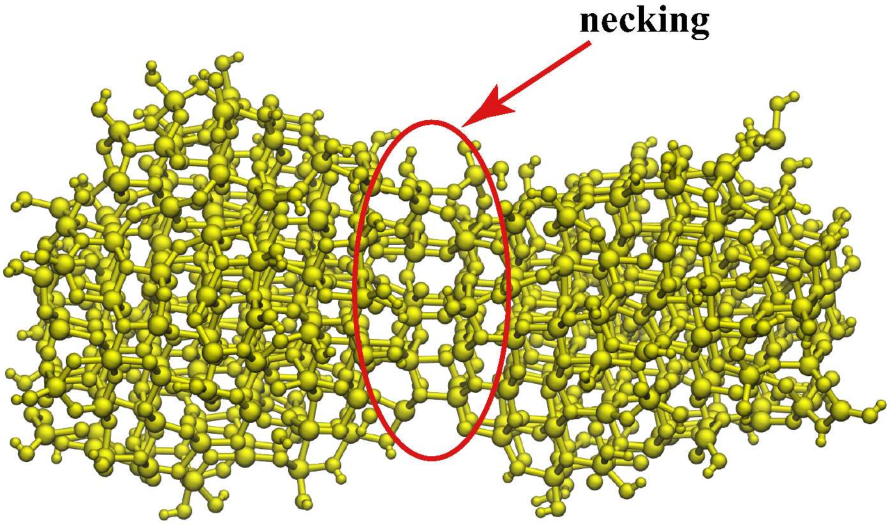
(a) Print (300 K)



(b) Curing (393 K)



(c) Burn-out (900 K)



(d) Sintering (1900 K)

Fig. S4: Snapshots of a BJP process. The Cr-oxide particles, water, and DEG molecules are shown in yellow, blue and red, respectively.

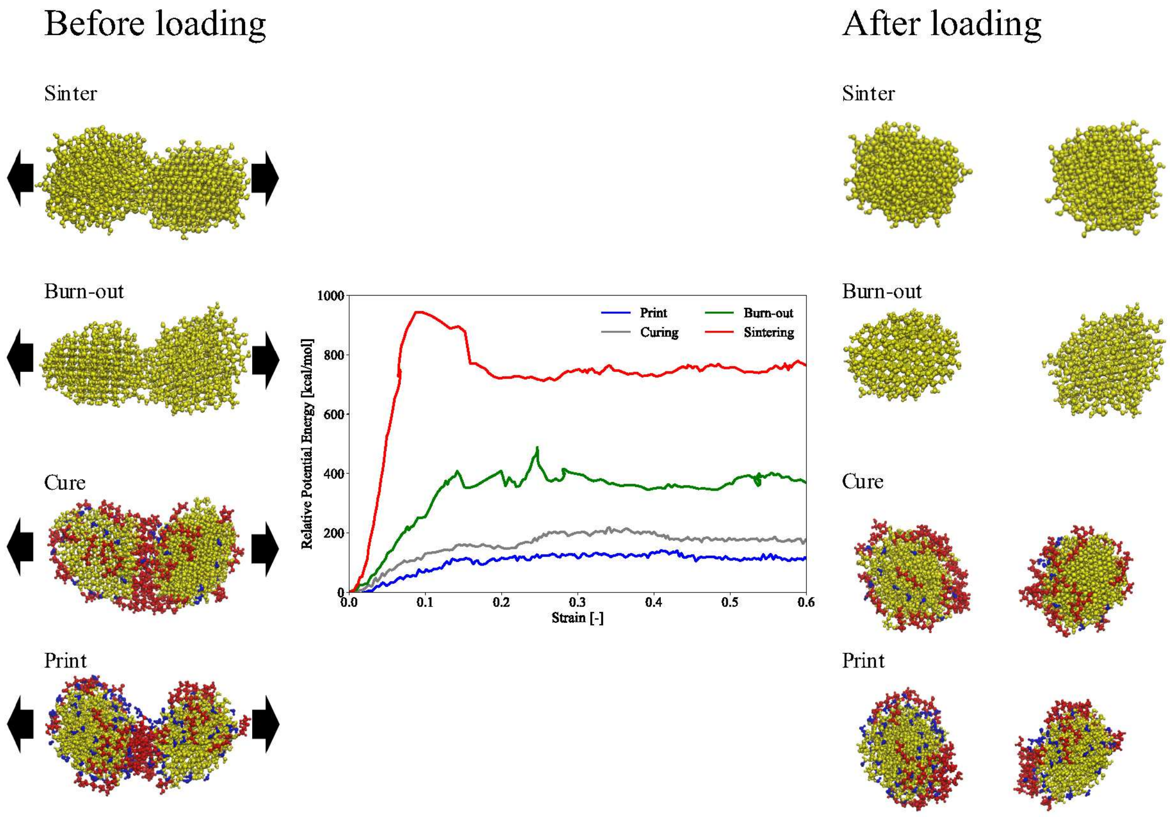
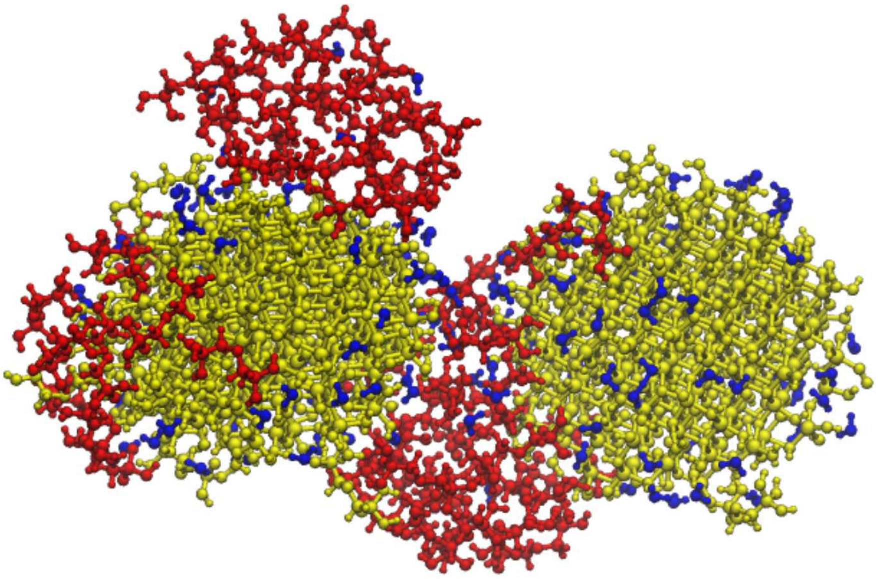
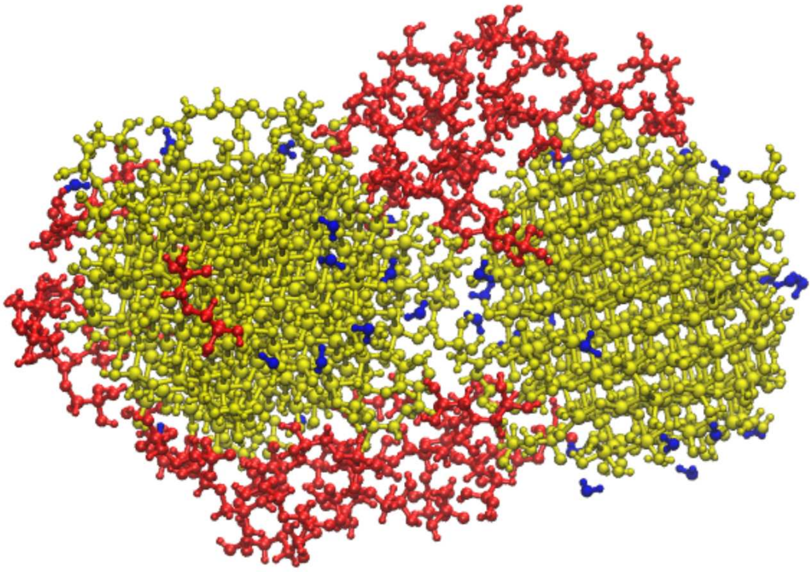


Fig. S5: Relative potential energy development under an external force, with the equilibrium state as the reference state. The strain is the ratio of the instantaneous center of mass distance over the center of mass distance at the equilibrium state. The Cr-oxide particles, water, and DEG molecules are shown in yellow, blue and red, respectively.

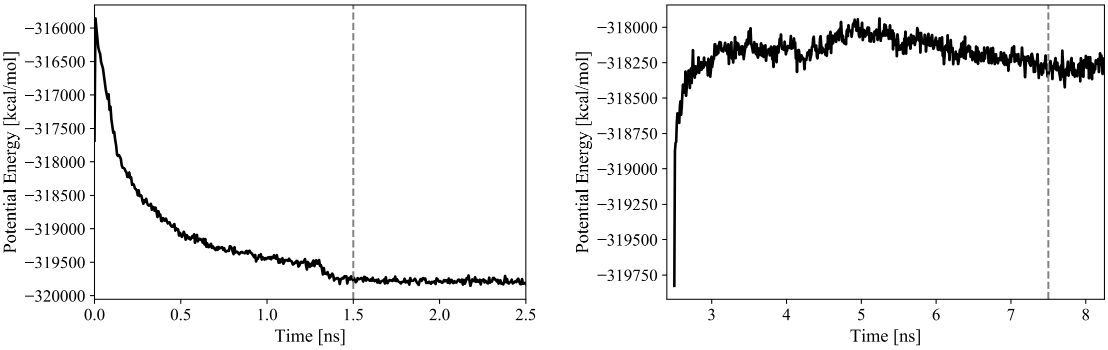


(a) Print



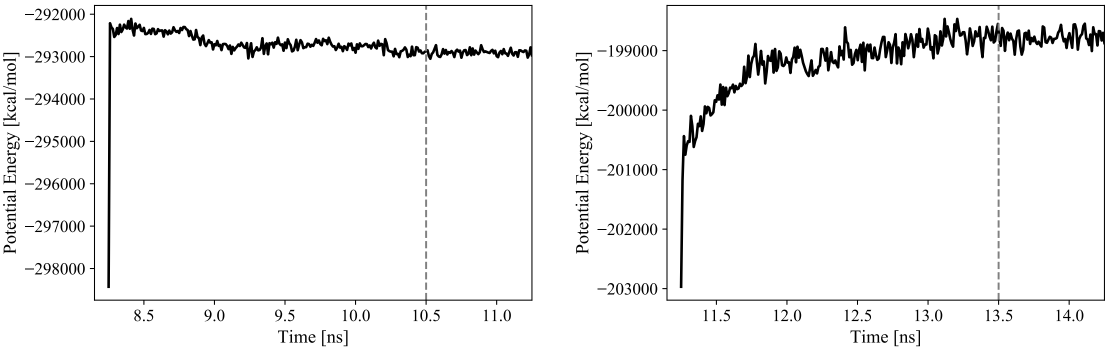
(b) Curing

Fig. S6: Spread of the binder species is facilitated by increasing temperature from 300 K to 393 K. We use a system of 160 water molecules, 60 1-(2,2,2-trihydroxyethoxy)ethane-2,2,2-triol and 2 Cr-oxide nanoparticles to illustrate this development. The Cr-oxide particles are shown in yellow, while the water and binder phase are highlighted in blue and red, respectively.



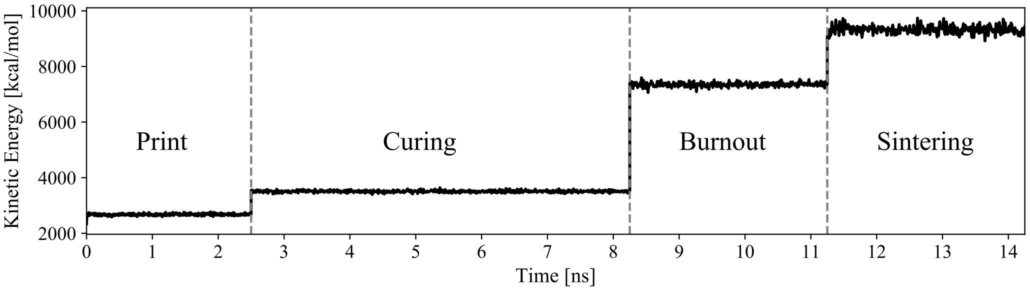
(a) Potential energy history of the print stage

(b) Potential energy history of the curing stage

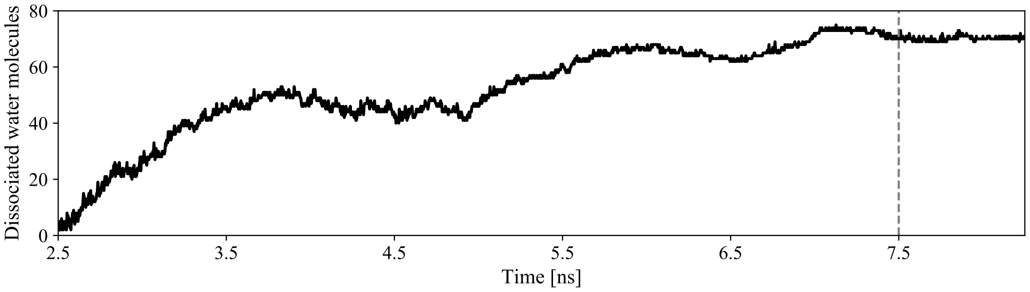


(c) Potential energy history of the burn-out stage

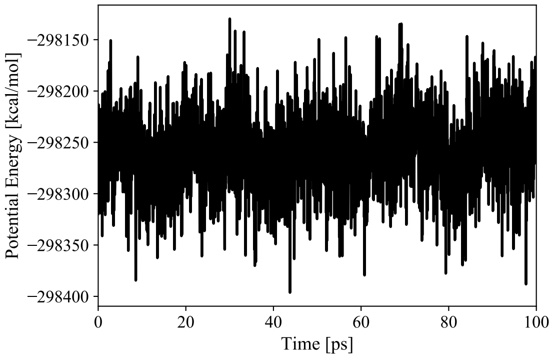
(d) Potential energy history of the sintering stage



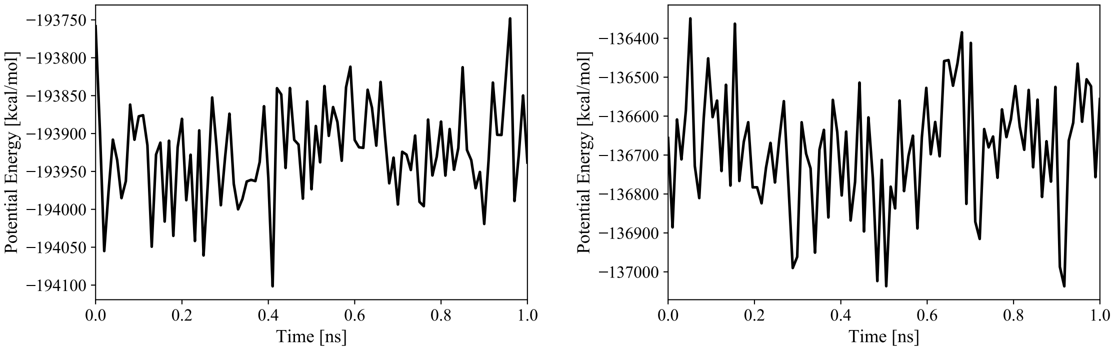
(e) Kinetic energy history



(f) The quantity of dissociated water vapor during curing



(g) Extra NVT-MD simulation for 100 ps at 393 K on the system without water vapor to verify whether the BJP part reaches equilibrium at 8.25 ns



(h) Extra NVT-MD simulation for 1 ns at 900 K on the system without gaseous species to verify whether the BJP part reaches equilibrium at 11.25 ns

(i) Extra NVT-MD simulation for 1 ns at 1900 K on the system without gaseous species to verify whether the BJP part reaches equilibrium at 14.25 ns

Fig. S7: History of potential energy and kinetic energy for each stage (a-e); Quantity of evaporated water molecules during curing (f). Extra NVT-MD simulations to verify whether the BJP part reaches the equilibrium state (g-i). It should be noted that the necessary pre-equilibration time varies from case to case. But in all cases, enough time is given until the system reaches its equilibrium state.