

Reaction and characterisation of a two-stage thermoset using molecular dynamics

Felix K. Schwab^{*a} and Colin Denniston^{b,c}

^{*} Corresponding author

^a Institute of Applied Materials (IAM-CMS), Karlsruhe Institute of Technology (KIT), Kaiserstrasse 12, 76131 Karlsruhe, Germany. E-mail: felix.schwab@kit.edu

^b Department of Applied Mathematics, University of Western Ontario (UWO), 1151 Richmond Street, London, ON, N6A 3K7, Canada.

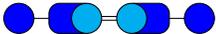
^c Department of Physics & Astronomy, University of Western Ontario (UWO), 1151 Richmond Street, London, ON, N6A 3K7, Canada.

Electronic Supplementary Information

Supplementary Information I: Resin System

To have extremely simple resin system as a minimal example, the virtual resin system is made up of small molecules with short backbone structures, see Table S1. Furthermore, each constituent is monodisperse. Hence, the listed number of molecules per component is

Table S1 Molecules used in the virtual resin system.

Virtual resin component	Schematic	Molecular structure	number of molecules
(P-)MDI		$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{OCN} - \text{C} - \text{C} - \text{C} - \text{NCO} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	57
UP		$\begin{array}{c} \text{H} \quad \quad \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{H} \\ \diagdown \quad \diagup \quad \quad \diagdown \quad \diagup \\ \text{C} = \text{C} - \text{C} = \text{C} \\ \diagup \quad \diagdown \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \quad \quad \text{H} \end{array}$	40
Ethylene		$\begin{array}{c} \text{H} \quad \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \quad \text{H} \end{array}$	262
Peroxide		$\text{H} - \overline{\text{O}} - \overline{\text{O}} - \text{H}$	4

directly related to the molecular structure shown in Table S1. The composition shown is a unit composition and serves as an input for the simulation setups of the virtual resin system.

The same unit composition applies to the commercial resin system, see Table S2. In contrast to the virtual resin system, the (P-)MDI and UP component are not monodisperse, both come in three different molecule variants. In the case of (P-)MDI these are chosen to

Table S2 Resin composition of the commercial resin system.

Component	number of molecules (total)	variants	attribute	number of molecules (specific)
(P-)MDI	57	3	$\left\{ \begin{array}{l} \text{functionality} = 2 \\ \text{functionality} = 3 \\ \text{functionality} = 4 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \\ 4 \\ 18 \end{array} \right.$
UP	40	3	$\left\{ \begin{array}{l} 1x \text{ basic structure} \\ 5x \text{ basic structure} \\ 10x \text{ basic structure} \end{array} \right.$	$\left\{ \begin{array}{l} 27 \\ 2 \\ 11 \end{array} \right.$
Styrene	262	1	—	262
Peroxide	4	1	—	4

give an overall functionality of about 2.7. The UP molecules come in three different lengths by repeating the basic molecule structure. With this the dispersity is increased analogously to the (P-)MDI, but under the prerequisite of keeping a functionality of 2.

Supplementary Information II: COMPASS Force-Field

Force-fields are used in molecular dynamics to model the interactions between atoms or particles. These interactions, collected in a potential energy E^{tot} , govern the movement and arrangement of the particles and atoms involved. A force-field describing the potential energy of molecules, which are bonded atoms, has to be modelled after molecule conformations and reciprocal influence of different molecules. Within a molecule each atom is influenced by its neighbouring atoms to which a chemical bond exists. From their relative position, showing in distances and angles, forces arise determining the atoms' positions. Furthermore, neighbouring atoms to which no chemical bond exists induce *van der Waals* and *Coulomb forces*, which also may have a long-range effect. Within this approach, a basic energy potential would be e.g. the energy of a bond between two atoms. This bond is usually described by a spring, which may be modelled through a Taylor series expansion around the equilibrium bond distance. The spring constants are then calculated from vibrational modes associated to the respective bond type, which are determined by experiments or simulations¹.

A suitable potential energy to describe polymer molecules is provided by the COMPASS force-field²⁻⁴. The molecular behaviour, governed by intra- and intermolecular forces, depends on relative *atom positions* r_{ij} and their combinations as *bond length* b_{ij} , *angle* φ_{ijk} , *dihedral* or *torsion angle* ϑ_{ijkl} and *out-of-plane angle* χ_{ijkl} . Superscripts denote the involved atoms and their position, e.g. $r_{ij} = r(x_i, x_j)$. Basic intra-molecular potential terms are constructed by the introduced distance and angles. Furthermore, the COMPASS force-field introduces intra-molecular cross-terms to allow for a more accurate molecule description. These terms give the total potential energy as

$$\begin{aligned}
 E^{\text{tot}} = & E^{\text{bonds}} \\
 & + E^{\text{angles}} + E^{\text{bond-bond}} + E^{\text{bond-angle}} \\
 & + E^{\text{dihedrals}} + E^{\text{middle-bond-torsion}} + E^{\text{end-bond-torsion}} + E^{\text{angle-torsion}} + E^{\text{angle-angle-torsion}} + E^{\text{bond-bond-13-torsion}} \\
 & + E^{\text{impropers}} + E^{\text{angle-angle}} \\
 & + E^{\text{vdW}} + E^{\text{Coulomb}}.
 \end{aligned} \tag{1}$$

The terms E^{vdW} and E^{Coulomb} introduce van der Waals and Coulomb forces, which add a Lennard-Jones potential of type 9-6 and an electrostatic behaviour to the system, respectively. These potential terms are called inter-molecular or non-bonded interactions. They act on atoms of different molecules and on atoms of the same molecule if they are not connected through an intra-molecular potential. By inserting all potential terms into Equation (1), the total potential energy is written as

$$\begin{aligned}
 E^{\text{tot}} = & \sum_{i,j} \left\{ K^{\text{K2}} (b_{ij} - b_{ij}^0)^2 + K^{\text{K3}} (b_{ij} - b_{ij}^0)^3 + K^{\text{K4}} (b_{ij} - b_{ij}^0)^4 \right\} \\
 & + \sum_{i,j,k} \left\{ A^{\text{A2}} (\varphi_{ijk} - \varphi_{ijk}^0)^2 + A^{\text{A3}} (\varphi_{ijk} - \varphi_{ijk}^0)^3 + A^{\text{A4}} (\varphi_{ijk} - \varphi_{ijk}^0)^4 \right. \\
 & \quad \left. + A^{\text{bb}} (b_{ij} - b_{ij}^0) (b_{jk} - b_{jk}^0) + A^{\text{ba1}} (b_{ij} - b_{ij}^0) (\varphi_{ijk} - \varphi_{ijk}^0) + A^{\text{ba2}} (b_{jk} - b_{jk}^0) (\varphi_{ijk} - \varphi_{ijk}^0) \right\} \\
 & + \sum_{i,j,k,l} \left\{ D^{\text{D1}} [1 - \cos(\vartheta_{ijkl})] + D^{\text{D2}} [1 - \cos(2\vartheta_{ijkl})] + D^{\text{D3}} [1 - \cos(3\vartheta_{ijkl})] \right. \\
 & \quad + (b_{jk} - b_{jk}^0) [D^{\text{mbt1}} \cos(\vartheta_{ijkl}) + D^{\text{mbt2}} \cos(2\vartheta_{ijkl}) + D^{\text{mbt3}} \cos(3\vartheta_{ijkl})] \\
 & \quad + (b_{ij} - b_{ij}^0) [D^{\text{ebt1}} \cos(\vartheta_{ijkl}) + D^{\text{ebt2}} \cos(2\vartheta_{ijkl}) + D^{\text{ebt3}} \cos(3\vartheta_{ijkl})] \\
 & \quad + (b_{kl} - b_{kl}^0) [D^{\text{ebt4}} \cos(\vartheta_{ijkl}) + D^{\text{ebt5}} \cos(2\vartheta_{ijkl}) + D^{\text{ebt6}} \cos(3\vartheta_{ijkl})] \\
 & \quad + (\varphi_{ijk} - \varphi_{ijk}^0) [D^{\text{at1}} \cos(\vartheta_{ijkl}) + D^{\text{at2}} \cos(2\vartheta_{ijkl}) + D^{\text{at3}} \cos(3\vartheta_{ijkl})] \\
 & \quad + (\varphi_{jkl} - \varphi_{jkl}^0) [D^{\text{at4}} \cos(\vartheta_{ijkl}) + D^{\text{at5}} \cos(2\vartheta_{ijkl}) + D^{\text{at6}} \cos(3\vartheta_{ijkl})] \\
 & \quad + D^{\text{aat}} (\varphi_{ijk} - \varphi_{ijk}^0) (\varphi_{jkl} - \varphi_{jkl}^0) \cos(\vartheta_{ijkl}) \\
 & \quad \left. + D^{\text{bb13}} (b_{ij} - b_{ij}^0) (b_{kl} - b_{kl}^0) \right\} \\
 & + \sum_{i,j,k,l} \left\{ I\chi_{ijkl}^2 \right. \\
 & \quad \left. + I^{\text{aa1}} (\varphi_{ijk} - \varphi_{ijk}^0) (\varphi_{kjl} - \varphi_{kjl}^0) + I^{\text{aa2}} (\varphi_{ijk} - \varphi_{ijk}^0) (\varphi_{ijl} - \varphi_{ijl}^0) + I^{\text{aa3}} (\varphi_{ijl} - \varphi_{ijl}^0) (\varphi_{kjl} - \varphi_{kjl}^0) \right\} \\
 & + \sum_{i,j} \left\{ \epsilon_{ij} \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\}.
 \end{aligned} \tag{2}$$

The parameters used in the potential terms exist for a wide range of molecular interactions and are listed in the work of Sun et al.²⁻⁴. In these references, the parameters are adjusted to different molecules and the resulting combination of model and parameters is validated on the basis of energetic behaviour.

Supplementary Information III: Reaction Algorithms

Algorithm S1 Bond dissociation

```

1: procedure BONDBREAK( $\Theta$ ,  $b^{\text{br}}$ )
2:   if  $\Theta < \Theta^{\text{min}}$  then
3:     return
4:   end if
5:   for all  $b$  in bondlist do
6:      $b^{\text{t}} \leftarrow \text{TYPE}(b)$ 
7:     if  $b^{\text{t}} == b^{\text{br}}$  then
8:        $(a^1, a^2) \leftarrow \text{ATOMS}(b)$ 
9:        $\Theta^{\text{l}} \leftarrow \text{COMPUTELOCALTEMPERATURE}(a^1, a^2)$ 
10:       $P \leftarrow \text{RANDOM}(0,1)$ 
11:       $F \leftarrow \text{ARRHENIUS}(a^1, a^2, b^{\text{br}}, \Theta^{\text{l}})$ 
12:      if  $P > F$  then
13:        DELETEBOND( $b$ )
14:      end if
15:    end if
16:  end for
17:  UPDATE()
18:  return
19: end procedure

```

$\triangleright \Theta$: current system temperature; b^{br} : bond type to break
 \triangleright Loop over all bonds
 \triangleright Get type of current bond b
 \triangleright Get atoms of current bond b
 $\triangleright P$: probability bond breaks
 $\triangleright F$: threshold preventing breakage
 \triangleright type-updates of affected atoms, bonds, angles, dihedrals, impropers

Algorithm S2 Bond formation

```

1: procedure BONDCREATE( $a$ ,  $b^{\text{cr}}$ )
2:    $a^{\text{t}} \leftarrow \text{TYPE}(a)$ 
3:   if  $a^{\text{t}}$  not part of  $b^{\text{cr}}$  then
4:     return
5:   end if
6:   for all  $a_n$  in NEIGHBOURS( $a$ ) do
7:      $a_n^{\text{t}} \leftarrow \text{TYPE}(a_n)$ 
8:     if  $(a^{\text{t}}$  and  $a_n^{\text{t}})$  form  $b^{\text{cr}}$  then
9:       if  $\text{DIST}(a, a_n) < d^{\text{max}}$  then
10:        return
11:      end if
12:       $\Theta^{\text{l}} \leftarrow \text{COMPUTELOCALTEMPERATURE}(a, a_n)$ 
13:       $P \leftarrow \text{RANDOM}(0,1)$ 
14:       $F \leftarrow \text{ARRHENIUS}(a, a_n, b^{\text{cr}}, \Theta^{\text{l}})$ 
15:      if  $P < F$  then
16:        ADDBOND( $a, a_n, b^{\text{cr}}$ )
17:        ADDTRANSIENT( $a, a_n, b^{\text{cr}}$ )
18:      end if
19:    end if
20:  end for
21:  UPDATE()
22:  return
23: end procedure

```

$\triangleright a$: current atom; b^{cr} : bond type to create
 \triangleright Get type of current atom a
 \triangleright Loop over all neighbour atoms a_n of atom a
 \triangleright Get type of neighbour atom a_n
 $\triangleright d^{\text{max}}$: max. allowed distance
 $\triangleright P$: probability bond forms
 $\triangleright F$: threshold for formation
 \triangleright check for side reaction and add to transient list
 \triangleright type-updates of affected atoms, bonds, angles, dihedrals, impropers

```

24: function CHECKTRANSIENT( $b^{\text{tr}}$ )
25:    $(a^1, a^2) \leftarrow \text{ATOMS}(b^{\text{tr}})$ 
26:    $\Theta^{\text{l}} \leftarrow \text{COMPUTELOCALTEMPERATURE}(a^1, a^2)$ 
27:    $P \leftarrow \text{RANDOM}(0,1)$ 
28:    $F \leftarrow \text{ARRHENIUS}(a^1, a^2, b^{\text{tr}}, \Theta^{\text{l}})$ 
29:   if  $P > F$  then
30:     return true
31:   else
32:     REMOVETRANSIENT( $b^{\text{tr}}$ )
33:     return false
34:   end if
35: end function

```

$\triangleright b^{\text{tr}}$: transient bond from transient bond list
 \triangleright Get atoms of transient bond b^{tr}
 $\triangleright P$: probability bond forms
 $\triangleright F$: threshold for formation
 \triangleright remove bond from transient list

Algorithm S3 Treatment of electrophile and nucleophile centres

```

1: function CHECKRADICAL(a)
2:   at ← TYPE(a)
3:   if at is radical then
4:     for all an in NEIGHBOURS(a) do
5:       ant ← TYPE(an)
6:       if (at and ant) are radical_pair then
7:         return COULOMBFORCE(a, an)
8:       else
9:         return 0.0
10:      end if
11:    end for
12:  else
13:    return 0.0
14:  end if
15: end function
    
```

▷ a: current atom
 ▷ Get type of current atom a
 ▷ radical: atom types involved in the radical reaction
 ▷ Loop over all neighbour atoms a_n of atom a
 ▷ Get type of neighbour atom a_n
 ▷ radical_pair: electrophile and nucleophile centre meant to form a bond
 ▷ Calculate additional attraction

Supplementary Information IV: Material Properties

In the following the values of different material properties calculated are listed. The values correspond to the depicted values in the three-dimensional plots in results section, hence they are calculated at a specific combination of temperature Θ and degree of cure ζ .

Table S3 Specific heat capacity of the virtual resin system $c_V(\Theta, \zeta)$ in $\text{J}/(\text{kgK})$

(Θ, ζ)	U0R0	U50R0	U50R20	U50R40	U50R60	U50R80	U50R100
273 K	2863	2929	2896	3493	3283	2888	2961
313 K	2896	2852	2326	2786	2778	2921	2914
398 K	—	2728	2365	3081	2775	2720	2723
438 K	—	2517	3122	2703	2841	2561	2758

Table S4 Specific heat capacity at constant volume as a weighted average of the small commercial resin systems, $c_V(\Theta, \zeta)$, in $\text{J}/(\text{kgK})$

(Θ, ζ)	U0R0 ⁺⁰ ₋₀	U50R0 ⁺⁰ ₋₀	U50R20 ⁺⁰ ₋₀	U50R40 ⁺⁶ ₋₅	U50R67 ⁺⁵ ₋₃	U50R82 ⁺⁵ ₋₂	U50R97 ⁺⁰ ₋₁
273 K	2257 ⁺⁹⁴ ₋₁₂₇	2441 ⁺²⁵² ₋₁₄₄	2362 ⁺¹⁴⁹ ₋₉₂	2104 ⁺³⁵³ ₋₂₄	2484 ⁺²²⁹ ₋₂₀₂	2306 ⁺⁸⁸ ₋₂₅₃	2124 ⁺³⁰⁸ ₋₂₂₄
313 K	2034 ⁺¹¹⁶ ₋₁₁₄	2165 ⁺⁶³ ₋₆₇	2337 ⁺⁷⁴ ₋₉₀	2020 ⁺⁴³⁷ ₋₆₃	2299 ⁺¹¹⁶ ₋₂₃₈	2137 ⁺²⁹⁹ ₋₁₈₀	2071 ⁺³³⁰ ₋₂₅₆
398 K	—	2017 ⁺¹⁶⁶ ₋₂₀₈	2273 ⁺¹³⁴ ₋₈₂	2110 ⁺¹⁷¹ ₋₃₆₉	2298 ⁺⁷⁴ ₋₉₃	2443 ⁺⁸⁸ ₋₂₆	2298 ⁺¹²⁷ ₋₁₄₃
438 K	—	2287 ⁺²⁰⁷ ₋₁₉₁	2246 ⁺⁵¹⁶ ₋₃₃₄	1959 ⁺⁴²⁷ ₋₃₄	2497 ⁺²⁸⁶ ₋₁₈₈	2464 ⁺³³ ₋₂₀	2696 ⁺⁶⁵⁸ ₋₁₆₆

Table S5 Isotropic thermal conductivity of the virtual resin system $\kappa^{\text{iso}}(\Theta, \zeta)$ in $\text{W}/(\text{mK})$

(Θ, ζ)	U0R0	U50R0	U50R20	U50R40	U50R60	U50R80	U50R100
273 K	1.456	1.126	0.912	0.678	0.498	0.426	0.385
313 K	2.643	1.602	1.218	0.854	0.638	0.480	0.441
398 K	—	0.108	0.165	1.604	0.888	0.506	0.430
438 K	—	0.086	0.121	1.208	1.360	0.771	0.508

Table S6 Isotropic thermal conductivity of the small commercial resin systems $\kappa^{\text{iso}}(\Theta, \zeta)$ in $\text{W}/(\text{mK})$

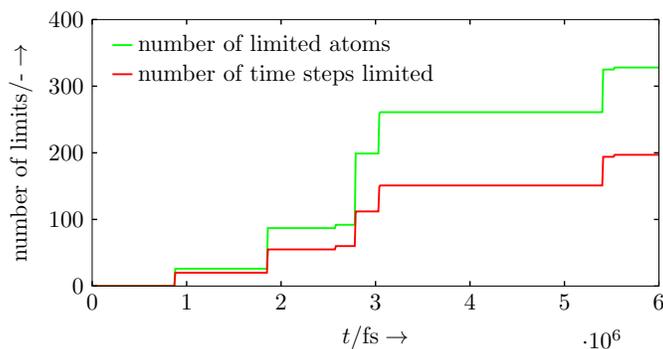
(Θ, ζ)	U0R0 ⁺⁰ ₋₀	U50R0 ⁺⁰ ₋₀	U50R20 ⁺⁰ ₋₀	U50R40 ⁺⁶ ₋₅	U50R67 ⁺⁵ ₋₃	U50R82 ⁺⁵ ₋₂	U50R97 ⁺⁰ ₋₁
273 K	0.210 ^{+0.002} _{-0.003}	0.225 ^{+0.005} _{-0.008}	0.225 ^{+0.008} _{-0.006}	0.226 ^{+0.012} _{-0.017}	0.230 ^{+0.011} _{-0.015}	0.239 ^{+0.018} _{-0.022}	0.259 ^{+0.010} _{-0.014}
313 K	0.215 ^{+0.006} _{-0.010}	0.225 ^{+0.016} _{-0.008}	0.231 ^{+0.014} _{-0.008}	0.233 ^{+0.012} _{-0.010}	0.233 ^{+0.010} _{-0.008}	0.234 ^{+0.004} _{-0.007}	0.246 ^{+0.010} _{-0.015}
398 K	—	0.225 ^{+0.001} _{-0.001}	0.230 ^{+0.024} _{-0.018}	0.223 ^{+0.007} _{-0.012}	0.243 ^{+0.022} _{-0.018}	0.246 ^{+0.012} _{-0.017}	0.261 ^{+0.011} _{-0.010}
438 K	—	0.210 ^{+0.015} _{-0.013}	0.224 ^{+0.013} _{-0.012}	0.231 ^{+0.010} _{-0.014}	0.238 ^{+0.029} _{-0.015}	0.254 ^{+0.015} _{-0.017}	0.235 ^{+0.012} _{-0.016}

Table S7 Bulk modulus of the large commercial resin system, $K(\Theta, \zeta)$, in MPa with uncertainty of the linear regression.

(Θ, ζ)	U0R0	U50R0	U50R20	U50R33	U50R67	U50R82	U50R95
273 K	2012 ± 13	2168 ± 14	2464 ± 15	2679 ± 18	3037 ± 19 ¹	3098 ± 21 ¹	3236 ± 20 ¹
313 K	1584 ± 10	1751 ± 11	2104 ± 15	2285 ± 16	2676 ± 17 ¹	2762 ± 18 ¹	2933 ± 21 ¹
398 K	—	1070 ± 9	1132 ± 9	1546 ± 11 ¹	1858 ± 13 ¹	2134 ± 15 ¹	2325 ± 16 ¹
438 K	—	781 ± 8	1093 ± 9 ¹	1203 ± 10 ¹	1530 ± 12 ¹	1750 ± 14 ¹	1961 ± 17 ¹

¹ with *fix nve/limit***Supplementary Information V: Bulk Modulus Calculation with *fix nve/limit***

In Table S7†, values marked with the numeral 1 were obtained by using *fix nve/limit* as a time integrator. The NEMD runs at higher degrees of cure and temperature showed irregular simulation failures by single, quickly accelerating atoms. Neither lowering the deformation amplitude or rate, nor applying numerical measures (e.g. multi-timescale integrator, *rRESPA*⁵) could remedy the simulation failures over the whole parameter range. Hence, the limitation of atom movement was applied, if an atom moves farther than a distance of 0.5 Å in one time step. As this violates the conservation of energy, the number of limited atoms was additionally evaluated. In Figure S1 this is depicted for the highest degree of cure and temperature.

**Figure S1** Amount of interventions of *fix nve/limit* for a system at $\Theta = 438$ K and a degree of cure of U50R95

Here, during a simulation of six million time steps only 328 atoms had to be limited, in a total of 192 time steps. Further examination showed, that almost all limited atoms were hydrogen atoms, hence atoms of low mass and not directly part of the polymer backbone. Considering the large system size (number of atoms in the domain), the number of limits are negligibly small, and thus no significant influence on the simulation outcome is expected.

Notes and references

- [1] T. Schlick, *Molecular Modeling and Simulation: An Interdisciplinary Guide*, Springer, New York, 2010, p. 723.
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