

Molecular dynamics simulation of vinyl ester resin crosslinking

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Molecular dynamics simulations of vinyl ester resin crosslinking

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Molecular dynamics simulations on an atomistic scale were performed to create a series of crosslinked vinyl ester resins, where the crosslink density was varied at a constant degree of conversion. Thermodynamic and mechanical properties were obtained as a function of the crosslink density. In this study, a new algorithm was developed to generate the crosslinking network by incorporating the correct regioselectivity (head-to-tail chain propagation), and simulated the actual monomer reactivity ratios during the cure. These features had never been achieved in previous simulations. Most previous crosslinking simulations have been performed on epoxy resins, which undergo step-growth type polymerization. Vinyl esters, in contrast, cure by free radical chain polymerization. In this study, vinyl ester crosslinking networks with conversions up to 98% were successfully achieved. Volume shrinkage, glass transition temperature, and Young's modulus of the equilibrated structures were calculated, where the resin's crosslink densities were varied. The isotropic Young's modulus was compared with available experimental data. This newly developed method holds great promise for generating other realistic thermoset and thermoplastic polymer systems containing two or more type of monomers.

I. Introduction

Vinyl ester (VE) resins have costs and mechanical properties intermediate between polyester and epoxy resins. They are widely used in marine and chemical tank applications because of their high corrosion resistance and water barrier properties [1, 2]. Fiberglass-reinforced VE materials have been used in boats and airplanes. Their largest growth market is for wind turbine blades [3]. Nanoreinforced VE polymer composite uses are increasing as significant mechanical property improvements have been realized [4]. The curing of VE resins is extremely complex and involves microphase separation. Tiny regions become more highly crosslinked and phase separate into microgels leading to complex internal diffusion and chemical kinetics that depend on the monomer composition, initiator concentration and the cure temperature protocol [5, 6]. To capture all these features is currently beyond the capability of MD simulations due to limitations on the system size and the need for continuous repeating unit cells. Real cured vinyl ester materials, while homogeneous at the macro scale, are nonhomogeneous at the micro scale. Molecular dynamics (MD) simulation can, however, be a tool to study the properties of homogeneous regions of

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cured VE resins; similar work has been reported for epoxy resins (i.e., EPON-862) crosslinking networks [7-9]. An atomistic simulation of an EPON-862/isophorone diamine network with only 900 atoms gave mechanical property predictions [10]. Two simulations of EPON-862/DETDA with about 20,000 atoms have been reported which predicted thermo-mechanical properties [11, 12].

Simulations of free radical addition homo-, co- or terpolymerizations to form either thermoplastics or thermosets are fundamentally different than step-growth polymerizations [13]. Each initiation step adds a large number of monomers to the chain (or network), typically in the hundreds, before termination or chain-transfer occurs. As chain growth and crosslinking proceeds, the growing radical's mobility decreases, but monomer diffusion to the radical site continues as a rapid rate. Then, as the crosslink density increases further, the rate of monomer diffusion drops and the reactive rates of chain growth, termination and chain transfer change in complex ways. Furthermore, at all stages of the polymerization, different vinyl monomers react with the growing chains at different rates. Also, different growing monomer radical chain ends exist during polymerization. When two different monomers (for example, the styrene and methacrylate type monomers found in VEs) are present, the terminal polymerization model (Eq. 1) is a good approximation [13, 14] of the rate of each monomer's incorporation into the cured matrix.

$$dM_1 / dM_2 = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)} \quad (1)$$

In this equation, M_1 represents the number of styrene molecules and M_2 represents the number of vinyl ester dimethacrylate molecules. Four reactions determine the rate of incorporation into the polymer of the two different monomer types in the terminal polymerization model.



However, knowledge of each rate constant is not required. Only the reactive reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are needed in the copolymerization equation, which describes the rate at which each type of monomer is incorporated into the polymer. An algorithm that reflects these rate constant ratios (r_1 , r_2) for styrene and the dimethacrylate VE monomers is required to account for monomer drift and to give realistic monomer sequence distributions in the polymer. The r_1 and r_2 values used were $r_1 = 0.485$ and $r_2 = 0.504$ [15]. These free radical polymerizations also differ from step-growth systems because they proceed only in head-to-tail regioselectivity during chain growth (see the following chemical equations). Thus, the algorithm used must also enforce this selectivity to achieve the correct molecular structure along the polymer chains.

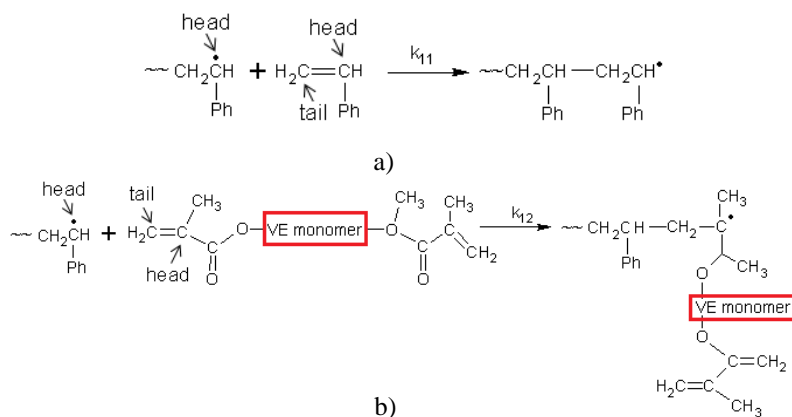


Figure 1. Head to tail regioselectivity during radical addition polymerization.

The faster rate of the growing chain $\sim\text{Sty}^\bullet$ radical's addition to vinyl ester methacrylates versus its addition to styrene ($r_1 = 0.485$) was accounted for by allowing a larger reactive volume around the active styrene head for finding a VE tail than for finding a styrene tail using the close contact bonding distance criteria. This criterion defines when a new bond between a growing radical chain's head can be made to a new monomer. It is used to calculate the closest distance between a head's active center and a tail atom. Spherical volumes around growing heads proportional to the rate constant reactivity ratios were used in which the tails of new monomers were located that could react with a growing head radical. These spherical volumes were defined by their respective radii from the growing radical center to the tail carbon of VE and styrene monomers, respectively. The same approach was used for imposing the r_2 rate ratio on a growing vinyl ester head. The growing radical was then allowed to form a bond with the closest monomer tail within the reactive spheres defined by these radii.

II. Simulation Models and Methods

Commercial Derakane 441-400 vinyl ester (VE) resin was used in this study. General VE chemical structure and molecular models are shown in Fig 2. The average number of Bisphenol-A groups, (n), in the dimethacrylate backbone is 1.62. Two specific vinyl ester monomers VE1 ($n = 1$) and VE2 ($n = 2$) were used in a mole ratio of 8/13. A total of 89 monomers (3154 atoms) including 68 styrene, eight VE1 and 13 VE2 molecules were used in the simulation, corresponding to 33 wt% of styrene. Subsequent calculations were performed later where the repeating cell size was increased to one containing twice molecules (136 styrene, 16 VE1 and 26 VE2 consisting of 6308 atoms). A few of these results are given at the bottom of Table 1.

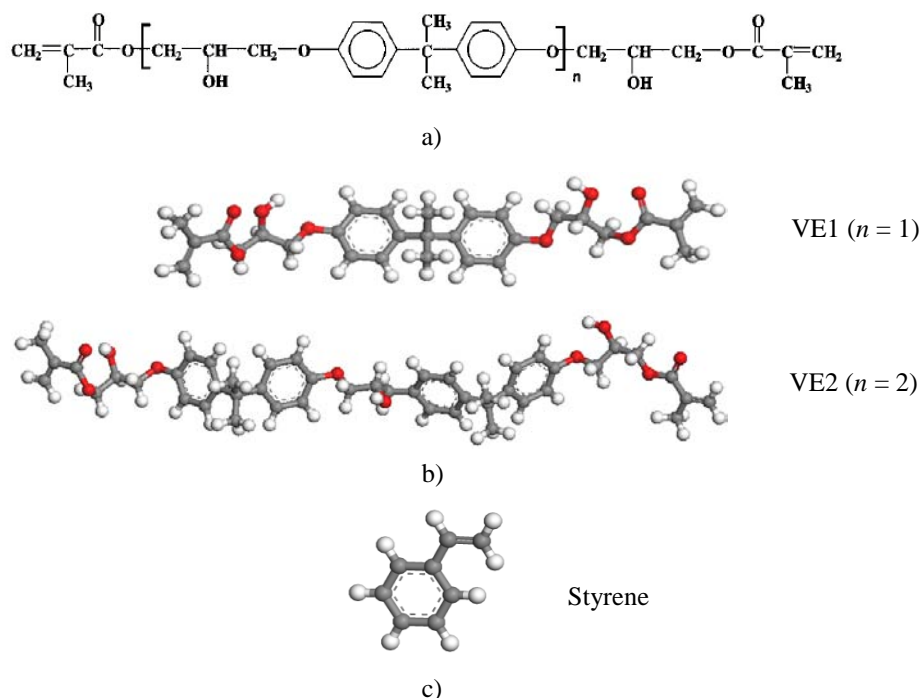


Figure 2. a) Chemical structures and molecular models of bisphenol-A-based dimethacrylate vinyl ester resin components. b) VE1 ($n = 1$), VE2 ($n = 2$) and c) styrene were generated with Materials Studio v5.0.

All molecular dynamics (MD) crosslinking simulations were performed with energy minimization (EM), NVT (constant number of atoms, volume and temperature) and NPT (constant number of atoms, pressure and temperature) at 300 K. The crosslinking simulations considered: 1) monomer reactivity ratios, 2) regioselectivity (head-to-tail growth) and 3) close-distance criteria. In order to apply monomer reactivity ratios in the simulations, the cutoff distances used were the radii of the respective reactive spherical volumes as described above. This forced the probability of finding the next styrene or VE tail to match the reactivity ratio values, dictated by rate constants, which depended on the activation energies and pre-exponential factors for each reaction type.

III. Results

A crosslinked vinyl ester resin was successfully generated with high conversion where 98% of the double bonds were consumed. This is high conversion, because complete conversion not obtained experimentally even with extended post curing. Two methods were used to grow the crosslinked system. (1) The first method (Method 1) involved starting a new chain when growth of the first chain slowed. When the growth of the second chain slowed, a third chain was initiated. This process was continued until 98% conversion was reached. Every chain has two reactive ends (a head and tail). In the second method, ten chains were used leaving 20 chain ends versus two chain ends in the first method. The more chain ends that exist, the lower the crosslink density is. Therefore, in the second method, the chain end heads present after reaching 98% conversion were forced to react with chain end tails progressively, followed by thermal relaxation. Thus, the number of chain ends was reduced stepwise from 20 to 2. This gave a series of resins with different crosslink densities at the same 98% conversion. The chain ends were then capped with hydrogen. Chain capping was done at the end of each crosslinking cycle so that no reactive ends existed when properties were calculated at each crosslink density studied. Mechanical properties were then computed for this series of cured resins. (2) A single chain (Method 2) was started and head to tail connections were made progressively with monomers available within the proscribed volumes. Then the system was thermally equilibrated, allowing both monomer and growing chain diffusion to proceed. This was followed by further chain growth using the closest monomer tails within the defined spheres. This process was repeated stepwise until 98% conversion is reached. Only one growing chain was used during the entire cure. This method is computationally intensive because the diffusion process slows with increasing conversion, accompanied by higher crosslinking density. The final crosslinking structure is shown in Fig 3. Some bonds are connected to the other neighboring cells (not visualized) across the cell boundaries, thus forming an extended periodic system.

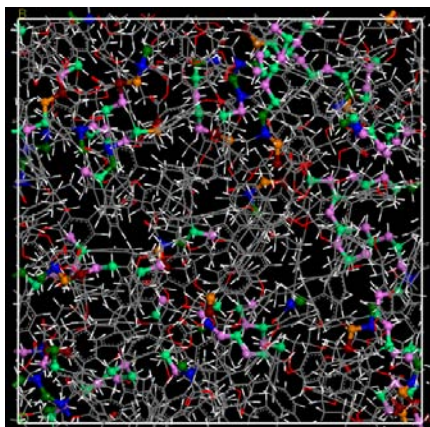


Figure 3. A VE crosslinked system generated by Method 1 at 98% conversion with two chain ends remaining that were capped by hydrogen. Balls represent the head and tail reactive ends connected by regioselectivity.

Density and volume shrinkage were computed versus each level of conversion (for curing by Methods 1 and 2) and also at 98% conversion. Derakane 441-400 vinyl ester resin was reported to shrink 7.5% after curing. This value was obtained from a data sheet provided by Ashland Co. The total volume shrinkage computed by Method 1 in this work was about 4.7% when 20 chain ends remained. After these 20 chain ends were reduced to 2 chain ends (i.e., higher crosslink density) the volume shrinkage increased to 7.8%. The volume shrinkage was 8.8% when a single chain was grown to 98% conversion (Method 2) with two chain ends remaining. This difference in volume shrinkage using multiple chains (7.8%, Method 1) for curing followed by connecting chain ends versus using a single chain growth (8.8%, Method 2) occurs because each particular crosslinking procedure will lead to a different crosslink pattern. The volume contractions are listed in Table 1.

The two computed volume shrinkages (7.8, 8.8%) obtained with the smaller unit cell using Methods 1 and 2 at the same conversion (98%) and number of chain ends (two) were both somewhat higher than the experimental value (7.5%). This is not surprising because the experimental curing will not reach 98% conversion, and real cured samples could contain some voids and defect sites. Furthermore, Method 1 links chain ends somewhat arbitrarily. If that linking were performed differently, small differences in mass density would occur. Finally, the absolute

crosslink density of the experimental cure is not known. Hence, it is expected that the calculated volume shrinkages should be higher than the experimental value because (1) the crosslink density in the simulated structure (98%) is higher than that achieved in experimental resins, and (2) no voids or defects sites are present in this model.

Volume shrinkages of the larger repeating unit cell (6308 atoms) were compared to those of the smaller repeating unit cell (3103 atoms). The crosslinking density of the VE network structure containing four chain ends in the larger unit cell will be the same as the crosslinking density with two chain ends in the smaller unit cell. Two computed volume shrinkage (8.8% and 8.4%) are very close to each other as shown in Table 1, suggesting that the smaller unit cell was sufficient to evaluate a homogeneous VE network structure. With only two chain ends present in the larger cell, the crosslinking density at 98% conversion will be greater than that in the smaller cell when two chain ends remain. Thus, a greater shrinkage (9.8%) is expected and confirmed in the last entry in Table 1.

Table 1. Volume shrinkage during curing by method two. Shrinkage versus conversion to 98% while increasing crosslink density by progressively combining chain ends.

Curing Method	Conversion (%)	Number of chain ends	Volume (\AA^3)	Volume shrinkage (%)
	Initial liquid system	—	33732.7	—
1	78	48	32749.1	2.9
1	86	30	32357.5	4.1
1	90	22	32262.5	4.3
1	98	20	32153.5	4.7
1	98	2	31101.6	7.8
2	98	2	30758.3	8.8
	Initial liquid system ^a	—	66955.7	—
2 ^a	98	4 ^b	61299.0	8.4
2 ^a	98	2 ^b	60342.8	9.8

^a These simulations were performed with a larger repeating unit cell containing 6308 atoms. ^b Two chain ends is a higher crosslinking density in the larger repeating unit cell since twice as many monomers were present. Four chain ends results in the same crosslinking density as two chain ends given in the smaller unit cell containing 3154 atoms.

Glass transition temperatures (T_g) were obtained by annealing MD simulations. The crosslinked structures were first heated to 600 K and were performed for 200 ps with constant pressure (NPT ensemble) simulations to relax the structures. These equilibrated structures at 600 K were cooled to 300 K at a rate of 50 K/200 ps at atmospheric pressure by the Berenson barostat method. MD determinations of glass transition temperatures are described well in the literature [16]. Density versus temperature plots for three crosslinked systems, all at 98% conversion, are shown in Fig 4. Two plots are shown for resins cured by Method 1 with 20 chain ends and two chain ends. T_g occurs where the slopes intercept at 424 K for the resin cured by Method 1 with 20 chain ends (98% conversion). Increasing the crosslink density by reducing the number of chain ends to two resulted in a $T_g = 426$ K. Finally, for the single chain growth cured resin (Method 2) with two chain ends, $T_g = 426$ K. This is close to the values obtained using Method 1 (424K, 426 K). The experimental T_g for Derakane 441-400 VE resin is $T_g = 410$ K. The calculated T_g values are not particularly sensitive to the crosslinking densities in these example resins. The glass transition temperatures for resins cured with both 20 and two chain ends structures are very similar at the same 98% conversion values. Ziaee *et al.* [5] showed that T_g values for post-cured VE systems were constant, regardless of which initial isothermal cure temperature was used. However, different initial cure conditions will influence the 3D polymer structure and conformations. This implies that the glass transition temperature was most strongly affected by the final degree of conversion. Therefore, T_g may be more related to the degree of conversion than to the crosslink density.

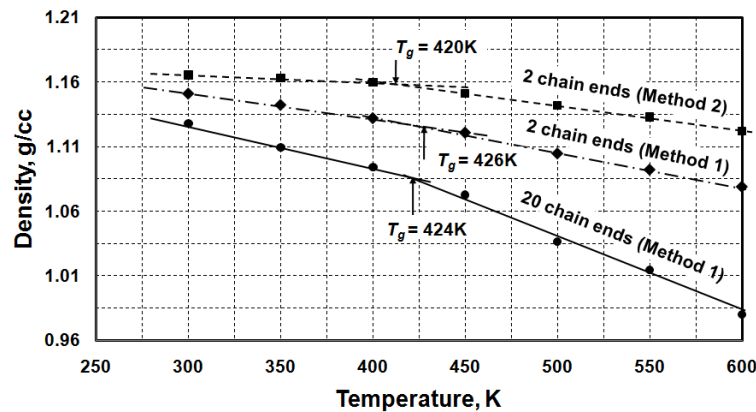


Figure 4. Glass transition temperature (T_g) for cured VE resins simulated by Methods 1 and 2 at 98% conversion. T_g values from Method 1 with different crosslink densities are very close to each other and also close to that predicted by Method 2. The experimental T_g for Derakane 441-400 VE resin is 410 K.

The isotropic Young's modulus was calculated for each of the final cured crosslinked VE structures. The Young's moduli for the series of VE resins at a constant 98% conversion cured by multiple chain growth (Method 1) are shown in Table 2 for increasing crosslink density. Increasing the matrix's connectivity with more crosslinks enhances its stiffness, with the Young's modulus increasing from 3.95 GPa to 5.79 GPa as chain ends were reduced to two. The simulation cannot mimic the real heterogeneous crosslinked structure of a VE resin, because micron sized periodic repeating unit cell (RUC) dimensions or larger would be needed. However, this study's approach can be used to model various homogeneous microstructure features and properties.

The Young's modulus calculated by the single chain curing method (Method 2) at 98% conversion (7.05 GPa) was about twice as high as the corresponding experimental value in Table 2. This single chain cure more closely corresponds to the way a real chain grows during VE curing. This simulation may better represent the formation of a microgel region which has a higher crosslink density than the average of the entire cured material. The experimental value represents the mechanical response of an entire heterogeneously structured experimental resin. Furthermore, the degree of conversion of the experimental resin may be less than 98% and most literature reports [16-18] do not give the percentage conversions of the monomers, making comparisons difficult. The double bond conversion degree of VE and styrene was reported to be over 90% with a high initial isothermal temperature used. Monomer conversions of 90-95% are unlikely to be as highly crosslinked as 98% conversion specimens will be.

The isothermal cure temperature affects both VE microgel regions and the continuous crosslinked matrix. Rey *et al.* [19] showed that high isothermal cure temperatures had an effect on creating small sized microgel regions. Furthermore, Ganglani *et al.* [20] showed theoretically that networks formed by high temperature initiation had more highly crosslinked matrices between the microgel domains, leading to the greater tensile strength. Finally, all structural features depend on the stoichiometry and structure of the monomers used.

Table 2. Young's modulus by VE resins cured by Method 1 and 2 to 98% conversion. Effect of crosslink density^a.

Curing Method	Chain ends present	Tensile modulus (Gpa)
1	20	3.95
1	16	4.11
1	8	4.94
1	2	5.79
2	2	7.05
Experimental VE result ^b	—	3.40

^a The VE resin models used in this work mimicked those in Derakane 441-400 VE resin. The multiple chain (Method 1) and single chain (Method 2) growth methods used here were progressively advanced curing to the point where the number of chain ends was two. Crosslink density continuously increases as the number of chain ends is lowered from 20 to 2. ^b Ashland Co. <http://www.derakane.com/derakaneControllerAction.do?methme=showTechnicalsDataSheets> (date accessed: March 19, 2012)

IV. Conclusions

The curing of vinyl ester (VE) resin, Derakane 441-400, was simulated by MD, employing an algorithm which, for the first time, enforces regioselectivity (head-to-tail chain growth), and monomer reactivity ratios. Thermodynamic and mechanical properties calculated represent homogeneous sections of cured VE. Thus, they do not represent yet the true extended nonhomogeneous network structure of real VEs. An immediate application of this chain growth algorithm is to study the copolymerization of two monofunctional monomers with quite different relative reactivity ratios. In such copolymerizations, the initially formed copolymers have a significantly different M_1/M_2 ratio and different triad and tetrad microstructural features due to monomer drift during conversion. Throughout the course of radical chain polymerizations, the individual polymer molecules which form at different points during the process have different individual compositions (ratios of the different monomers and specific monomer sequence distributions). This occurs due to the monomer composition drift as a function of conversion. It is the blend of all these individual polymer molecules that determine the final material properties.

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