Molecular dynamics simulation of vinyl ester resin crosslinking

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I. Introduction

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. Then the thermodynamic and mechanical properties were calculated as a function of crosslink density. In this study, a new algorithm was developed to generate the crosslinking network with real chemical features incorporated, including the correct regioselectivity (head-to-tail chain propagation), and the actual monomer reactivity ratios. These have not been yet employed in previous simulations. Most previous crosslinking simulations have been performed on epoxy resins which are step-growth type polymerizations. Vinyl esters, in contrast, cure by free radical chain polymerizations. In this study, vinyl ester crosslinking networks with conversions up to 98% were successfully achieved. Properties calculated include volume shrinkage, glass transition temperature, coefficient of volumetric thermal expansion and tensile elastic constants of the equilibrated structures, 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.

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 airplanes and 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

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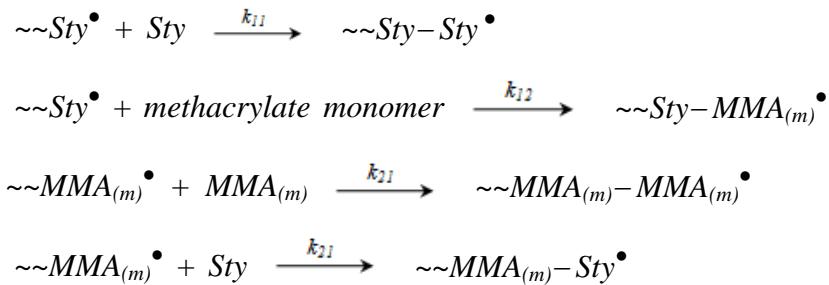[4] Professor, Chemistry, Mailstop 9573 Hand Laboratory Rm 3337 Mississippi State, MS 39762

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separate 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 sizes and need for continuous repeating unit cells. Real cured vinyl ester materials are inhomogeneous at the micro level. MD simulation can, however, be a tool to study the properties of homogeneous regions of cured VE resins as has done for the epoxy resins (i.e. EPON-862) crosslinking networks [7-9]. An atomistic simulation of a 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 rapidly. Then, as the crosslink density further increases, the rate of monomer diffusion drops and the relative 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 present in VEs) are present, the terminal polymerization model (Eq. 1) is a good approximation [13, 14].

$$dM_1 / dM_2 = \frac{M_1(r_1 M_1 + M_2)}{M_2(r_2 M_2 + M_1)} \tag{1}$$

In the current case, M_1 is styrene and M_2 is the vinyl ester methacrylate molecule(s). Four reactions determine the rate of incorporation of the two different monomer types in the terminal polymerization model.

$$\sim\sim Sty^\bullet + Sty \xrightarrow{k_{11}} \sim\sim Sty - Sty^\bullet$$

$$\sim\sim Sty^\bullet + methacrylate\ monomer \xrightarrow{k_{12}} \sim\sim Sty - MMA_{(m)}^\bullet$$

$$\sim\sim MMA_{(m)}^\bullet + MMA_{(m)} \xrightarrow{k_{21}} \sim\sim MMA_{(m)} - MMA_{(m)}^\bullet$$

$$\sim\sim MMA_{(m)}^\bullet + Sty \xrightarrow{k_{21}} \sim\sim MMA_{(m)} - Sty^\bullet$$

However, only the relative 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 of each type of monomer's incorporation into the polymer. An algorithm that reflects these rate constant ratios (r_1, r_2) for styrene and the methacrylated 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

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chemical equations). Thus, the algorithm used must also enforce this selectivity to achieve the correct molecular structure along the polymer chains.
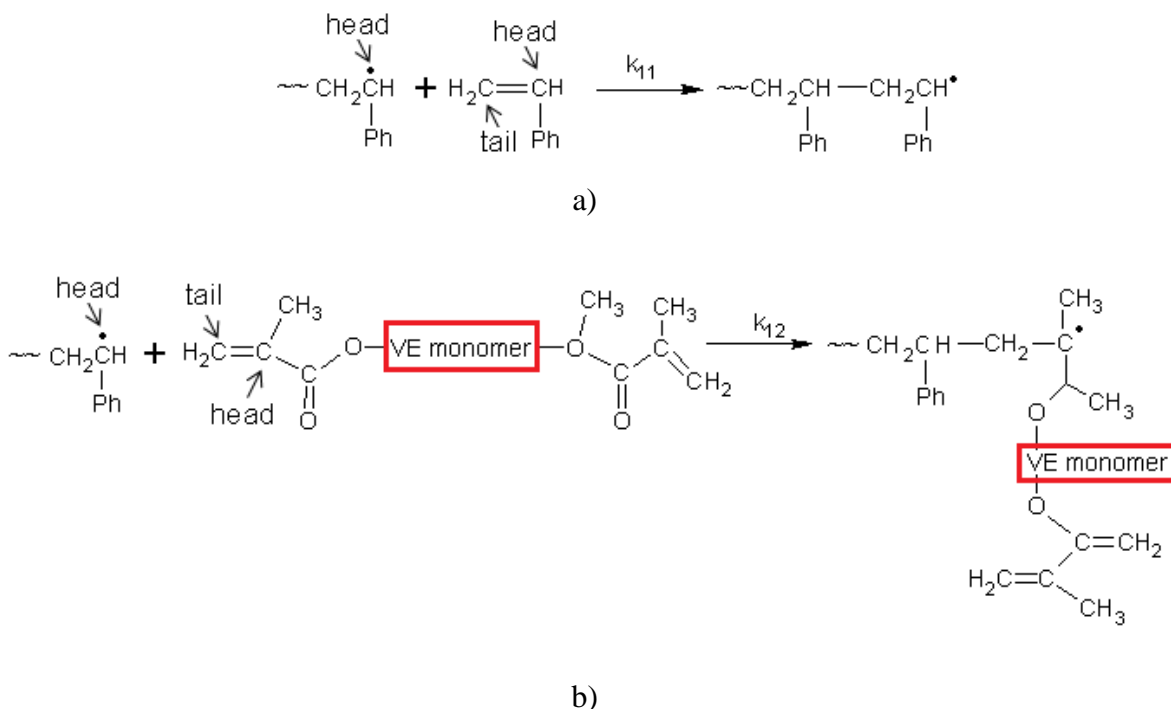

a)

b)

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

The faster rate of the growing chain $\sim Sty^{\bullet}$ 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 criteria 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 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 (3153 atoms) including 68 styrenes, 8 VE1 and 13 VE2 molecules were used in the simulation, corresponding to 33 wt% of styrene.
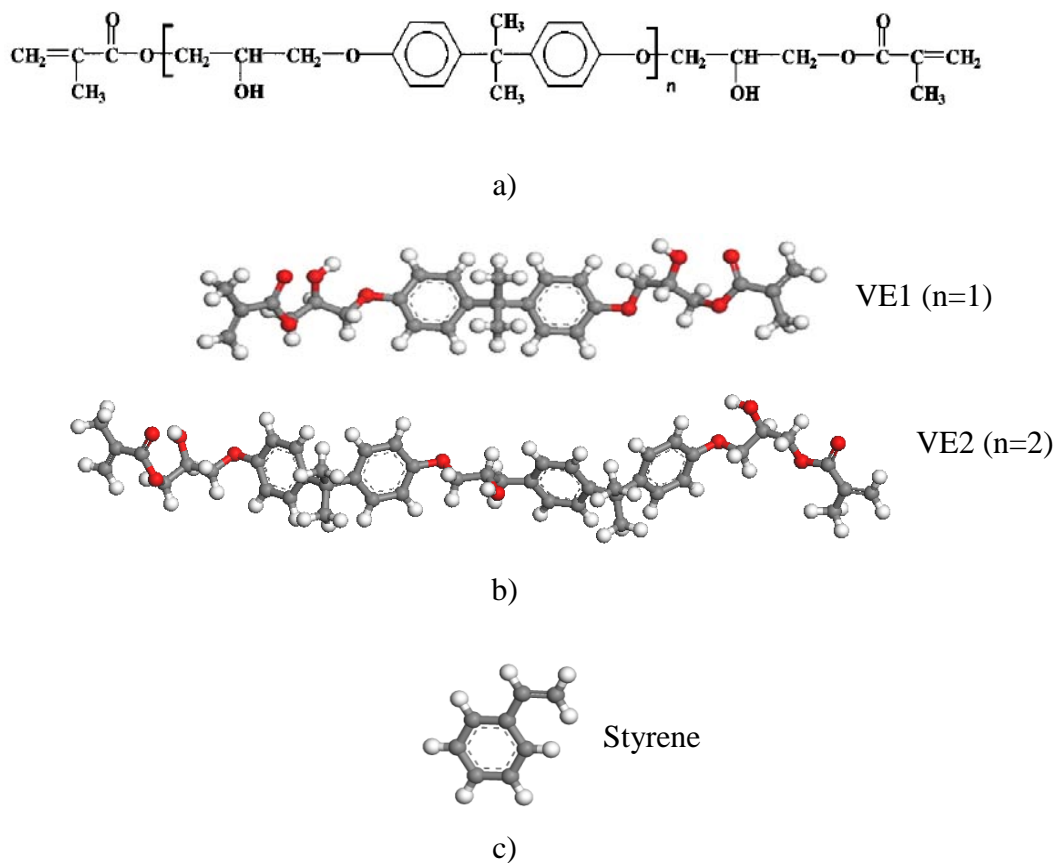

a)

 VE1 (n=1)

 VE2 (n=2)

b)

 Styrene

c)

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 Material Studio v5.0.

All molecular dynamics (MD) crosslinking simulations were performed with energy minimization (EM), NVT (constant volume and temperature) and NPT (constant pressure and temperature) at 300 K. The crosslinking simulations considered: 1) monomer reactivity ratios, 2) regioselectivity (head-to-tail chain growth) and 3) close-distance criteria. In order to apply monomer reactivity ratios into 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 value.

III. Results

A crosslinked vinyl ester resin was successfully generated with high conversion where 98% of the double bonds were consumed. This conversion is reasonable, because a full conversion not obtained experimentally even with extended post curing. Two methods were used to grow the

crosslinked system. (1) A single chain 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. This method is computationally intensive because the diffusion process slows with increasing conversion, accompanied by higher crosslinking density. (2) The second method involves starting a new chain when growth of the first chain slows. When the growth of the second chain slows, a third chain is initiated. This process is continued until 98% conversion is 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 was 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. Mechanical properties were then computed for this series of cured resins. 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.
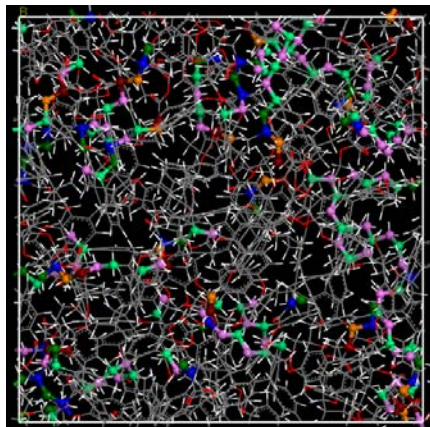

Figure 3. A crosslinked model of molecular system generated by method two at 98% conversion with 2 chain ends remaining that were capped by hydrogen.

Density and volume shrinkage were computed versus conversion (for curing by method 2) and also at 98% conversion versus the number of chain ends remaining. Derakane 441-400 vinyl ester resin was reported to shrink 7%[1] after curing. This value was obtained from a data sheet provided by Ashland Co. The final volume shrinkage computed here 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 was 6.4%. The volume contractions are listed in Table 1.

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[1] http://www.derakane.com/derakaneControllerAction.do?method=showTechincalDataSheets

Table 1. Volume shrinkage as curing proceeds by method two as a function of conversion to 98% followed by increasing crosslink density by combining chain ends progressively.

Conversion (%)	Number of chain ends	Volume (Å^3)	Volume shrinkage (%)
Initial liquid system		33732.7	
78	48	32749.1	2.9
86	30	32357.5	4.1
90	22	32262.5	4.3
98	20	32153.5	4.7
98	2	31559.6	6.4

Glass transition (T_g) temperatures were obtained by annealing MD simulations. The crosslinked structures were heated to 600 K and then the constant pressure (NPT ensemble) simulations were performed for 200 ps to relax the structure. This equilibrated structure was cooled to 300 K at a rate of 10K/200 ps at atmospheric pressure by the Berenson barostat method. MD determinations of glass transition temperatures are well described in a literature [16]. Density versus temperature plots are shown in Fig 7. The T_g occurs at the intercept of the two slopes at 424 K for the resin with 20 chain ends (98% conversion). Increasing the crosslink density by reducing the number of chain ends to two gave $T_g =$ K. The experimental T_g for Derakane 441-400 VE resin (410 K) is compared with the simulated T_g in Fig 4. The tensile modulus for the series of VE resins cured by method two are shown in Table2 for increasing crosslink densities, all at 98% conversion. The increasing crosslink densities are indicated by the decreasing number of chain ends, from 20 to 2.
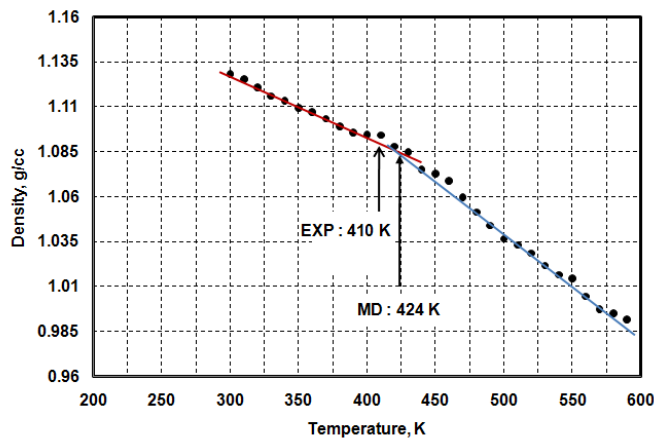

Figure 4. Glass transition temperature (T_g) for cured vinyl ester simulated at two crosslink densities, both at 98% conversion. The experimental T_g value found for Derakane 441-400 was from a data sheet provided by Ashland Co.

IV. Conclusions

The curing of vinyl ester (VE) resin, Derakane 441-400, was simulated by MD, employing algorithm which, for the first time, enforces regioselectivity (head-to-tail chain growth), and monomer relativity ratios. Properties calculated represent homogeneous sections of cured VE. Thus, they do not represent yet the true extended inhomogeneous network structures of real VEs. This new algorithm can be employed for other thermoplastic or thermoset systems.

Acknowledgments

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