

Analysis of Computer-synthesized Cross-linked Polymers Using the ReaxFF Force Field

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Abstract

The purpose of this study is to analyze the results of computer-synthesized cross-linked polymers using the ReaxFF force field. Monomers from glycidyl derivatives of 3,5,7,3'4'-pentahydroxyflavone (quercetin) cured with diethylenetriamine (DETA) were used for polymer synthesis. The ReaxFF method was chosen for its effectiveness in simulating chemical reactions and molecular dynamics in complex systems. It is known for its ability to capture intricate reaction mechanisms. The study found that the choice of geometry optimization method had a significant impact on polymer densities. The FIRE method yielded the best results. Calculated values for the densities and glass transition temperatures (T_g) of the resulting polymers showed good correlation with experimental data, indicating the method's reliability in predicting certain physical properties. The investigation highlights the importance of accurately interpreting the chemical structure of cross-linked polymers in computer simulations to predict their properties.

Keywords

Cross-linked polymers; molecular dynamics; crosslinking simulation; thermomechanical properties; reactive force field

1. Introduction

Currently, there is a high demand for functional materials with specific physical and chemical properties in various industries [1-6]. Special attention is given to developing functional materials using cross-linked polymers [7-11]. This is because cross-linked polymers have high manufacturability, a wide range of physicochemical properties, and good long-term stability. Given the importance of using cross-linked polymers and functional materials based on them in various fields of industry, the design and synthesis of such polymers are very crucial tasks.

However, designing and synthesizing functional materials with the necessary properties for a specific application can be a long and expensive process. Therefore, computer simulation methods are widely used to expedite the discovery of new functional materials and reduce costs. To achieve accurate results through computer simulation that correlate well with experiments, it is crucial to use the correct algorithms. This is particularly important for cross-linked polymers that have both a chemical (3D) network and a physical network formed by intramolecular hydrogen bonds between different functional groups in the monomers.

Polymers based on glycidyl derivatives of 3,5,7,3'4'-pentahydroxyflavone (quercetin) are promising for obtaining new functional materials. These polymers have various advantages that make them suitable for use in photonics, optoelectronics, analytical chemistry, and other fields. Additionally, they are environmentally friendly and can be synthesized from renewable sources of raw materials [12].

Based on the above, the purpose of the investigation was to synthesize cross-linked polymers using computer technology, specifically glycidyl derivatives of quercetin. 3'-triglycidyl-3,5-dihydroxyflavone (3GEQ) and 7,3,4',3'-tetraglycidyl-5-hydroxyflavone (4GEQ), cured with diethylenetriamine (DETA) through molecular

dynamics (MD) simulations. The results were analyzed by assessing physical parameters of the polymers, such as density (ρ) and glass transition temperature (T_g), and comparing the calculated data with experimental data.

ReaxFF (Reactive Force Field) is a method for molecular dynamics that enables effective calculation. Previous articles have investigated epoxy resin based on bisphenol A (DGEBA) with a hardener DETA using this method, and a good correlation was obtained [13]. Therefore, ReaxFF was chosen to compare theoretical calculations with the already obtained experimental ones. The computer simulation method is used to study chemical reactions and molecular dynamics in complex systems, including chemical reactions, surfaces, and molecular dynamics under various conditions. This method is particularly useful for studying complex reaction mechanisms that may be difficult to model using traditional methods [15-20]. ReaxFF is a parameterized force field that considers reactive potentials between atoms in a molecule, including electrostatic, valence, and non-valence interactions. The parameters of ReaxFF are trained using experimental data and/or quantum-chemical calculations, which allows for the consideration of chemical reaction specificity in various systems.

The ReaxFF is a powerful molecular dynamics tool that fills the gap between classical force fields and quantum chemical methods. It preserves the computational efficiency of traditional models while allowing the modeling of bond breaking and bond formation (intra- and inter-molecular bonds), which is necessary for correct modeling of the synthesis of cross-linked polymers. Thus, today, the ReaxFF is one of the powerful methods to precisely calculate the cross-linked polymers. The ReaxFF method has a great result for epoxides to study reaction mechanisms involving epoxy (glycidyl) groups, including ring opening, polymerization, post-cured reactions, and other processes. This method can help understand the kinetics and thermodynamics of these reactions, as well as the influence of various conditions, such as temperature and pressure, on the chemical modification of cross-linked polymers obtained with epoxy chemistry [21-23].

2. Experimental part/methods

2.1 Materials

The glycidyl derivatives of quercetin, namely 7,4'-diglycidyloxy-3,5,3'-trihydroxyflavone (2GEQ), 7,4',3'-triglycidyloxy-3,5-dihydroxyflavone (3GEQ), and 7,3,4',3'-tetraglycidyloxy-5-hydroxyflavone (4GEQ), were used for computer simulation [13]. The curing agent used was diethylenetriamine (DETA). The chemical structures of the monomers are shown in Figure 1.

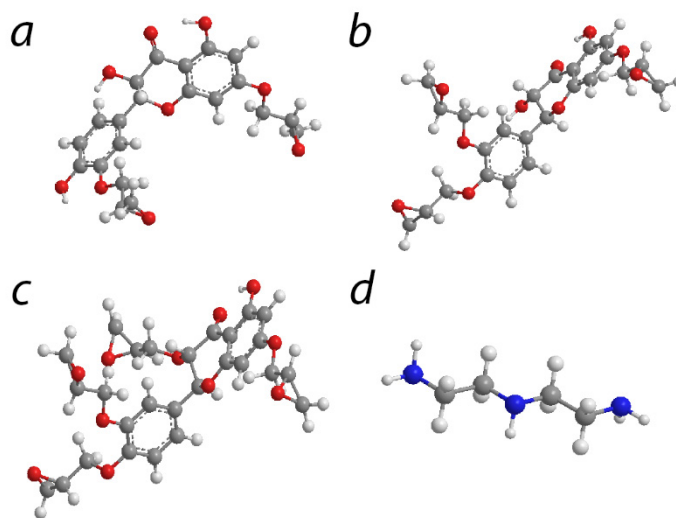


Figure 1. Chemical structures of monomers and harder for: computer synthesis a) 7,4'-diglycidyloxy-3,5,3'-trihydroxyflavone (2GEQ); b) 7,4',3'-triglycidyloxy-3,5-dihydroxyflavone (3GEQ); c) 7,3,4',3'- tetraglycidyloxy -5- hydroxyflavone (4GEQ); d) N^1 -(2-Aminoethyl)ethane-1,2-diamine (DETA).

2.2 Computer details and simulation procedure

The reaction between the epoxide (glycidyl) compounds and the amines was studied by ReaxFF, which is included in the program package Amsterdam Model Suite (AMS) developed by Software for Chemistry & Materials, using

the CHNO-2017_weak45 force field, which was re-optimized for this purpose. For the study, model polymers were used, consisting of 20 monomer units and 10 hardener molecules [15, 16]. The lattice vectors for the simulation box were $32 \text{ \AA} \times 32 \text{ \AA} \times 32 \text{ \AA}$. This force field was developed to improve the description of weak interactions between functionalized hydrocarbons and water in the condensed phase. It has been demonstrated to accurately reproduce the properties of functionalized hydrocarbon systems and hydrocarbon-water mixtures. The force field reparameterization procedure maintained the hydrocarbon and water molecule parameters from the CHON-2017_weak force field without changes. However, the C-O, C-N, and N-H bond terms, angle terms of oxygen and nitrogen atoms, and the nitrogen hydrogen bonding parameters were optimized to improve their ability to reproduce coupling reactions between epoxide and amine [16, 24]. The calculations also considered the influence of the hydrogen bond H-O. The bond lengths between nitrogen and carbon remained unchanged, with an R_{\min} of 2.5 \AA and an R_{\max} of 4.0 \AA . For carbon and oxygen, the bond lengths ranged from 1.2 \AA to 3.0 \AA , while for oxygen and hydrogen, the hydrogen bond lengths ranged from 3.0 \AA to 5.5 \AA . The force parameters (R_{12} , F_1 , and F_2) for the bonds were as follows: O-C with 1.95 \AA , 313.8 kJ/mol , and 0.75 \AA^{-2} ; O-H with 1.05 \AA , 1046 kJ/mol , and 0.75 \AA^{-2} ; and C-N with 1.5 \AA , 1255.2 kJ/mol , and 0.75 \AA^{-2} . All reactions were conducted during NVT simulations using a Berendsen thermostat with a temperature damping constant of 100 fs .

The computer synthesis time was increased by 150,000 steps, which allows to chemical reaction to proceed completely. Time of 1 step is 0.25 fs . Following the main procedure, the FIRE method (fast internal relaxation method) was used for geometry optimization before the annealing procedure. This method was chosen because it gives the best correlation between theoretical and experimental data. The annealing procedure was carried out three times in the temperature range of 298.15 to 598.15 K . Each annealing cycle involved heating up by 25 K over $30,000$ steps and sampling the density over $10,000$ steps. The process was repeated until reaching 598.15 K , then reversed to cool down to 298.15 K again.

The polymer's density was calculated after each annealing procedure. The glass transition temperature was determined by finding the intersection of two straight lines fitted by linear regression to the densities for the first and last five temperatures [16].

The accuracy of the results was verified by comparing the density and glass transition temperature of the obtained polymers to the experimental ones.

3. Results and discussion

The process of synthesizing cross-linked polymers based on glycidyl derivatives of quercetin and amines involves an open-ring polymerization process between the two groups [14]. The interaction between amines and glycidyl groups can be simplified as follows:

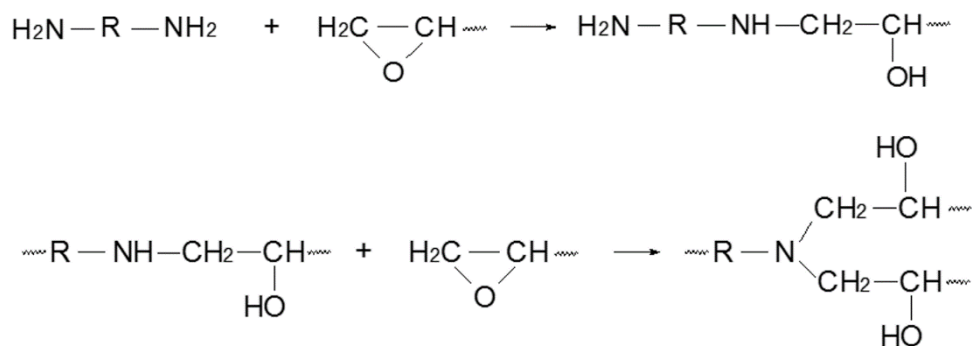


Figure 2. The open-ring polymerization scheme of glycidyl group-containing monomers with amines.

The secondary amino group reacts with the epoxy (glycidyl) group to form a three-dimensional polymer network (Figure 2). If the initial monomer has other reactive groups (such as hydroxyl or carboxyl), it can also form a physical network of intramolecular hydrogen bonds in addition to the main chemical network.

Computer synthesis results indicate that the resulting polymers have very low densities of 261 kg/m^3 , 261 kg/m^3 , and 371 kg/m^3 for poly(2GEQ), poly(3GEQ), and poly(4GEQ), respectively, at the end of the main cross-linking reaction. Furthermore, altering the reaction time from $150,000$ steps to $250,000$ steps does not increase the density values. Consequently, the next step involved optimizing the geometry of the macromolecules using the FIRE method.

The FIRE method is the most suitable for optimizing geometry before the hardening procedure. Figure 3 displays the cross-linked structure of the polymers after the annealing procedure. After optimizing geometry using this method and carrying out the triple quenching procedure, the density of the resulting polymers reached the maximum values shown in Table 1. However, experimentally determined polymer densities are higher than those shown in Table 1.

The low-density values of polymers obtained through computer modeling can be attributed to the presence of reactive glycidyl also hydroxyl groups in quercetin-containing polymers. These groups create two types of networks: a physical network based on intramolecular hydrogen bonds and a chemical network formed during polymerization. According to the information provided, the total polymer density is the combination of the physical and chemical network densities. However, the ReaxFF force field does not consider the physical density component, resulting in an underestimation of the synthesized network polymers' densities.

To overcome the ReaxFF limitation, the force field algorithm should be modified to accommodate both types of networks.

Table 1. Parameters of synthesized crosslinked polymers

Polymers	ρ_{calc} , kg/m ³	ρ_{exp} , kg/m ³	$T_{g(\text{calc})}$, K	$T_{g(\text{exp})}$, K
poly(2GEQ)	1325	1595	466	391
poly(3GEQ)	1312	1539	465	390
poly(4GEQ)	1299	1540	458	353

Based on the computer synthesis data, the glass transition temperatures of the studied simulated polymers were determined according to the method described earlier using the plot of the dependence of densities vs. temperature [16].

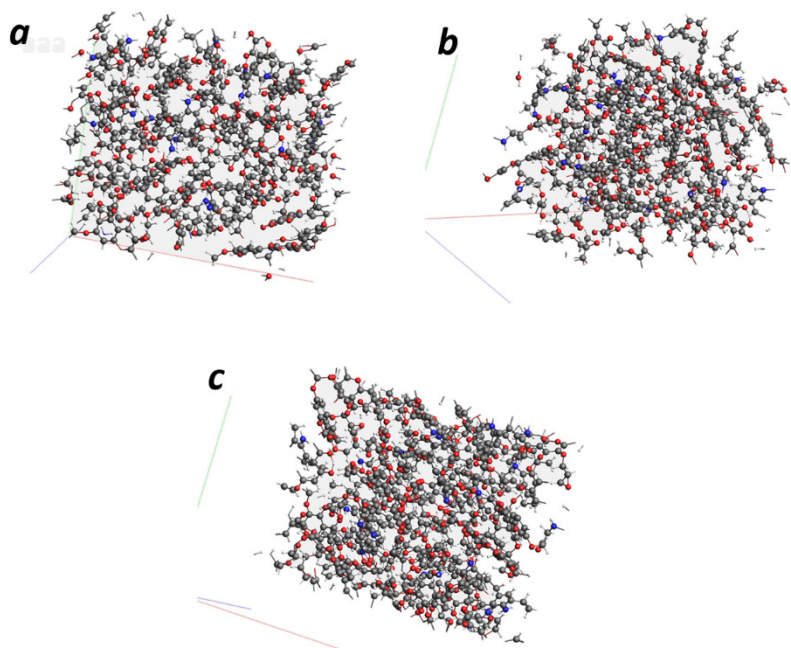


Figure 3. The crosslinked structure of polymers based on glycidyl ethers of 3,5,7,3'4'-pentahydroxyflavone after the annealing procedure: a) poly(2GEQ), b) poly(3GEQ), c) poly(4GEQ).

The glass transition temperature (T_g) (refer to Table 1) exhibits an opposite trend. The calculated T_g values are higher than the experimentally determined values. It is important to note that the experimentally determined T_g values of polymers are influenced by various factors such as pressure, heating rate, measurement methods, and peculiarities in the chemical structure. This confirms the assumption that the physical network of hydrogen bonds has an influence on the T_g values. The physical network only exists at low temperatures and does not significantly

affect the determination of the glass transition temperature of the synthesized polymers. A comparative analysis of calculated and experimental data shows that although the densities and glass transition temperatures of polymers differ, the trends between polymers remain unchanged. For example, poly(4GEQ) has the lowest T_g values among the three, suggesting that it may have a lower bulk density or a higher cross-link density.

To evaluate the agreement between calculated and experimental data, the Pearson coefficient was utilized. This coefficient measures the directionality of the relationship between two values. Figures 4 and 5 display the correlation between experimental and calculated data for determining the densities and glass transition temperatures of network polymers based on glycidyl ethers of quercetin. The comparison of experimental and calculated data reveals a strong linear correlation.

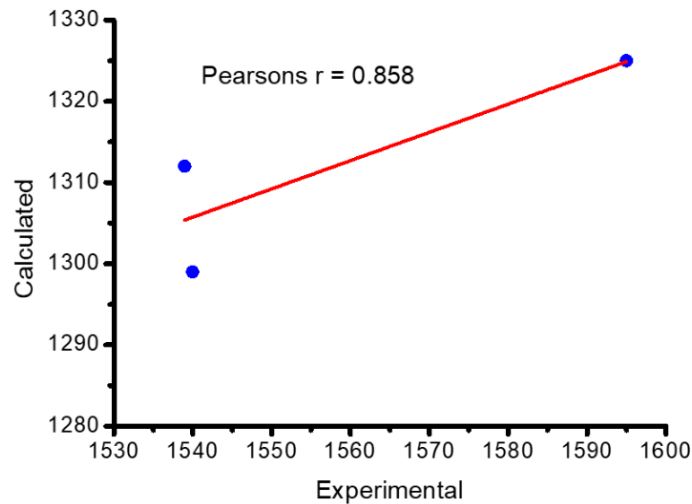


Figure 4. The correlation between experimental and calculated data for determining cross-linked polymer densities (ρ).

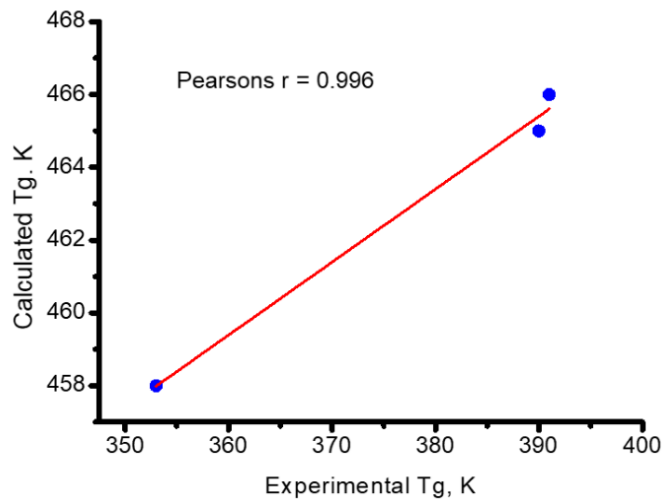


Figure 5. The correlation between experimental and calculated data for the determination of the cross-linked polymer glass-transition temperatures (T_g).

4. Conclusion

Thus, based on the conducted research, we can conclude that the use of ReaxFF force field in the computer synthesis of cross-linked polymers provides valuable insights for predicting the complex process of polymerization. This method adequately predicts some physical properties, such as glass transition temperature and density. However, discrepancies in the values of these physical parameters suggest limitations in accounting for the contribution of physical networks that exist in ReaxFF. The FIRE optimization method showed good results, highlighting the need for careful selection of simulation parameters. The correlation between experimental and calculated data was

approximately 0.85-0.9, confirming the reliability of the approach and its potential to guide experimental efforts in polymer design. Theoretical calculations are a promising and attractive alternative to experiments for predicting the chemical properties of crosslinked polymers with sufficient accuracy.

The findings of this study highlight the potential of reactive molecular dynamics simulations using ReaxFF as a powerful tool for predicting key physical and thermal properties of cross-linked polymers prior to their experimental synthesis. This computational approach offers a cost-effective and time-efficient strategy for designing advanced polymeric materials with tailored properties, particularly from renewable and environmentally friendly sources. Future research should focus on improving force field accuracy for systems with physical and chemical networks and improving optimization mechanisms for getting more precise data. From an industrial perspective, this methodology can be used to accelerate the development of a crosslinked polymer system with specified properties.

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