



## Research paper

# A multiscale model for the synthesis of thermosetting resins: From the addition reaction to cross-linked network formation

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## HIGHLIGHTS

- A multi-scale model simulated the influence of conditions on thermosetting resins.
- We simulated the effect on the structure and physical properties.
- We focused on the synthesis of the phenol formaldehyde resin.
- The comprehensive reaction model included the addition and condensation reactions.
- The effectiveness of the reported model was validated.

## ARTICLE INFO

## Keywords:

Thermosetting resin  
Multiscale model  
Polymerization  
Cross-linked network  
Molecular dynamics

## ABSTRACT

A multi-scale model that can simulate the influence of the synthetic conditions (e.g., molar ratio) on the structure and physical properties of thermosetting resins (e.g., phenol resin) through the introduction of a comprehensive reaction model that includes the addition reaction was developed and reported herein. The effectiveness of the model was validated by verifying the influence of the primary synthetic index, i.e., the molar ratio, on the physical and thermal properties (i.e., density and glass transition temperature) of Resol resins. This model can aid in developing more efficient and suitable synthetic conditions to obtain products exhibiting the desired material properties.

## 1. Introduction

As a class of synthetic thermosetting polymers, phenol resin exhibits a range of properties determined by the chemistry of its constituent monomers and how these monomers combine with each other in a three-dimensional network structure upon heating [1]. Compared to the continuum model, atomic-level simulations enable us to examine this cross-linking process and obtain information relating to the microscopic response from the fundamental chemical structure and the dynamics of each atom, which ultimately determine the macro-mechanical properties of the polymer. Indeed, several groups [2,3] have employed atomic-level molecular dynamics (MD) simulations to discuss the physical properties of phenol resin. However, all previous models have ignored or simplified the chemical reaction process, where the linear polymer chain has been directly used as the initial molecule

in the system, or where the reaction is considered to be a direct condensation reaction, thereby rendering examination of the influence of the synthetic conditions rather challenging. Thus, the effect of the molar ratio and the monomers employed on the prepolymer size cannot be predicted. Due to the influence of these factors on estimation of the physical properties (e.g., density and glass transition temperature [4]) of a polymer, the importance of the addition reaction to the cross-linked structure appears to have been underestimated.

A model which can discuss the influence of the synthetic conditions is therefore required. More specifically, this model should be able to clarify the relationship between the synthetic conditions, the resulting polymeric structure, and the physical properties. We also expect that this could reduce the cost of the synthetic process, while allowing the design of resins exhibiting desirable properties.

In recent years, very few studies have focused on the synthetic

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<https://doi.org/10.1016/j.cplett.2019.02.012>

Received 18 September 2018; Received in revised form 3 February 2019; Accepted 4 February 2019

Available online 14 February 2019

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model due to the difficulty in representing the chemical reaction that results in formation of the three-dimensional cross-linked structure [5]. In 2001, the reactive force field ReaxFF [6] was developed for MD simulations to enable chemical reactions involving bond formation and breakage to take place. However, such simulations are particularly time consuming. The large-scale model is only employed to simulate systems containing  $\sim 10,000$  atoms [7]. This contrasts to the nonreactive force field, which can be applied to billion atoms systems [8]. Another approach is the use of Monte Carlo (MC) simulations, which have been employed since the 1950s for building polymer networks. One of the main advantages of MC over MD simulations is that the MC simulations are rapid, even for fully atomistic modeling [9]. Notably, MC models based on kinetic theory are becoming popular [10,11], as such models built for polymer networks can be used to represent the various distributions of the final product following the polymerization reaction. However, the chemical reaction hypothesis based on sphere capture is limited, as description of the non-bonded interactions between atoms is challenging, and these interactions play a crucial role in describing the physical cross-linking reaction and the resulting configuration. In contrast, the use of MD models with a force field based on van der Waals and electrostatic interactions can solve this problem.

Thus, to address the above issues, we herein report the development of a multi-scale model based on quantum chemistry calculations, MC simulations, and MD simulations to reproduce the polymerization process of phenol resin. Indeed, the MC/MD model is identical to that previously presented by our group for the cross-linked epoxy resin [12,13]. However, in this case, we adopt a complex reaction model based on quantum chemistry combined with the MC/MD model. More specifically, we consider the two reaction steps involved in the polymerization process [14], namely the addition of formaldehyde to the *ortho*- and *para*-phenol positions, and the subsequent condensation reaction. Furthermore, a range of monomer molar ratios are examined due to the importance of this variable in determining the network cross-linking structure [15].

## 2. Materials and methods

### 2.1. Formation of a Resol resin

Although the highly cross-linked phenol formaldehyde (PF) resin is commercially valuable, once the highly intractable network has been formed, it cannot be molded due to the irreversible changes involved in its formation. The preparation process is therefore carried out in two stages, namely preparation of the prepolymer, and subsequent growth polymerization. More specifically, the desired prepolymers are firstly obtained in an alkaline medium through the reaction of formaldehyde with the *ortho*- and *para*-positions of the phenol substrate, as shown in Fig. 1(a). Subsequently, during growth polymerization, the cross-linked network structure is formed through condensation of the prepolymers and the elimination of water, as indicated in Fig. 1(b).

### 2.2. Quantum chemistry simulations for the activation energy

We initially studied the reactions at the *ortho*- and *para*- positions of phenol using the transition state theory. The activation energy of these reactions was elucidated using the Molecular Orbital method, with the HF/3-21G level of theory being employed for the transition state. The solvation environment was mimicked by implicit water molecules (i.e., the solvent) using the polarizable continuum model (PCM) [16] in a quantum chemistry package program, Gaussian 09 [17]. Detailed information regarding the method employed is summarized in Table 1. The geometric structures for formaldehyde ( $\text{H}_2\text{CO}$ ), phenoxide ion ( $\text{C}_6\text{H}_5\text{O}^-$ ), and the reaction products ( $\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{OH})^-$ ) were optimized, and frequency calculations were used to confirm all structures were at their true minimums. The kinetics of the reaction were then revealed by optimizing the transition state of the reaction, where

intrinsic reaction coordinate calculations were carried out to confirm the reaction pathway. In addition, the Global Reaction Mapping Method (GRRM) was employed to find transition states by uphill walking from equilibrium structures by anharmonic downward distortion following algorithm [18]. The activation energies were then calculated by taking the energy difference between the transition state and the reactants. Such activation energy simulation work has also been carried out previously [19].

### 2.3. The polymerization process by MC and MD simulations

During the PF polymerization process, the different monomers react with one another to form the prepolymers, which then react to give the final polymer [15]. To reproduce this process, quantum chemistry was initially used to calculate the activation energies (the reaction energy barriers), which was converted to give the reaction probability. Subsequently, combination of the MC algorithm with the reaction probability was used to reproduce this random event. Finally, the force field theory in the MD simulation was applied to find the minimum total potential energy state of the system.

In the MC/MD simulation employed to reproduce the cross-linking reaction of the phenol resin system, the dynamics (relaxation) calculation and the recombination of covalent bonds that are associated with the reaction are repeatedly calculated as follows. Firstly, all pairs of reaction sites are determined between a phenol and a formaldehyde molecule within  $4 \text{ \AA}$  of one another, which is achieved using the radial distribution functions. Secondly, MC calculations are used to determine whether a reaction occurs for each pair or not. In this stage, the random number ( $P$ ), which ranges from 0 to 1, compares to the Arrhenius type reaction probability ( $K$ ):

$$K = A \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

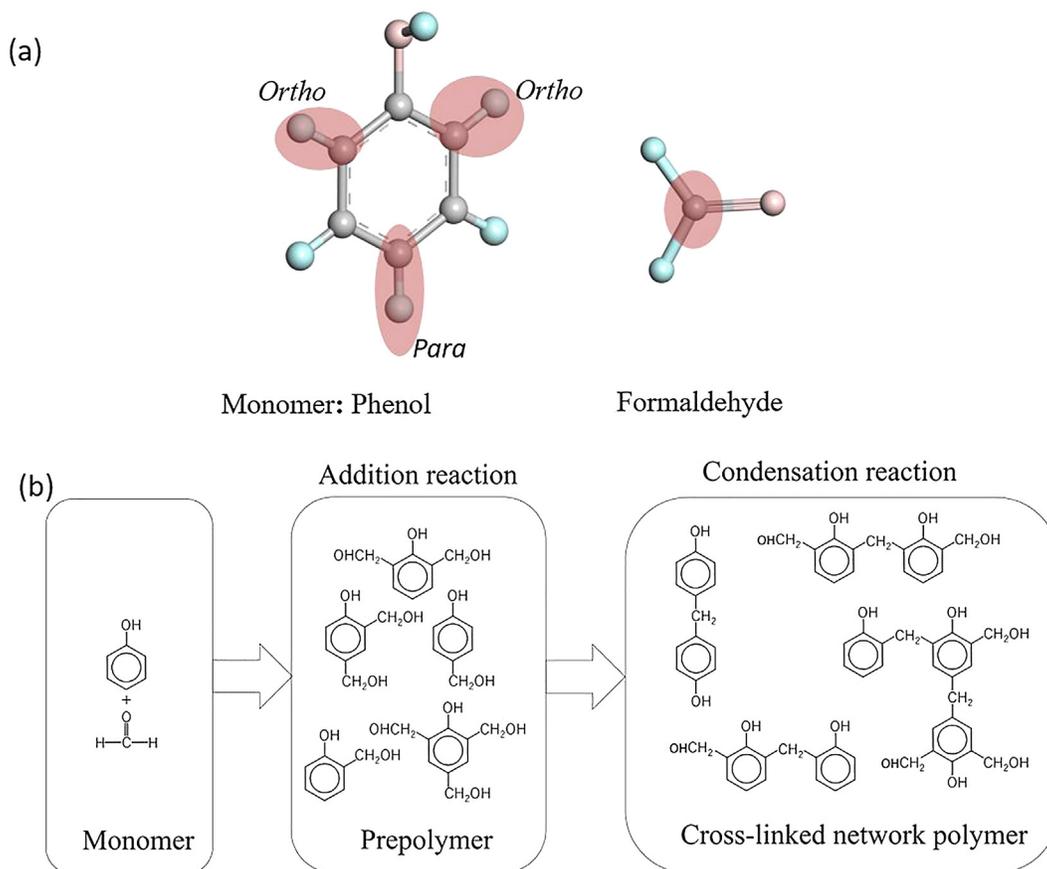
where  $R$  is the gas constant,  $T$  is the local temperature obtained from the reacting molecules,  $E_a$  is the activation energy obtained from the GRRM calculations, and  $A$  is an acceleration factor ( $10^{18}$ ) employed to bridge the time gap between an actual reaction (hour scale) and the MD simulation (picosecond scale). In the subsequent step, bond breakage and bond creation are considered to occur simultaneously if the random number is greater than the reaction probability (i.e.,  $P > K$ ). Finally, geometrical optimization and relaxation calculations for the system are performed over 2 ps. By repeating the above steps under iso-thermal (298 K) and iso-pressure (1 atm) conditions, we can obtain phenol resin systems with their corresponding curing conversions ( $\alpha$ ), which are defined by:

$$\alpha = \frac{f_{\text{react}}}{f_{\text{total}}}, \quad (2)$$

where  $f_{\text{total}}$  is the number of the phenol units in molecule before reaction, and  $f_{\text{react}}$  is that of the reacted phenol molecular during the cross-linking process. It should be noted that the water molecule formed during the condensation reaction (see Fig. 2) is omitted for simplicity.

Following the cross-linking simulation, we evaluated the thermal properties (density and glass-transition temperature) for the system with each curing conversion. The density ( $\rho$ ) is defined by the total weight of the particle to the cell volume, which is obtained by relaxation dynamics under the NPT ( $P = 1 \text{ atm}$  and  $T = 298 \text{ K}$ ) ensemble. The glass-transition temperature ( $T_g$ ) is obtained by finding the intersection temperature of two straight lines on volume vs temperature plots in which each data point is a result of the relaxation dynamics under the NPT ensemble where  $T$  is increased from 220 to 580 K while maintaining  $P$  at 1 atm.

As mentioned above, our MD simulation procedure is divided into two stages, namely the curing dynamics for obtaining the polymerization structure, and the relaxation dynamics to determine the thermal properties. In the case of curing dynamics, the COMPASS II force field



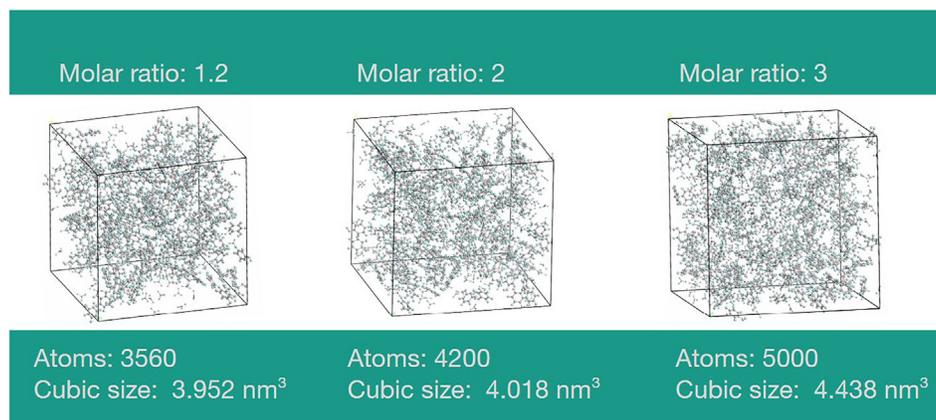
**Fig. 1.** (a) Chemical structures of the phenol and formaldehyde substrates/monomers employed for preparation of the phenol resin. The reactive positions of phenol and formaldehyde are shaded in red. (b) During the polymerization process, prepolymer formation takes place through addition reactions between the monomers. The various prepolymers then react via a condensation reaction to eliminate water and form a cross-linked network structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

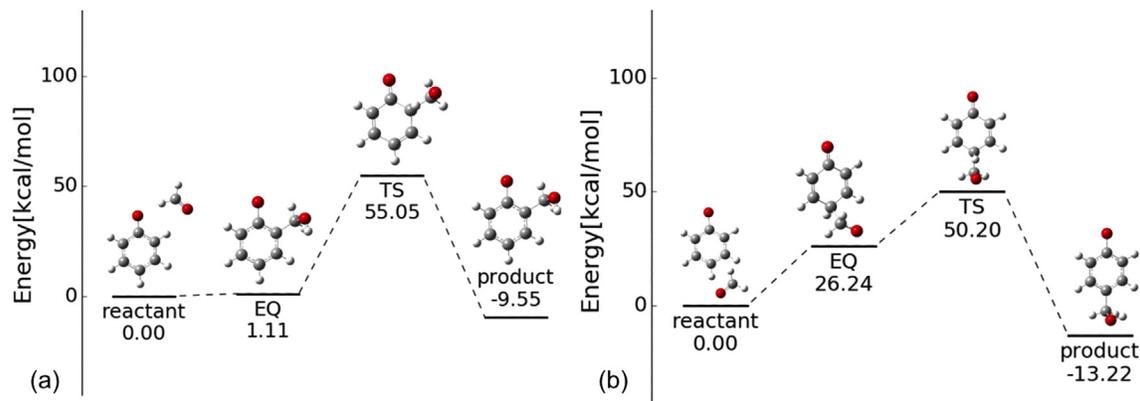
Quantum chemistry computational conditions employed based on the Molecular Orbital method for determination of the activation energy.

Calculation	GRRM11 with Gaussian09
Level of Theory	HF/3-21G
Spin	Singlet
Environment	Alkaline, Charge is -1

[21] was applied and the Materials Studio 8.0 was utilized. In contrast, to calculate the thermal properties, the TEAM force field was employed along with the LAMMPS software package. To validate the effectiveness of this quantum mechanics/MC/MD model, the influence of the primary synthetic index, i.e., the molar ratio, on the mechanical properties (i.e., the Resol glass transition temperature ( $T_g$ )) was verified. More specifically, formaldehyde/phenol molar ratios of 1.2, 1.4, 1.5, 1.6, 2, 2.5, and 3 were examined, which are the typical molar ratios employed in the synthesis of Resol resin [20], and the atom numbers of phenol was kept as constant, 2400. Fig. 2 shows snapshots of the three



**Fig. 2.** Example snapshots of each equilibrium structure in the initial conditions with molar ratios of 1.2, 2, and 3, and atom numbers ranging from 3560 to 5000. The bulk size is on the nanometer scale.



**Fig. 3.** The activation energies and heats of formation for the addition reactions as determined by GRRM calculations. (a) In the reaction at the *ortho*-position, the activation energy is 55.05 kcal/mol and the heat of formation is 9.55 kcal/mol. (b) In the reaction at the *para*-position, the activation energy is 50.20 kcal/mol and the heat of formation is 13.22 kcal/mol.

equilibrium structures in the initial conditions with different molar ratios and atom numbers.

### 3. Results and discussions

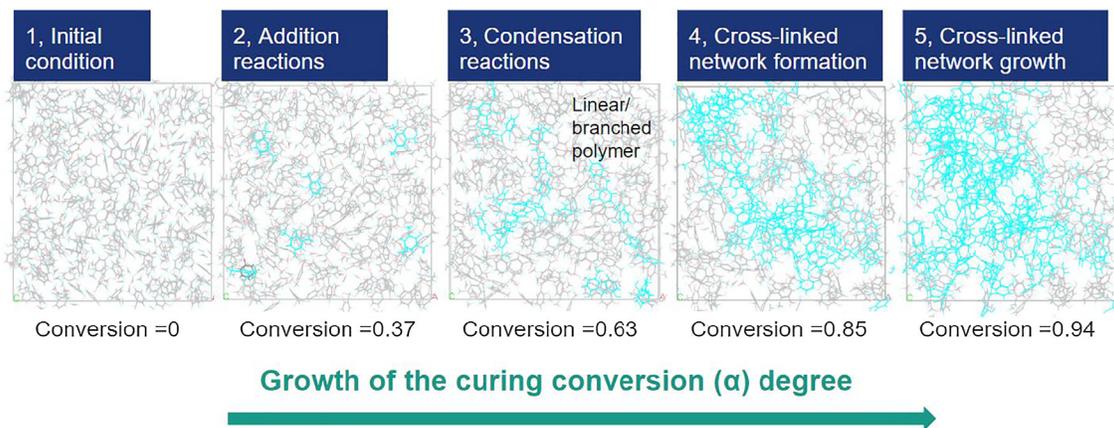
The activation energy and heat of formation of the addition reactions taking place at the phenolic *ortho*- and *para*- positions under alkaline conditions were predicted using the GRRM tool, as shown in Fig. 3(a) and (b). More specifically, the activation energy for the *ortho*-position is 55.05 kcal/mol, while that of the *para*- position is 50.20 kcal/mol, indicating that the probability of a reaction occurring at these two positions is similar, because the activation energy can be interpreted as the magnitude of the energy barrier to the reaction. The activation energies of the other types of prepolymers, such as *o,o*-, *o,p*-, and *o,o,p*-, have been reported in Ref. [22], and the simulation results suggested that the reaction probability at the *ortho*-position was significantly higher than that at the *para*-position based on the obtained activation energies. Indeed, almost twice the amount of energy is required for reaction at the *para*-position under acidic conditions. These results can therefore account for the fact that different resin structures are formed in the reaction between phenol with formaldehyde under different pH conditions [15]. More specifically, Novolac, which has a linear polymeric chain structure, is prepared under acidic conditions, while Resol, which has a network polymer structure, is synthesized under alkaline conditions.

For the synthesis of phenol resin, the polymerization processes were

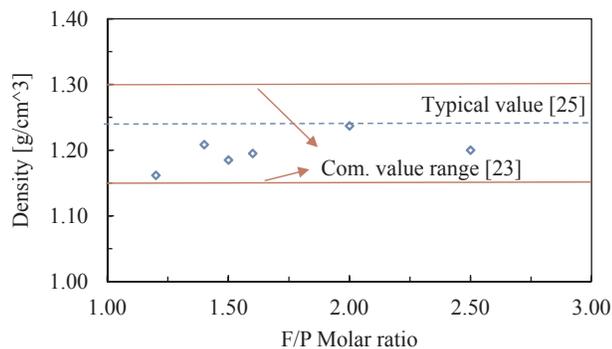
observed using this multi-scale model, and the variation in the atomic system was reported, as shown in Fig. 4. The monomers were randomly distributed in the initial atomic system (Fig. 4(a)), where a formaldehyde:phenol molar ratio of 2 was employed along with a bulk size of a 4.018 nm<sup>3</sup> cubic cell with 4200 atoms. Thus, the addition reactions in the *para*- and *ortho*-positions tended to occur following growth of the polymerization degree, and in this state (see Fig. 4(b)), small molecules were the predominant species. Subsequently (Fig. 4(c)), the prepolymers reacted with one another to give linear and branched polymers. When the polymerization reaction was allowed to proceed until close to completion, large-scale molecular and network structures were formed. These results indicate that the polymerization process involving both addition and condensation reactions is successfully reproduced in our quantum mechanics/MC/MD multiscale model.

The room temperature (298 K) density results simulated under different synthetic conditions (i.e., formaldehyde to phenol molar ratios ranging from 1.2 to 2.5) are shown in Fig. 5. Importantly, our results agree with commercial values ranging from 1.15 to 1.3 g/cm<sup>3</sup> [23] and experimentally measured values reported previously [24]. In contrast, previously reported simulated density results that do not consider the addition reaction were < 1.15 [2,3], while the simulated density results where the addition reaction was included are closer to the typical PF density data, i.e., 1.24 g/cm<sup>3</sup> [25].

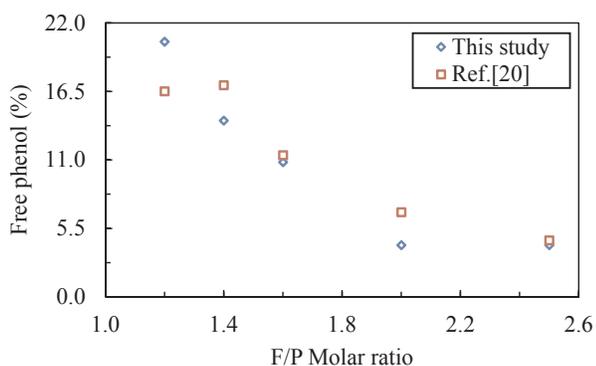
Different Resol resins were then characterized based on the free phenol content following preparation, and the simulation result is shown in Fig. 6 along with a comparison with previously reported



**Fig. 4.** Constructed molecular structure of the 4.018 nm<sup>3</sup> cubic cell with 4200 atoms in various reaction conversion stages (formaldehyde to phenol molar ratio = 2): (a) Initial condition prior to reaction; (b) Addition reaction with 37% curing conversion; (c) Formation of linear and branched polymer chains following condensation with 63% curing conversion; (d) and (e) Polymerization continued until the reaction approaches completion to give large-scale molecular and network structures.



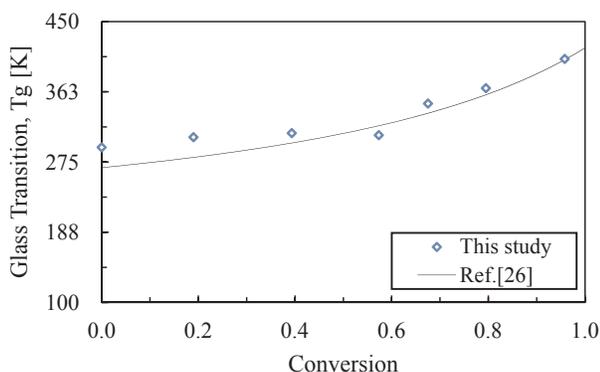
**Fig. 5.** The density simulation was performed under different synthetic conditions (i.e., formaldehyde to phenol molar ratios of 1.2–2.5). Literature values for the commercial [23] and simulated results are also shown for comparison.



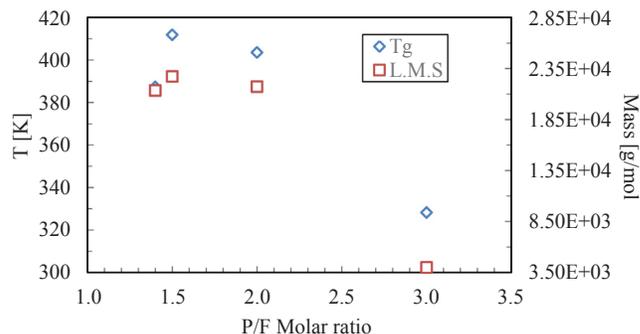
**Fig. 6.** Different resol resins were characterized based on their free phenol contents following preparation, and the simulation results are compared with previously reported experimental data [20]. The variation trend of the free phenol with the increasing molar ratio agree well with the experimental data.

experimental data [20]. As shown, the free phenol content tended to decrease with an increasing molar ratio in both cases, and from both the experimental and simulation results, it was apparent that phenol existed in the system following completion of the polymerization reaction. These results also suggest that the synthetic model should consider the addition reaction, where the initial reactants are the monomers.

The  $T_g$  values were then predicted for the various curing conversions, and the results are presented in Fig. 7. More specifically, the free volume approach and two fitting curves were used to calculate  $T_g$ , where we used the least squares error method to determine the two fitting curves, and the Perez model was fit using  $T_{g0} = 268$  K, and



**Fig. 7.**  $T_g$  was predicted with variation in the curing conversion. The Perez model was fit using  $T_{g0} = 268$  K, and  $T_{g\infty} = 434$  K,  $\lambda = 0.41$ , as described in the literature [26]. The estimation of  $T_g$  agrees well with the results of the Perez model and with typical experimental results at 423 K [25].



**Fig. 8.** Simulation results for the  $T_g$  and the largest molecular size (L.M.S) at different molar ratios. These results conform with the literature explanation [27] that the formation of large molecules can increase the number of strong intermolecular forces. In contrast, the presence of small molecules that can diffuse within the cross-linked system can reduce  $T_g$ .

$T_{g\infty} = 434$  K,  $\lambda = 0.41$ , as described in the literature [26]. Indeed, our estimation of  $T_g$  agrees well with the results of the Perez model and with typical experimental results at 423 K [23].

It should also be noted that molecular size can influence the value of  $T_g$ . Thus, the simulation results for  $T_g$  and for the largest molecular size (L.M.S) under different molar ratios were compared, as presented in Fig. 8. The obtained results suggest that the L.M.S exhibits a positive correlation with the  $T_g$ , where larger molecules increase the value of  $T_g$ . These results conform with the literature explanation [27] that the formation of large molecules can increase the number of strong intermolecular forces. In contrast, the presence of small molecules that can diffuse within the cross-linked system can reduce  $T_g$ . Such trends have been studied previously [4,28].

#### 4. Conclusions

We herein reported the development of an atomic-level model that can simulate the influence of synthetic conditions (i.e., the molar ratio and pH) on the physical and thermal properties of the phenol resin, phenol formaldehyde (PF). This model clarified the relationship between the synthetic conditions employed, the structure formation, and the physical and thermal properties of the resin by considering a comprehensive reaction model that includes both the addition and condensation reactions. The effectiveness of the reported model was then validated by verifying the influence of the primary synthetic index (i.e., the molar ratio) on the physical and thermal properties of the Resol resins, including the glass transition temperature, density. In addition, the computing cost was reduced through the adoption of a multi-scale model, which combined quantum chemistry calculations, Monte Carlo simulations, and molecular dynamics simulations. This model would be expected to contribute to reducing costs in the synthesis of PF resins by the removal of trial and error, and should also aid in determining suitable synthetic conditions for obtaining the desired material properties.

#### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

We thank Dr. Yamashita for his fruitful discussions. We also acknowledge the support of the Cross-ministerial Strategic Innovation Promotion Program, Tohoku University Center for Gender Equality Promotion (TUMUG) and the vitally important encouragement and

support of the University of Washington-Tohoku University: Academic Open Space (UW-TU:AOS). N. K and T. O. express gratitude for a research grant from the Institute for Quantum Chemical Exploration (IQCE).

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