



Large-scale molecular dynamics simulation of crosslinked phenolic resins using pseudo-reaction model



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ABSTRACT

We constructed and characterized a network structure of crosslinked phenolic resins using a large-scale atomistic molecular dynamics simulation with a pseudo-reaction algorithm. The atomic configuration of the reaction products was controlled by the reaction probabilities and initial molecular structures. The crosslinked structure obtained from phenols as initial molecules agreed well with experimental results in terms of the branching structure of the phenolic units and the methylene linkages, molecular weight distributions, densities, and scattering functions at various reaction conversions. The calculated structure factor for phenolic resins indicated inhomogeneous crosslinking, which expanded as the reaction proceeded after gelation. Voronoi tessellation analysis of the change in the occupation volume of the phenolic units after crosslinking indicated that the initial molecular configuration influenced the resulting crosslinked structure. The experimental molecular weight distribution before gelation and the scattering function were well reproduced by a large-scale simulation with 232,000 atoms.

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1. Introduction

Phenolic resins are widely used thermosetting plastics in a variety of industries including the aerospace, automotive, housing, and semiconductor industries [1–3]; this is because of their excellent properties such as high mechanical strength, thermal stability, insulating properties, and solvent resistance that are derived from their highly crosslinked structures. Crosslinked structure and inhomogeneity in cured thermosetting resins are recognized as a key factor in controlling the material properties of thermosetting resins [3,4], as well as polymer networks of gels and rubbers [5,6]. In phenolic resins, several network models have been proposed including structural defects [7,8] and microgel structures [9]. Much effort has been devoted mainly to fractographic

observation using electron microscopy [10–13]. Conversely, there is no strong evidence to date for inhomogeneous crosslinking in crosslinked phenolic resins. To characterize the chemical structures and understand the reaction behaviors of phenolic resins, many investigations have been performed using experimental analyses such as liquid- [14–17] and solid-state nuclear magnetic resonance (NMR) spectroscopy [18–20], proton pulse NMR spectroscopy [21], infrared absorption spectroscopy [22] and thermal analyses [23–27]. Statistical techniques have also been developed and applied to phenolic resins before gelation using theoretical [28–31] and kinetic models [32]. However, most of these analyses have been limited to soluble resins, and crosslinked structures are still poorly understood.

Scattering analysis has also been used as an indispensable technique to analyze crosslinked networks [33–35]. We applied dynamic light scattering (DLS) [36,37] and small-angle X-ray and neutron scattering (SAXS and SANS, respectively) [38–41] to understand the structures and gelation mechanisms of phenolic resins from soluble novolac resins to highly cured networks. A structural inhomogeneity in the phenolic network was clearly observed in loosely crosslinked phenolic resin just after the gel point by SAXS

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with a solvent swelling technique [39,40]. The scattering functions obtained were described by the Ornstein–Zernike equation and squared Lorentzian equations with a correlation length of several nanometers.

Molecular simulations are powerful tools for investigating the relationships between the structures and properties of thermosetting resins because they can obtain structural information that cannot be found by chemical analysis due to difficulties associated with insolubility and infusibility. Computational approaches to thermosetting resins have been limited to a small molecular model before gelation due to the hardware and algorithm limitations that existed until the early 2000s [42,43]. Conversely, since the pioneering work of Yarovsky and Evans [44], there have been many reports on methodologies for constructing models of crosslinked structures and their application to existing materials, especially epoxy resins [45–48]. To construct a crosslinking network, a pseudo-reaction is generally used between unreacted functional groups on molecules in a simulation box. Here a pseudo-reaction is a simplified recombination process emulating a real chemical reaction, in which a change in electronic structure is not considered with respect to strict *ab initio* calculations because of the computational cost. For molecular modeling of a crosslinked network, coarse-graining of atomic structures [46,47] and reverse mapping techniques [48] are also applied with the pseudo-reaction to consider longer dynamics or reduce the computational cost.

We previously demonstrated a crosslinking procedure for phenolic resins and predicted their thermal and mechanical properties using atomistic MD simulation with pseudo-crosslinking [49]. In that study, a crosslinked structure of phenolic resin was constructed from amorphous structures of linear novolac chains consisting of nine phenolic rings and all *ortho*–*ortho'* methylene linkages (Fig. 1(c)) by pseudo-crosslinking between unreacted *ortho* and *para* carbons on phenolic rings. In addition, a computational condition was established to characterize thermal and mechanical properties, such as the density, glass transition temperature, Poisson ratio, and tensile modulus. Here we adopted a DREIDING force field [50] and partial charges estimated from B3LYP/6-31G (d,p) calculations as parameters for the phenolic resins.

These methodologies, which were used in our previous study,

are indeed effective in achieving the above-mentioned purpose, but they involve two problems that need to be overcome. The first problem is poor quantitative values of the physical properties of the constructed network structure. The estimated values of the density and tensile modulus were lower than the experimental values. The supposed reason for these discrepancies is inadequacy of the DREIDING force field parameters and applied partial charges based on the B3LYP with the 6-31G(d) basis sets for the phenolic resins, which resulted in weak nonbonding attractive interactions. The second problem is the possibility of inadequacies in the constructed structure. In our previous study, the molecular configuration of the precursor was not taken into account, whereas many experimental studies have shown dependencies on the molecular weight distribution (MWD) [3,26,51–53] and the *ortho/para* ratio in the methylene linkage [1,2,25] on the curing behavior and the thermal and mechanical properties of cured resins. Therefore, such diversity in molecular configurations should be considered in order to understand the relationships between structures and material properties in crosslinked resins. Monk et al. investigated the mechanical and thermal properties of a crosslinked network from linear novolac resins consisting of nine phenolic rings and all *ortho*–*para'* (Fig. 1(b)) and *ortho*–*ortho'* (Fig. 1(c)) methylene linkages using a procedure similar to ours [54,55]. They investigated the dependencies of the density and mechanical properties of network structures on crosslinking reaction conditions with an all-atom OPLS force field [56] and found that these values were strongly influenced by the initial configuration before the reaction. However, the final densities of highly crosslinked structures tended to be lower than the experimental values. These results suggest that this crosslinking approach from linear novolac chains is not suitable for obtaining a realistic crosslinked structure. To check this assumption, detailed structural analysis and verification of the crosslinked network are required. The verification of a constructed structure is a common but important problem in computer simulation. Most reports concerning crosslinked thermosetting resins have discussed the validities of generated structures from the viewpoint of material properties, such as density, glass transition temperature, and elastic constants [45], but such a comparison is not sufficient to guarantee the accuracy of a crosslinked structure.

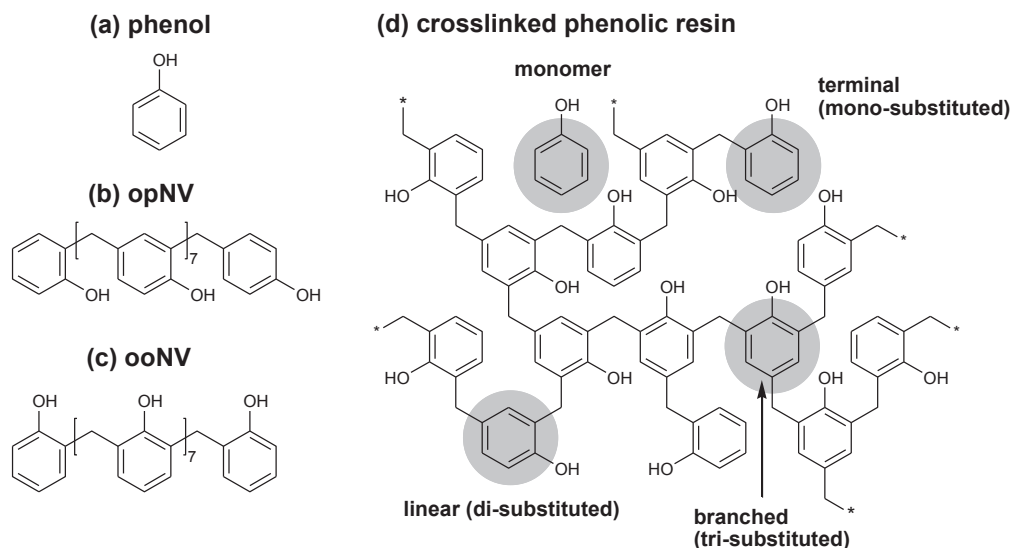


Fig. 1. Chemical structures of initial molecules used in simulation: (a) phenol, (b) opNV (linear chain containing nine phenol rings with *o*–*p'* methylene linkages), and (c) ooNV (linear chain containing nine phenol rings with *o*–*o'* methylene linkages). (d) Example of crosslinked phenolic resin.

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