Simulation Avancée des Réseaux Polymères Époxydes : Analyse Comparative des Algorithmes de Réticulation et des Modifications Topologiques dans LAMMPS

Advanced Simulation of Epoxy Polymer Networks : Comparative Analysis of Crosslinking Algorithms and Topological Modifications in LAMMPS

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Résumé

Dans cette étude, nous nous concentrons sur la génération et l'analyse de la topologie des réseaux polymères des résines époxydes, en particulier des molécules DGEBA et DETDA, en utilisant deux approches de réticulation dans le logiciel de simulation LAMMPS. La première méthode utilise l'approche REACTER pour simuler le processus de réticulation, tandis que la seconde approche emploie une version modifiée de la commande bond/create pour assurer une mise à jour dynamique de la topologie des molécules après la formation des liaisons. Cette modification améliore la précision et la fiabilité des structures de réseau simulées. Les deux méthodologies sont évaluées pour comparer leur efficacité à capturer le processus de formation des réseaux, avec un accent particulier sur leur pertinence pour caractériser les relations microstructure-propriétés et le comportement mécanique. Les résultats apportent des informations sur les avantages et les limites de chaque approche pour la simulation des systèmes polymères réticulés, avec des implications potentielles pour la conception de matériaux époxydes biosourcés à haute performance.

Abstract

In this study, we focus on generating and analyzing the polymer network topology of epoxy resins, specifically DGEBA and DETDA molecules, using two crosslinking approaches within the LAMMPS simulation software. The first method utilizes the REACTER approach to simulate the curing process, while the second approach employs a modified version of the bond/create to ensure the topology of molecules is dynamically updated after bond formation. This modification enhances the precision and reliability of the simulated network structures. Both methodologies are evaluated to compare their effectiveness in capturing the network formation process, with an emphasis on their suitability for characterizing microstructure-property relationships and mechanical behavior. The results provide insights into the advantages and limitations of each approach for simulating crosslinked polymer systems, with potential implications for the design of high performance bio-sourced epoxy materials.

Mots Clés : Epoxy bio-sourcée, Dynamique moléculaire, Réticulation
Keywords : Bio-sourced epoxy, molecular dynamic, crosslinking

1. Introduction

Epoxy resins are widely used in advanced materials due to their excellent mechanical properties, thermal stability, and chemical resistance. Simulating their polymer network formation provides crucial insights into their microstructure-property relationships, enabling the development of high-performance materials, including bio-sourced alternatives. A key challenge in molecular dynamics (MD) simulations of epoxy networks is accurately representing the crosslinking process[1] and the resulting topological changes in the network.

This study investigates two crosslinking approaches within the LAMMPS software[2] : the REACTER method, known for its precise reaction dynamics, and a modified version of the bond/create command, which dynamically updates molecular topology during crosslinking. By comparing these methods, we aim to evaluate their performance in capturing network formation and characterizing the mechanical behavior of epoxy polymers.

2. Materials and Methods

2.1. System description

The simulation system consists of 64 DETDA molecules and 128 DGEBA molecules, chosen to mimic a typical epoxy network formulation. The molecules were pre-equilibrated in a cubic simulation box under periodic boundary conditions. The initial configurations were generated using Avogadro software [3] for modeling the two molecules ; then, we used moltemplate software [4] to generate the system inside the box and to generate the force field parameters at the same time.

DGEBA

DETDA

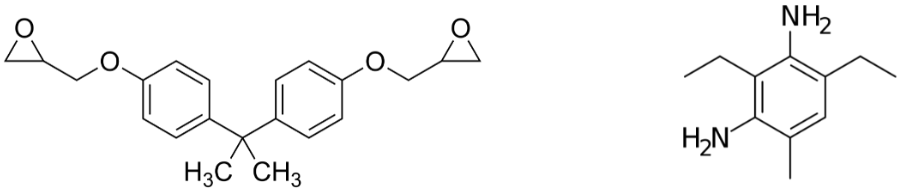
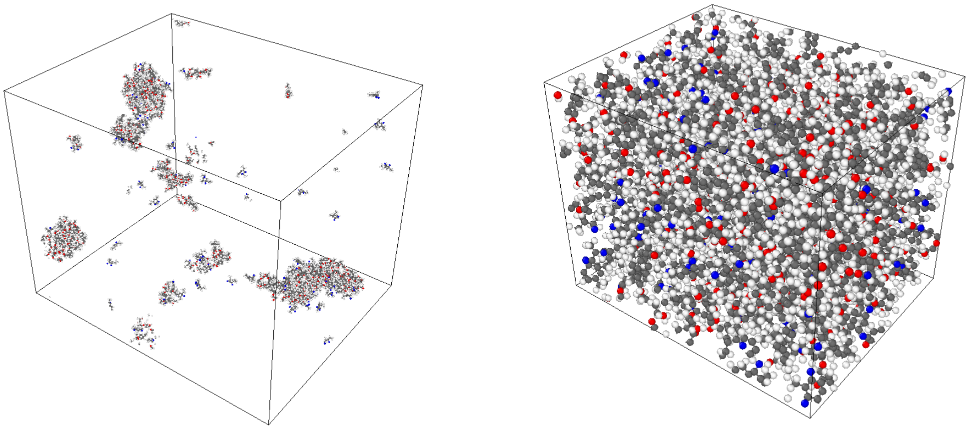


Fig. 1. – Chemical representation of DGEBA and DETDA molecules.

To initiate the crosslinking process, the system was relaxed in two distinct stages. The first stage involved thorough mixing of the molecules using an NVT ensemble at 300 K for 0.2 ns, ensuring homogeneous distribution. Subsequently, the second stage employed an NPT ensemble at 300 K for 0.2 ns, allowing the system to equilibrate and achieve a pre-crosslinking density close to 1 g/cm^3.

2.2. Crosslinking

From a molecular dynamics (MD) simulation perspective, the crosslinking process can be modeled by introducing reactive potentials or reaction algorithms that form bonds between polymer chains or monomers as they approach within a critical distance. Initially, polymer strands with reactive end-groups are placed in the simulation box. During the MD run, reactive force fields or custom bonding rules are applied so that when conditions for bond formation are met—such as close proximity and proper orientation—new bonds are created [5]. This approach enables monitoring the time evolution of the network structure, including the number of crosslinks, cluster connectivity, and the eventual formation of a gel-like network. From the resulting crosslinked structure, key parameters such as crosslink density, molecular weight between crosslinks, and mechanical properties can be extracted and correlated to experimental conditions [5]. Notably, this method provides atomistic-level insights that complement continuum-level models and experimental data.



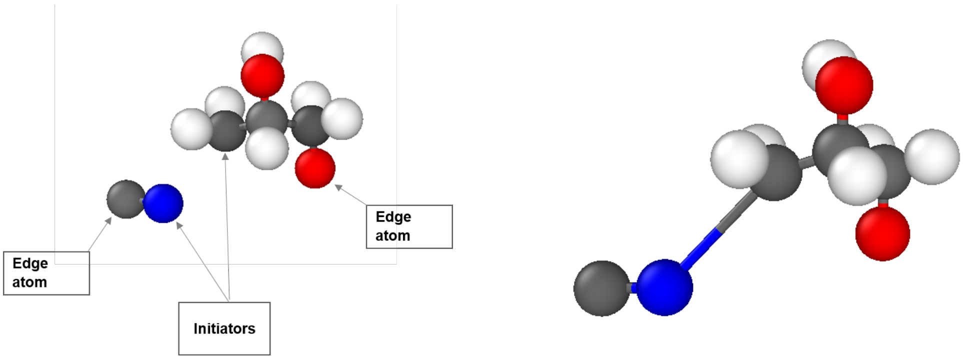
(a) *Simulation box after applying NVT* (b) *Simulation box after applying NPT*

Fig. 2. – Simulation box after relaxation.

2.2.1. REACTER approach

The REACTER [6] method employs the fix_bond_react [2] command to simulate curing reactions. This approach accounts for detailed reaction mechanisms, ensuring realistic bond formation dynamics.

In our case, to simulate the bond formation between the epoxyde group and amine group to generate the polymer network, we created four template files.



(a) *First template file* (b) *Second template file*

Fig. 3. – Template files.

2.2.2. Bond Create approach

The fix_bond_create [2] command in LAMMPS is a powerful tool for dynamically creating bonds between pairs of atoms during a simulation. This command is particularly useful for modeling processes such as the cross-linking of polymers or the formation of a percolation network.

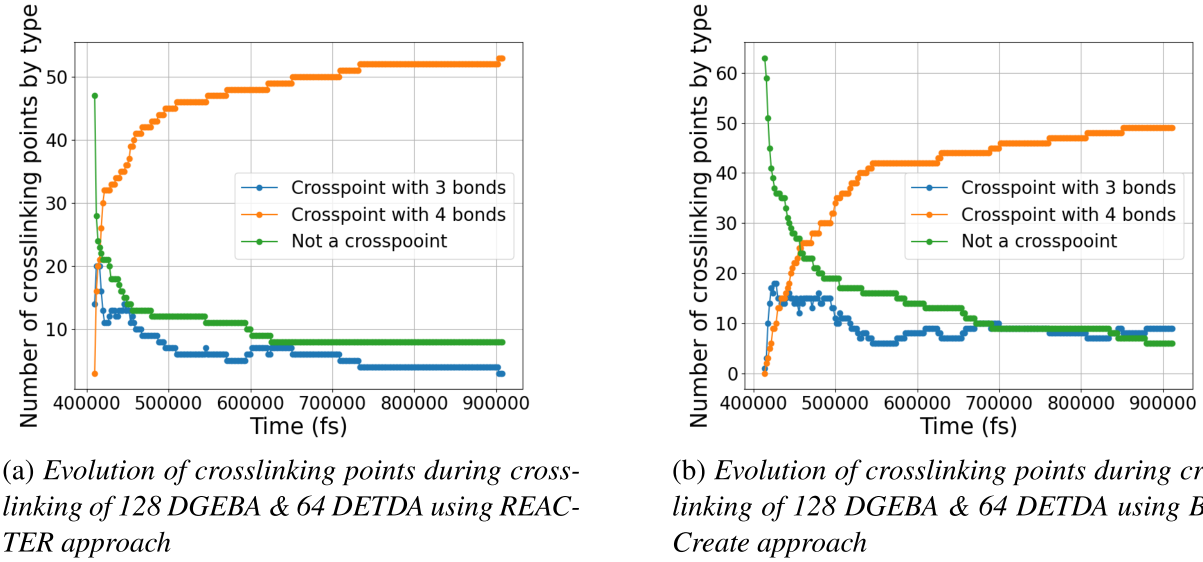
A customized version of the fix_bond_create [2] command was implemented to update molecular topology dynamically. This modification ensures that newly formed bonds are incorporated into the simulation's topology, allowing for more accurate representation of the evolving polymer network.

2.3. Post-processing techniques

The post-processing of polymer networks is a critical step that involves a comprehensive analysis of the network's topology to evaluate its structural properties and performance. For this purpose, we employed an advanced topology reconstruction method based on Depth-First Search (DFS). This algorithm enables the systematic traversal of the polymer network, starting from any atom, to reconstruct the topology and extract detailed information about each branch and connection within the system.

3. Results and discussions

3.1. Crosslinking points analysis



(a) *Evolution of crosslinking points during crosslinking of 128 DGEBA & 64 DETDA using REACTER approach*

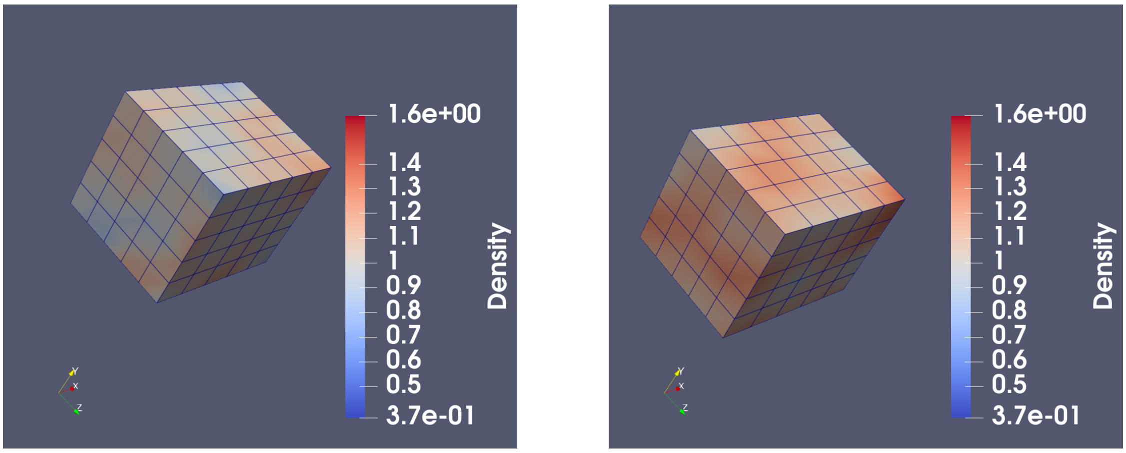
(b) *Evolution of crosslinking points during crosslinking of 128 DGEBA & 64 DETDA using Bond Create approach*

Fig. 4. – Evolution of crosslinking points by type.

These two plots in figure 4 show how the number of sites in three categories evolves over time :

- * Not a crosslinking point (Green) : Atoms with only two bonds (typical "chain" connections).
- * Crosslinking point with 3 bonds (Blue) : A branching point, but not fully crosslinked.
- * Crosspoint with 4 bonds (Orange) : A fully crosslinked node (tetra-functional junction).

3.2. Local density analysis



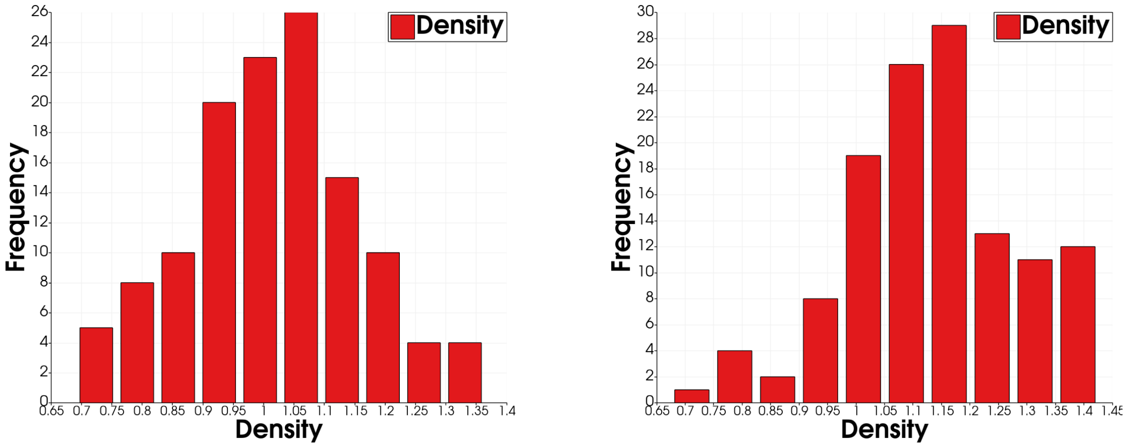
(a) *REACTER approach*

(b) *Bond Create approach*

Fig. 5. – Smoothing using Cell Data to Point Data in paraview of the final frame.

From these volumetric plots in figure 5, we can see how the system's density varies spatially by subdividing the simulation box into discrete subvolumes (or "voxels") and then computing the density in each smaller region. The color scale ranges from roughly $0.37 g/cm^3$ (blue) up to $1.6 g/cm^3$ (red).

That is a fairly broad distribution, revealing that the material is not homogeneous : some areas are substantially denser than others. This could be due to local clustering of atoms, crosslinked regions, or voids/pore-like spaces.



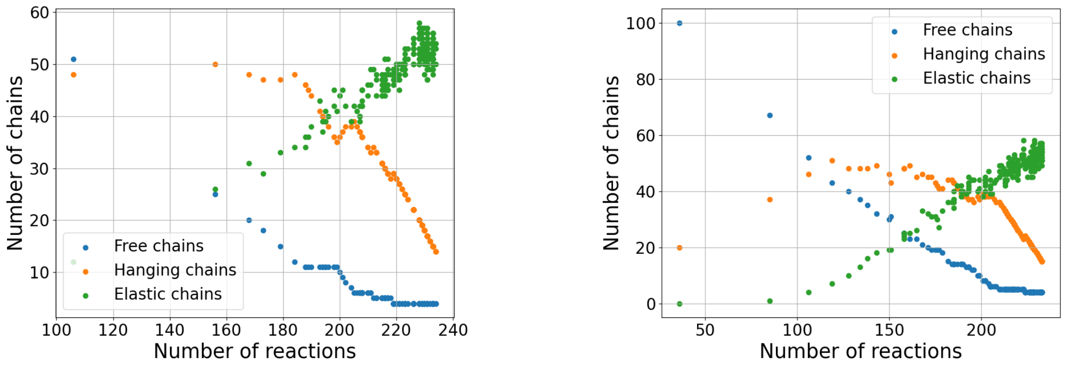
(a) *REACTER approach*

(b) *Bond Create approach*

Fig. 6. – Histogram of local densities frequency.

In figure 6 one can see that each histogram shows a single broad peak around $1.05 - 1.15 g/cm^3$. Although most subvolumes cluster near $\sim 1.1 g/cm^3$, there's a noticeable tail on both sides, reaching below 0.8 and above 1.3 – 1.4. This confirms significant local variation in density, even in the "steady" state.

3.3. Chain analysis



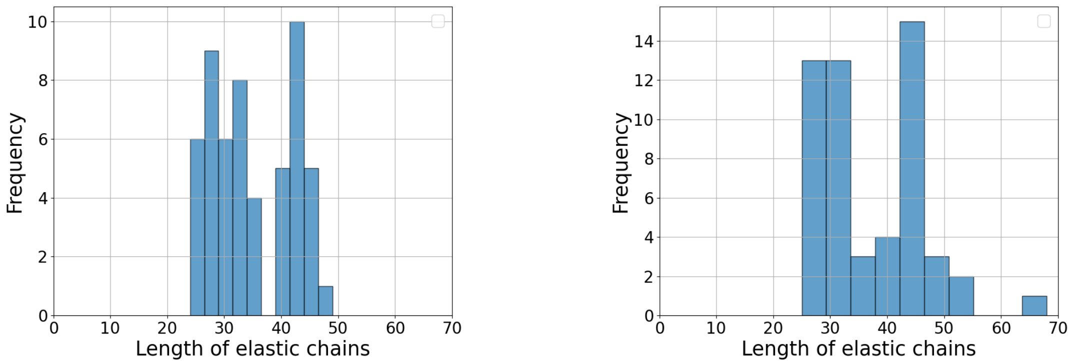
(a) *REACTER approach*

(b) *Bond Create approach*

Fig. 7. – Evolution of number of chains by type.

As the number of reactions increases in figure 7, the system evolves from a collection of many small, free chains into a smaller number of larger, more complex networks dominated by elastic chains. Initially loose structures become increasingly interconnected, reducing the count of free and hanging chains while increasing the presence of elastic (fully crosslinked) chains.

From the Chain Length Distributions in figure 8, despite increasing molecular size and complexity, the system tends to form elastic chains within a constrained length range. The peak around 30–40 units suggests an inherent limiting mechanism that prevents indefinite chain extension, possibly due to reaction kinetics, steric factors, or network crosslinking patterns.



(a) *REACTER approach*

(b) *Bond Create approach*

Fig. 8. – Histogram of elastic chain lengths frequency (length here represents the number of atoms in a direct path between two crosslinking points).

4. General conclusion

Across all the results—spanning molecular growth trends, chain classification, crosslink formation, and local density distributions—a consistent picture emerges of how these polymer networks develop and mature under two different reaction algorithms (REACTER vs. Bond Create). Regardless of the reaction algorithm used, the system transitions from many small polymer fragments into a heavily crosslinked, three-dimensional network. The bulk properties—like average density and final crosslink count—stabilize to similar values in both approaches. Local variations in density and chain connectivity remain, reflecting an inhomogeneous polymer architecture. Overall, the final networks are robustly crosslinked, with differences between REACTER and Bond Create confined primarily to how quickly they reach that end state.

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