



Process Modelling of Composites using a Multiscale Framework

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Abstract

During the processing of high-performance thermoset polymer matrix composites, chemical reactions occur during elevated pressure and temperature cycles, causing the constituent monomers to crosslink and form a molecular network that gradually can sustain stress. As the crosslinking process progresses, the material naturally experiences a gradual shrinkage due to the increase in covalent bonds in the network, causing the formation of residual stresses. Similarly, the shrinkage of semi-crystalline thermoplastics during the crystalline growth phase of the processing cycle can cause shrinkage of the resin also resulting in residual stresses. The goal of this research is to use molecular dynamics, micromechanical modelling, and finite element analysis to predict the residual stresses in composite laminates and optimize processing parameters to minimize the residual stress. This paper will present some examples of our team's multiscale process modelling for epoxy, polybenzoxazine, and PEEK polymer systems.

Keywords: Multiscale modeling; Molecular modeling; Computational Chemistry; ICME; MGI

1. Introduction

During the processing of high-performance thermoset polymer matrix composites, chemical reactions occur during elevated pressure and temperature cycles, causing the constituent monomers to crosslink and form a molecular network that gradually can sustain stress. As the crosslinking process progresses, the material naturally experiences a gradual shrinkage due to the increase in covalent bonds in the network, causing the formation of residual stresses. Similarly, the shrinkage of semi-crystalline thermoplastics during the crystalline growth phase of the processing cycle can cause shrinkage of the resin also resulting in residual stresses.

Once the fully cured (thermosets) or fully processed (thermoplastics) composite completes the processing cycle and is brought to room temperature, the thermal expansion mismatch of the fibers and matrix cause additional residual stresses to form. These compounded residual stresses can compromise the mechanical integrity of the composite material. Computational process modelling needs to be utilized to optimize processing parameters to reduce residual stresses and increase the composite material durability.

Computational process modeling is greatly complicated by the multiscale nature of the composite material. At the molecular level, the degree of cure (crystallinity) controls the local shrinkage and thermal-mechanical properties of the thermoset (thermoplastic). At the microscopic level, the local fiber architecture and packing affect the magnitudes and locations of residual stress concentrations. At the macroscopic level, the layup sequence controls the nature of crack initiation and propagation due to residual stresses.

The goal of this research is to use molecular dynamics (MD), micromechanical modelling, and finite element analysis (FEA) to predict the residual stresses in composite laminates and optimize processing parameters to minimize the residual stress [1-5]. MD is used to predict the polymer shrinkage and thermomechanical properties as a function of cure (for thermosets) or crystallization

(for thermoplastics). This information is used as input into FEA to predict the residual stresses on the microscopic level resulting from the complete cure process. FEA is subsequently used to predict residual deformations and performance of composite structures for aerospace applications. Experimental characterization is used to validate the computational modelling. This paper will present some examples of our team's multiscale process modelling for epoxy, polybenzoxazine (PBZ), and PEEK polymer systems.

2. Molecular modelling of epoxy

Figure 1 shows the molecular structure of the DGEBF epoxy monomer and DETDA amine monomer used in the simulated epoxy system. Following the procedure described by Patil et al [4], the monomers were used to simulate a bulk epoxy resin in a MD simulation box, and the reactive groups were subjected to a simulated cure (Figure 1, upper right). During the simulated curing the largest and second-largest clusters were tracked as two different measures of gel point (Figure 1, lower right).

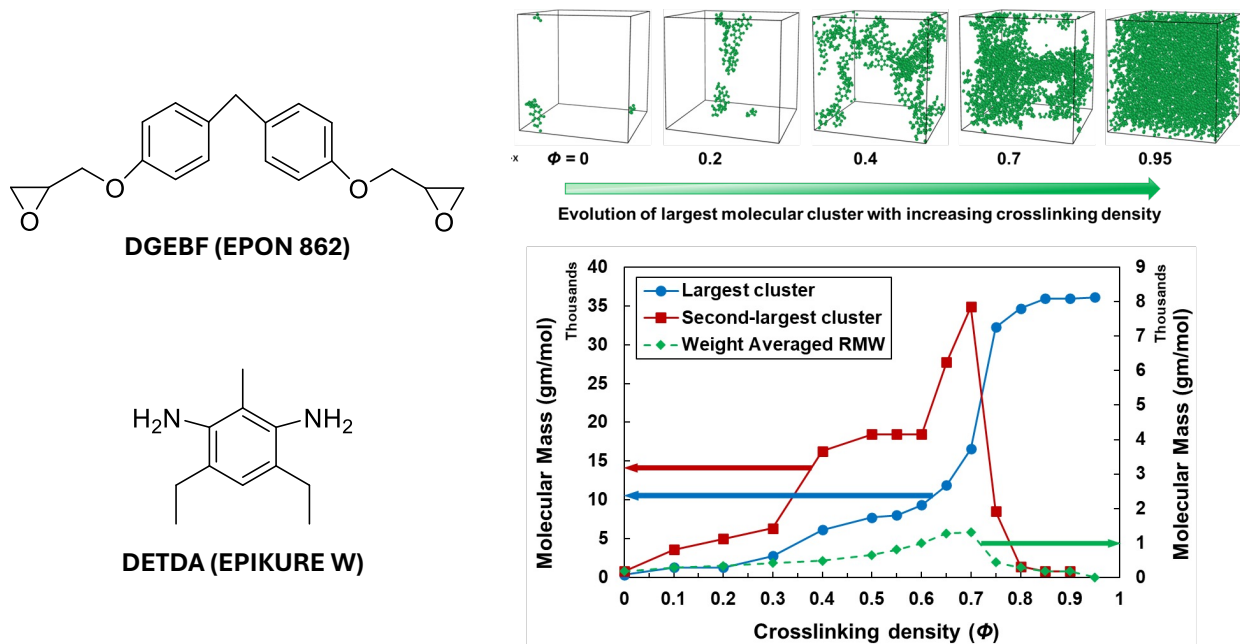


Figure 1 – Epoxy monomers (left), evolution of cluster growth during the curing process (upper right and lower right). From Patil et al [4].

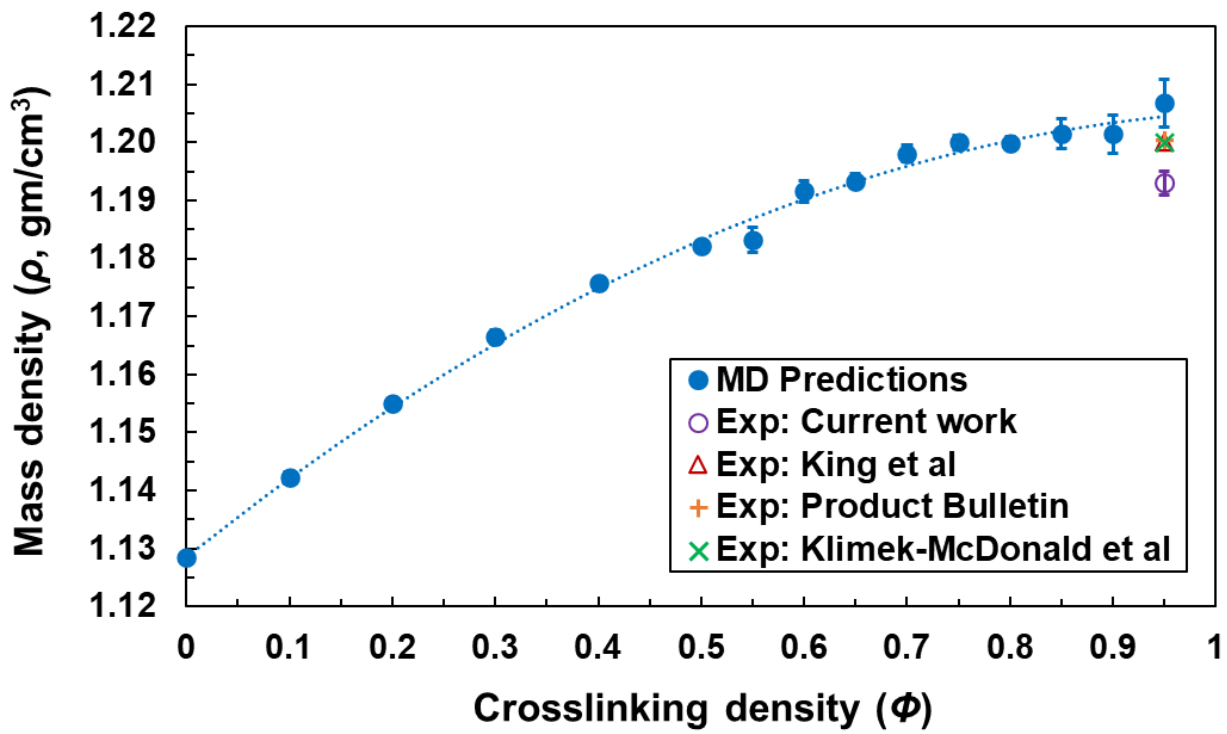


Figure 2 – Evolution of mass density during cure of epoxy. From Patil et al [4].

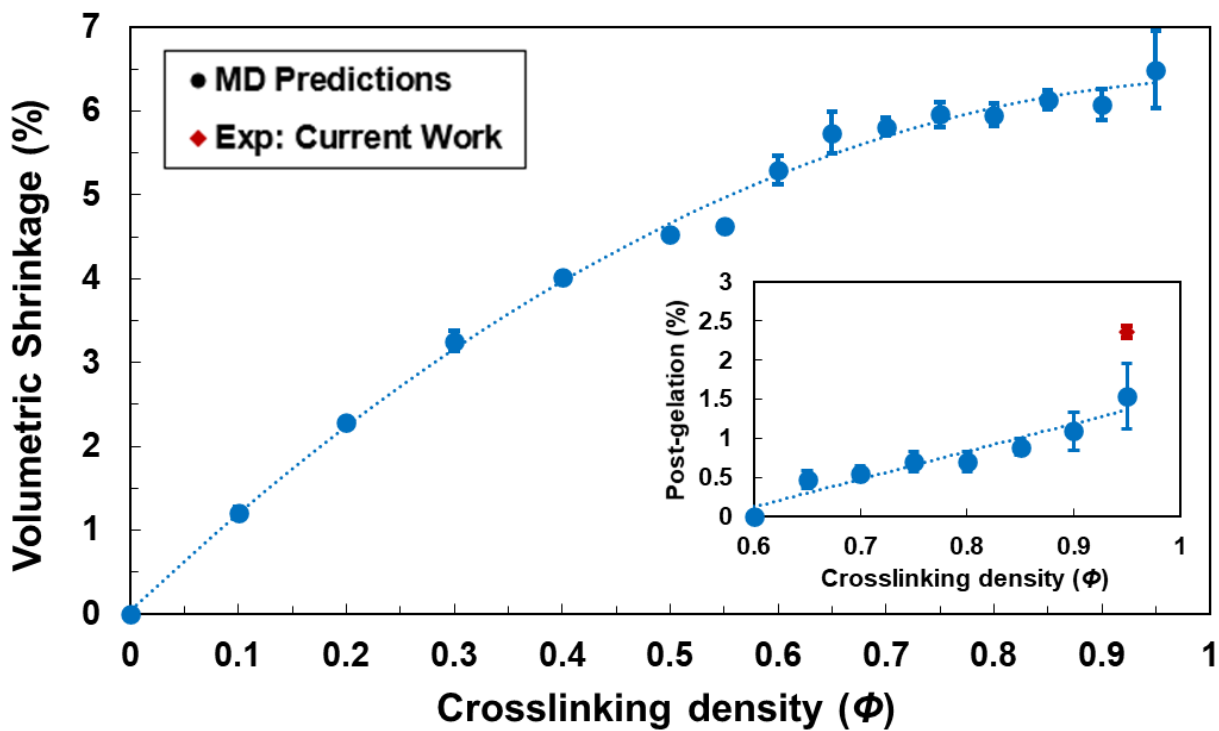


Figure 3 – Evolution of volume shrinkage and post-gelation volume shrinkage (inset) during cure of epoxy. From Patil et al [4].

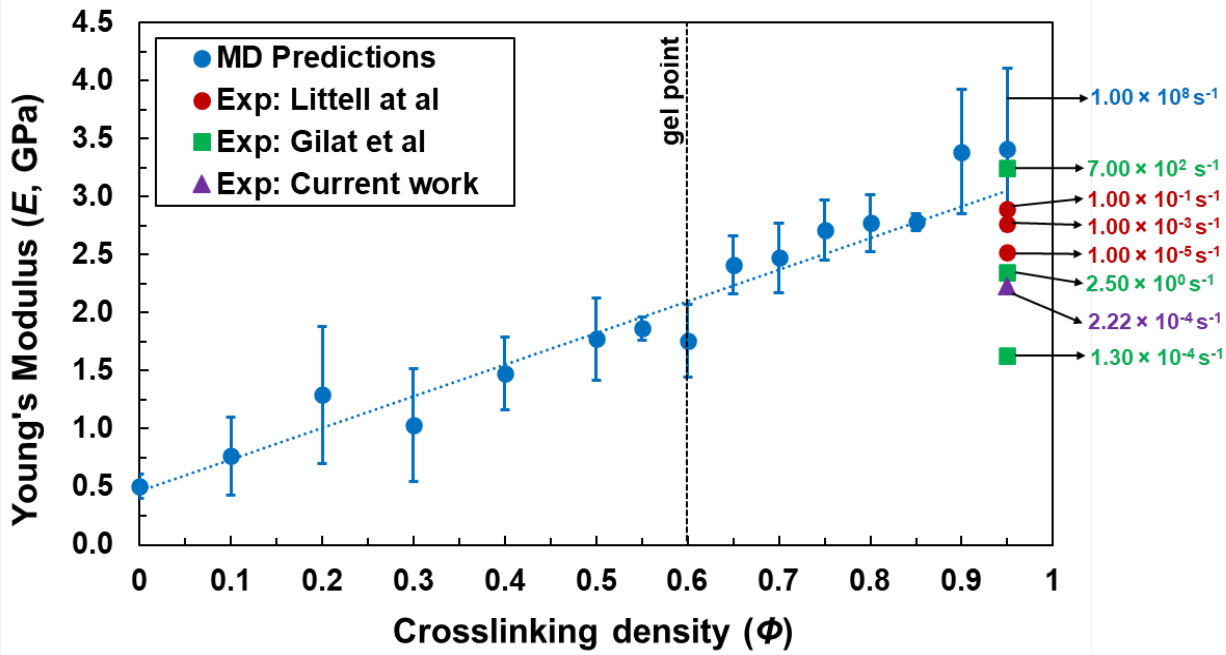


Figure 4 – Evolution of Young's modulus during cure of epoxy. From Patil et al [4].

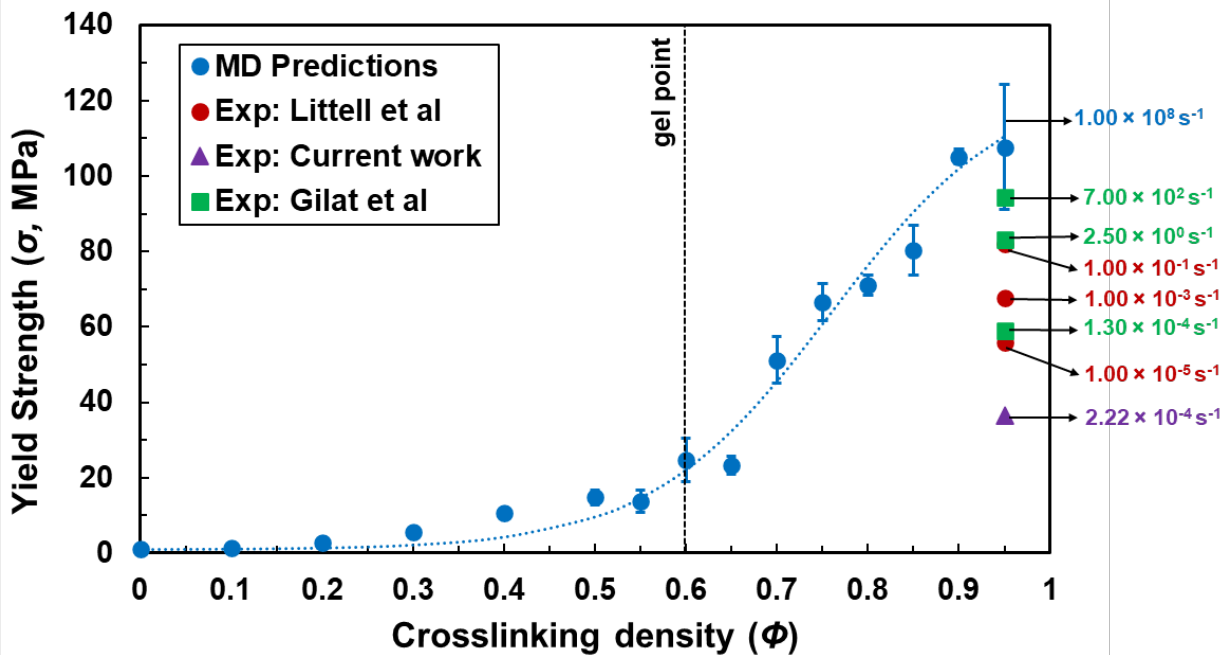


Figure 5 – Evolution of yield strength during cure of epoxy. From Patil et al [4].

The evolution of several properties were simulated as a function of cure. Figures 2, 3, 4, and 5 show the evolution of mass density, volumetric shrinkage, Young's modulus, and yield strength, respectively. Also included on the figures is experimental data, if available [6-9]. The figures show good agreement with the experimental data (considering the strain rate discrepancy) for all of these metrics.

3. Molecular modelling of PBZ

Figure 6 shows the molecular modelling steps performed by Gaikwad et al [1] for PBZ. The benzoxazine monomer was simulated in a MD simulation box and subsequently crosslinked to form PBZ (Figure 6 - top). The MD simulation boxes were subjected to shear and bulk deformations (Figure 6 - bottom) to predict the elastic and yield properties as a function of the degree of cure. Figure 7 shows the corresponding volumetric shrinkage. Both the total volumetric shrinkage and the post-gelation shrinkage are nearly zero for the full range of cure, which is experimentally observed with

PBZ [10]. This agreement between experiment and simulations for a well-known zero-shrinkage resin validates the MD modelling methodology for the PBZ and other simulated resin systems.

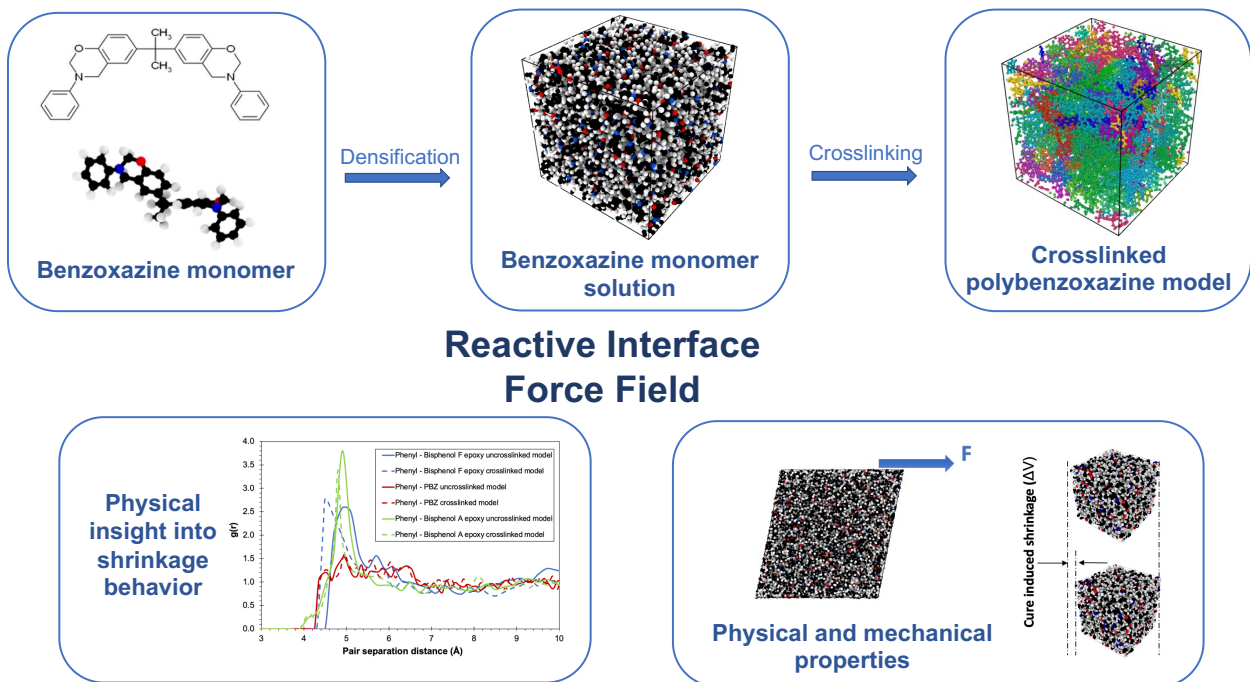


Figure 6 – Molecular modelling of PBZ resin. From Gaikwad et al [1].

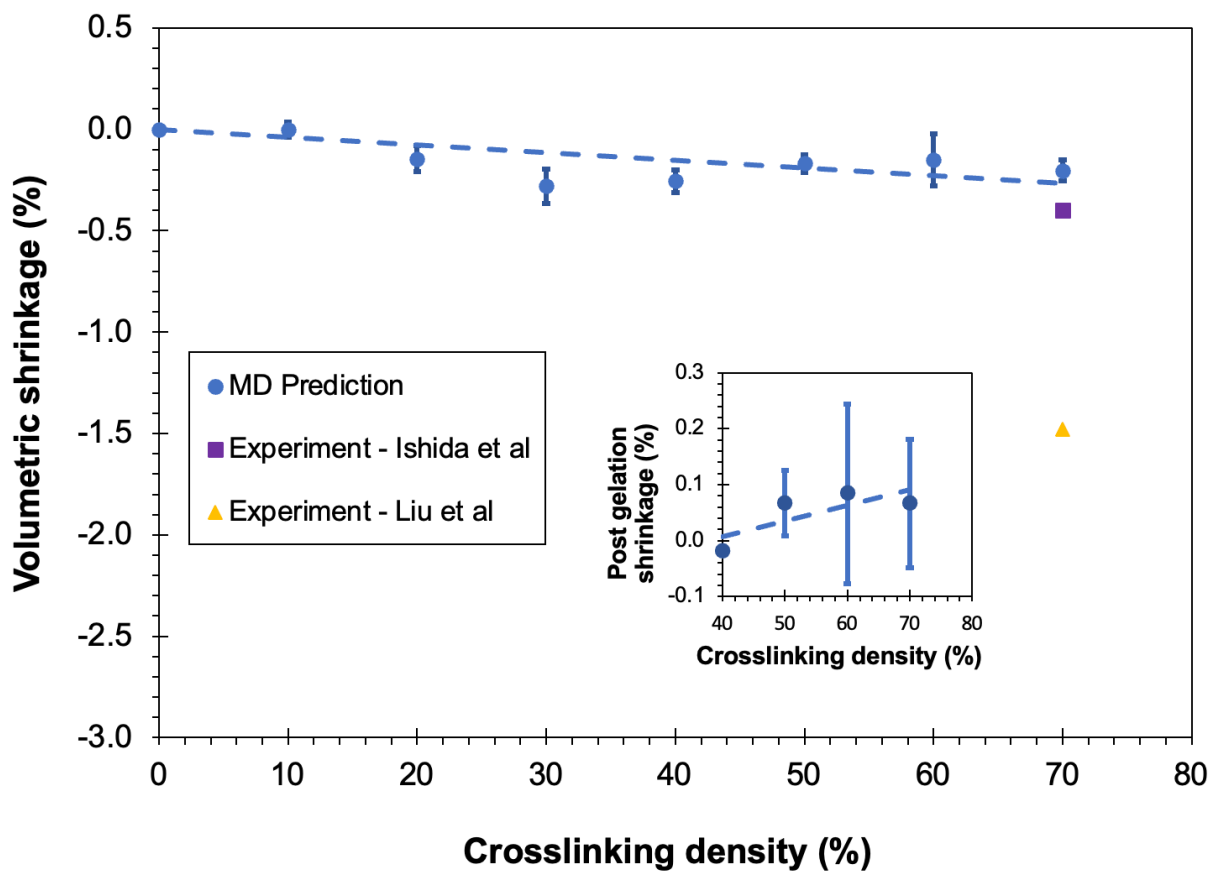


Figure 7 – Volumetric shrinkage of PBZ resin. From Gaikwad et al [1].

4. Molecular and micromechanical modelling of PEEK

Figure 8 shows the multiscale modelling methodology for PEEK, as performed by Kashmari et al [2]. MD models of the amorphous and crystalline phases of PEEK were built and simulated to get the correspond elastic and thermal properties (Figure 8 - top left). Micromechanical simulation was performed to predict the corresponding thermo-elastic properties of the semi-crystalline material. Once the properties of the semi-crystalline form of PEEK were predicted as a function of crystallinity content, the crystallization kinetics were coupled with the properties to predict the evolution of the thermo-mechanical properties of semi-crystalline PEEK as a function of processing time and temperature (Figure 8, lower left and right).

Figure 9 shows the detailed evolution of the volumetric shrinkage, Young's modulus, and thermal expansion coefficient of PEEK (resulting from crystallization) as a function of processing time and temperature. The data shows that both processing time and temperature have a significant effect on the corresponding PEEK properties.

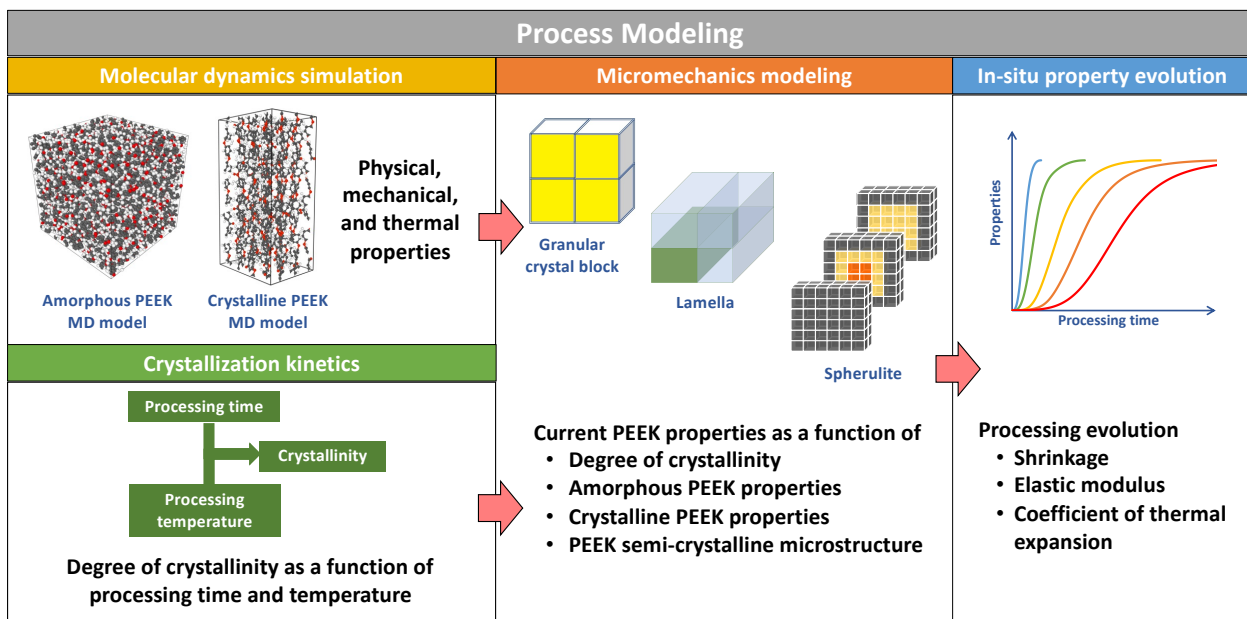


Figure 8 – Multiscale modelling of PEEK. From Kashmari et al [2].

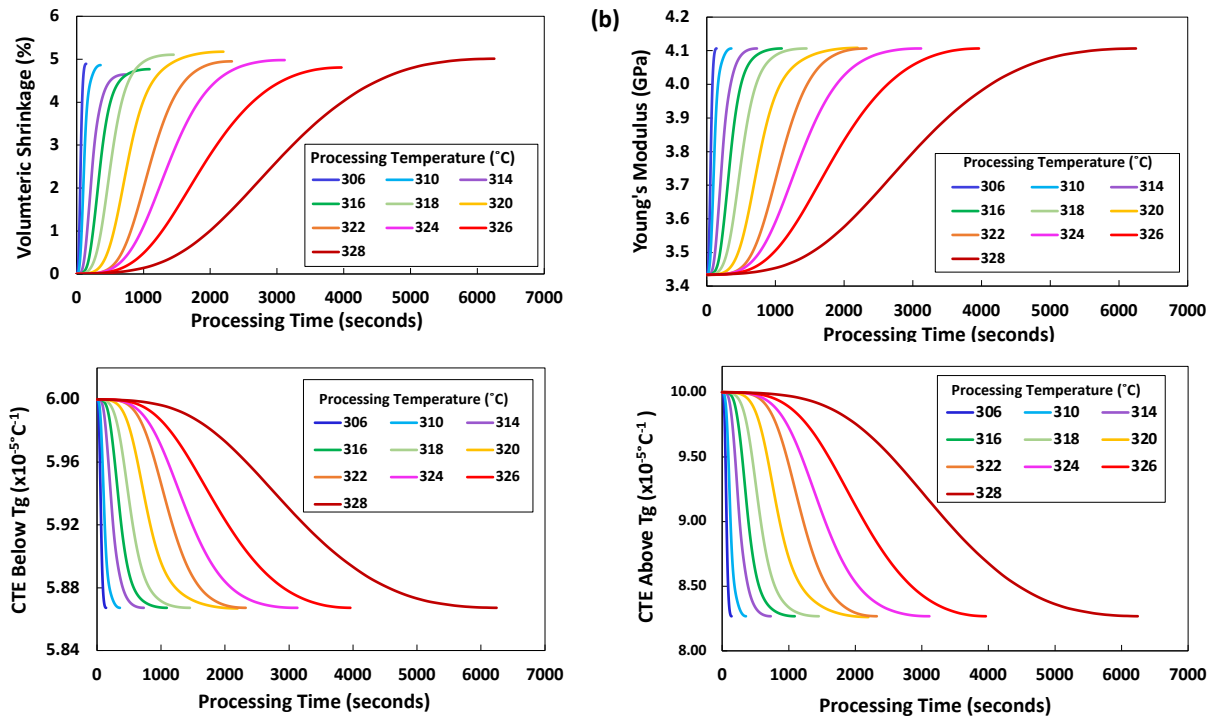


Figure 9 – Evolution of PEEK properties as a function of processing time and temperature. From Kashmari et al [2].

5. Conclusions

This research demonstrates that multiscale modelling can be used to accurately determine resin properties as a function of degree of cure (thermosets) or crystallization (thermoplastics). Coupled with cure and crystallization kinetics, respectively, the evolution of properties as a function of processing time and temperature can be established. This information can be used in higher-length scale micromechanics and FEA analysis to predict the evolution of residual stresses from cure shrinkage, crystallization shrinkage, and thermal shrinkage in composite laminates. This information can be carried forward into composite structures, such that the processing parameters and the component design can be optimized for minimized residual stresses and maximised product performance. These tools are ideal for ICME and MGI approaches for rapid material and structural development.

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