Computational design of thermoset nanocomposite coatings: Methodological study on coating development and testing

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Thermoset nanocomposites (TSNCs) may offer significantly improved performance over conventional thermoset materials, and thus are attractive for wide industrial applications, especially in the coating industry. Design of TSNCs via experiment, however, faces various technical challenges due to design complexity. Computational design can provide deep insights and identify superior design solutions through exploring opportunities in a usually huge design space. This paper introduces a generic computational methodology for the design, characterization, and testing of TSNC-based coatings. A distinct feature of the methodology is its capability of generating quantitative correlations among material formulation, processing condition, coating microstructure and property, coating performance, and processing efficiency. The correlations can enable a comprehensive analysis for optimal TSNC coating design. Case studies will demonstrate the methodological efficacy and attractiveness.

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1. Introduction

Development of thermoset nanocomposites (TSNCs) for coating applications has drawn increasing attention over recent years. This type of nanocomposites is usually designed by adding a small amount of organo-modified inorganic nanoparticles into a conventional thermoset resin. The resulting material is then applied to a substrate and cured at an elevated temperature to form a coating layer. TSNCs, when compared with conventional thermostet polymers, are capable of substantially improving coating performance, in terms of coating’s mechanical, barrier and flame-retardant properties, and even possessing new functionalities, e.g., self-cleaning and self-healing. It is believed that TSNCs will have wide industrial applications (Kotsikova, 2007).

In TSNC development, a deep understanding of the dependence of coating properties on material composition is essential. Various experimental efforts have been made to reveal the dependence. Nobel et al. (2007) developed a number of waterborne nanocomposite resins for automotive coating applications. It was found that an incorporation of needle-shaped Boehmite, disc-shaped Laponite, or plate-shaped Montmorillonite into an aqueous acrylic resin could increase dramatically the stiffness of the cured film and make the rheology of the binder more adjustable. Jalili et al. (2007) investigated a number of nanocomposite polyurethane coatings. It was shown that adding 4–8 wt% of hydrophobic nano-silica to a two-pack acrylic polyol polyurethane clearcoat could enhance the coating’s morphological, rheological, mechanical, and optical properties. Hosseinpour et al. (2005) showed that an acrylic-melamine resin filled with spherical, polar-surface-treated alumina particles could improve greatly the mechanical performance of the coating. The existing studies have improved the understanding on TSNC materials and their correlation to the properties of the nanostructured coatings. However, due to the existence of a large number of adjustable material parameters, the identification of an optimal formulation solely through experiments is extremely challenging. It must be pointed out that computational material design can provide us with impressive freedom and control over the investigated material parameters and product properties through allowing virtually any number of in silico experiments. Moreover, computational modeling and simulation should greatly facilitate identification of vast correlations among material, microstructure, property, and performance. Nevertheless, there has been no such a computational methodology available for investigating TSNCs.

The known computational studies on polymer nanocomposite materials are nearly all for thermoplastic nanocomposites (TPNCs) (see Zeng et al., 2008), Molecular dynamics (MD) simulation (Starr et al., 2002; Bedrov et al., 2003) and lattice and off-lattice Monte Carlo (MC) simulations (Vacatello, 2001, 2002; Zhang and Archer, 2004; Ozmusul et al., 2005; Dionne et al., 2006) are among the techniques used to investigate polymer chain conformation, nanoscale interactions, and material structural evolution and properties. Investigation of TSNCs is much more challenging. First,
the polymeric material structural complexity in terms of the molecular weight distribution and the functional group distribution must be taken into account. Second, multiple inter-correlated chemical and physical phenomena occurred during the coating formation process have to be properly characterized. Note that a thermoset material must undergo a crosslinking reaction process in coating formation, but this is not the case for a thermoplastic material application.

Most of the computational studies on structure–property correlations for polymer nanocomposites are focused on model-based mechanical property quantification. The continuum-based micromechanics methods (e.g., Eshelby, Halpin-Tsai, and finite element based) and the non-continuum-based nanomechanics methods (e.g., MC, MD, and molecular mechanics based) are the two major types of techniques (Valavala and Odegard, 2005). Recently, multiscale methods received a great deal of attention (Sheng et al., 2004; Zeng et al., 2008), since they can characterize appropriately the hierarchical morphology of polymer nanocomposites, which is essential for accurate prediction of material properties. It has been noted by experimentalists that the detailed knowledge of the structure of crosslinked polymer network matrix is essential for developing structure–property relationships in TSNC systems (Bharadwaj et al., 2002; Nobel et al., 2007; Pluart et al., 2005). However, the known computational methods are insufficient in studying TSNCs, because they either address thermoplastic polymer matrix only or neglect detailed information about the microstructure of polymer matrix.

As the goal of this work is to extend the fundamental knowledge and conduct optimal design of TSNC coatings; a main focus of this paper is to develop a comprehensive computational methodology for in silico synthesis (fabrication), characterization, and testing of TSNC coatings. This methodology should establish systematic correlations between material formulation, processing condition, coating microstructure, property, and performance. In the following text, a coarse-grained modeling method is introduced for TSNCs characterization at the outset. Then, a detailed simulation method for generating TSNC coating samples is described. Succeedingly, a unique microstructure characterization method is presented in order to gain insights into the structure–property correlation. After that, a computational tensile test method is proposed, which can be used to reveal the stress–strain behavior and evaluate the scratch resistance performance of the coatings. The methodological efficacy will be demonstrated through a comprehensive study on the design and analysis of a TSNC material.

2. General modeling of TSNCs

To fully characterize TSNCs, a modeling method must be capable of describing the polymeric material and nanoparticles in a 3D space of a computational environment and quantifying the interactions between them.

2.1. Polymer network model

Kremer and Grest (1990) introduced a coarse-grained bead-spring (CGBS) model. In that model, each polymer chain is represented by a sequence of equal-size beads (i.e., effective monomers) connected by anharmonic springs (i.e., bonds). In this work, the original CGBS model is extended, where each crosslinker is represented by a bead with the same size as an effective monomer, and a bond created by reactions connects an effective monomer and a crosslinker by the same type of spring in a precursor polymer chain.

The potential energy between each pair of non-bonded polymer beads and nanoparticles is defined as follows:

\[ I_{ij}^{nn} = 4 \varepsilon_{nn}^{pp} \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6, r_{min}^{nn} \leq r_{ij} \leq r_{max}^{nn} \]

where \( r_{ij} \) is the distance between beads \( i \) and \( j \); \( \varepsilon_{nn}^{pp} \) is an energy parameter; \( \sigma \) is a distance parameter; \( r_{min}^{nn} \) and \( r_{max}^{nn} \) are, respectively, the minimum distance and the cut-off distance between any two polymer beads. Note that the potential energy is set to zero when \( r_{ij} > r_{max}^{nn} \).

The potential energy between each pair of bonded beads and nanoparticles is defined as follows:

\[ I_{ij}^{nb} = \frac{-\mu}{2 \sigma^2} \left( \psi_{nb}^{max} \right)^2 \ln \left( 1 - \left( \frac{r_{ij}}{r_{nb}^{max}} \right)^2 \right) + 4 \varepsilon_{nb}^{pp} \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6, r_{min}^{nb} \leq r_{ij} \leq r_{max}^{nb} \]

where \( \mu \) is a spring constant; \( \psi_{nb}^{max} \) is the maximum allowable bond length.

2.2. Nanoparticle model

In this work, only spherical nanoparticles are investigated. Each nanoparticle is represented by a single (spherical) bead. The polymer beads interact with the nanoparticle beads through the following potential (Vacatello, 2001, 2002):

\[ I_{ij}^{mm} = 4 \varepsilon_{mm}^{pp} \left( \frac{\sigma}{r_{ij} - R_{np}} \right)^{12} - \left( \frac{\sigma}{r_{ij} - R_{np}} \right)^6, r_{min}^{mm} \leq r_{ij} \leq r_{max}^{mm} \]

where \( I_{ij}^{mm} \) is the potential energy shared by polymer bead \( i \) and nanoparticle bead \( j \); \( \varepsilon_{mm}^{pp} \) is an energy parameter, whose value is related to the size ratio of a nanoparticle bead to a polymer bead; \( R_{np} \) is the nanoparticle radius; \( r_{min}^{mm} \) and \( r_{max}^{mm} \) are, respectively, the minimum distance and the cut-off distance between a nanoparticle bead and a polymer bead.

The interaction potential between two bonded nanoparticles can be evaluated as

\[ I_{ij}^{nn} = 4 \varepsilon_{nn}^{nn} \left( \frac{\sigma}{r_{ij} - 2R_{np}} \right)^{12} - \left( \frac{\sigma}{r_{ij} - 2R_{np}} \right)^6, r_{min}^{nn} \leq r_{ij} \leq r_{max}^{nn} \]

where \( I_{ij}^{nn} \) is the potential energy shared by nanoparticle beads \( i \) and \( j \); \( \varepsilon_{nn}^{nn} \) is an energy parameter; \( r_{min}^{nn} \) and \( r_{max}^{nn} \) are, respectively, the minimum distance and the cut-off distance between two nanoparticle beads.

Note that the values of the minimum distance and the cut-off distance in Eqs. (1)-(4) are determined based on the potential energy. At the minimum distance, the potential energy should be larger than 50\( \varepsilon_{nn}^{pp} \). At the cut-off distance, the absolute value of the potential energy should be smaller than 0.017\( \varepsilon_{nn}^{pp} \). Also note that in this work, instead of modeling a nanoparticle as a cluster of beads (Starr et al., 2002; Cho and Sun, 2007), each nanoparticle is simplified as a single bead. It can help decrease the number of interaction potentials to be calculated in the simulation; thereby improving computational efficiency. However, the simplification may not be applicable to the cases where nanoparticles are significantly larger than the polymer beads and the shape change of nanoparticles is not negligible. In such circumstances, the treatment of a nanoparticle as a cluster of beads should be preferred.
3. TSNC coating development

As stated above, a critical need for computational design of TSNC coatings is to establish comprehensive correlations among TSNC material, processing condition, coating microstructure, property, and performance (see Fig. 1). Thus, the first essential task is to capture and understand the material’s microstructural evolution information obtainable from the coating formation process. A number of methods are available for studying TPNCs where the microstructure is a mono-dispersed thermoplastic polymer matrix that contains regularly distributed nanoparticles (Starr et al., 2002; Zhang and Archer, 2004). The known methods are not applicable to the study of TSNCs where the microstructure is a crosslinked polymer network containing randomly distributed nanoparticles. This requires development of a new simulation method that can resolve the following problems: (i) how to take into account the special characteristics of thermoset polymers, (ii) how to impose processing conditions, (iii) how to form polymer networks that interact with nanoparticles, and (iv) how to evaluate the effect of polymer network formation on the distribution of nanoparticles.

3.1. Simulation overview

In this work, an off-lattice MC simulation method is developed for TSNC coating development. There are two reasons for choosing MC rather than MD based method. The first is a concern of time scale. Note that a crucial step in preparing a TSNC coating sample is a polymer network formation through crosslinking reactions, for which the time scale involved is in the order of $10^3$ s; this has a multiple-order difference from MD simulation (a time step in the order of $10^{-15}$ s). The second reason for choosing MC rather than MD based method is a concern of length scale. MD simulation can be difficult for studying a polymer–nanoparticle system that contains long chains (> 100 effective units in a polymer chain) and large particles (> 10σ in diameter) (Zhang and Archer, 2004).

Metropolis algorithm: The Metropolis algorithm is directly adopted in the simulation (Metropolis et al., 1953). By this method, system microstructure evolution is realized through a trial move involving either an entity displacement or a volume change. The probability of accepting a trial configuration in the Markov chain can be expressed as (Allen and Tildesley, 1987)

$$p = \min \left\{ 1, \exp \left( -\frac{E^{\text{trial}} - E^{\text{now}} + P(V^{\text{trial}} - V^{\text{now}})}{k_B T} \right) \right\} \tag{5}$$

where $E^{\text{trial}}$ and $E^{\text{now}}$ are, respectively, the potential energy of the trial configuration and that of the current one; $V^{\text{trial}}$ and $V^{\text{now}}$ are, respectively, the volume of the trial configuration and that of the current one; $k_B$ is Boltzmann’s constant; $T$ is the system temperature; $P$ is the pressure; $N$ is the total number of entities in the system.

Periodic boundary condition (PBC): For all simulations, the PBC must be applied to all the faces of the simulation box in order to ensure the validity of the MC simulation results extendable to the entire system at the macro-scale. The PBC implies that when leaving the simulation box from one side (or face), the entity will enter the same box but from the opposite side.

Simulation procedure: A TSNC coating sample can be formed through a three-stage process. The first stage involves system set-up and then system equilibration in an NVT ensemble. In the second stage, crosslinking reactions and then another system equilibration in the NVT ensemble should be implemented. In the last stage, the system undergoes cool down and proceeds to equilibration in the NPT ensemble. These stages are delineated below.

3.2. Simulation system set-up

To setup a simulation system, all the involved system entities, including polymers and nanoparticles, must be created in a specified simulation box.

Polymeric material creation: The distribution of polymer molecular weights and functional groups is critical for thermoset polymer characterization. This disqualifies the simulation entity creation methods for the systems of monodispersed end-linked polymers (Gina et al., 2000) or those for the systems of monodispersed thermoplastic polymers (Zhang and Archer, 2004; Cho and Sun, 2007). Very recently, Xiao and Huang (2009) introduced a method for creating precursor polymer chains and crosslinker molecules for studying the design of paints—a type of TSNC material. That method is directly adopted in this work.

Nanoparticle creation and dimensional determination of simulation box: The total number of nanoparticles ($N^n$) can be determined as follows:

$$N^n = \text{int} \left( \frac{3\rho^p(N_m^m + N_f^m)}{4\rho^p(1 - \phi^a)\pi(R)^2} \right)$$

where $\rho^p$ is the number density of polymeric materials; $N_m^m$ and $N_f^m$ are, respectively, the total number of effective monomers and that of crosslinkers; $R$ and $\phi^a$ are, respectively, the radius and volume fraction of nanoparticles.

For a regular cubic simulation box, its initial edge length can then be calculated as

$$L_0 = \sqrt[3]{\frac{N_m^m\pi4}{3\phi^a}} R$$

For each entity created in the simulation box, a unique index is assigned to it. For convenience, the entity numbers from 1 to $N_m^m$ are reserved for $N_m^m$ effective monomers, the numbers from $N_m^m + 1$ to $N_m^m + N_f^m$.
to \(N^m + N^r\) are given to \(N^r\) crosslinkers, and the numbers from \(N^m + N^r + 1\) to \(N^m + N^r + N^p\) are assigned to \(N^p\) nanoparticles.

### 3.3. Initial configuration generation

An initial system configuration can be generated by properly placing all the entities including nanoparticles, precursor polymer chains, and crosslinkers into the simulation box. The placement should satisfy three restrictions: (a) the distance between any two adjacent entities should be sufficient to avoid an extraordinarily high steric repulsion in between, (b) the distance between any pair of bonded polymer beads cannot exceed the maximum bond length, and (c) polymer chain backfolding must be prevented through separating every other polymer bead in the same precursor polymer chain so that the distance in between can be larger than a preset minimum distance \(r^\text{min}\). According to Kremer and Grest (1990), this third restriction can ensure basically a right polymer chain persistence length.

**Entity placement:** To ensure an efficient placement, the large entities (i.e., nanoparticles) should be first placed randomly into the simulation box where restriction (a) is applied. Then, the polymeric materials are placed in two steps: (i) to generate a queue of polymer chains according to their lengths, where the longest chain is at the beginning, and the molecules of individual effective monomers and crosslinkers not involved in any chain in the end and (ii) to place the entities from the top of the queue one by one into the simulation box by following the procedure below. Needless to say, every placement must satisfy the restrictions listed above.

#### Step 1. Place the first polymer bead of a chain in the queue to a randomly selected feasible location in the box.

#### Step 2. Identify the next polymer bead (e.g., bead \(i\)) of the chain in the queue and try to place it to a feasible location that is specified by the following equation:

\[
\mathbf{r}_i = \mathbf{r}_{i-1} + \Delta \mathbf{r}
\]

where \(\mathbf{r}_{i-1}\) is the position vector of the most recently placed polymer bead (i.e., bead \(i-1\), whose relative position to the polymer bead \(i\) is given by \(\Delta \mathbf{r}\)

\[
\Delta \mathbf{r} = (l_0^i \sin \theta_1 \cos \theta_2, \ l_0^i \sin \theta_1 \sin \theta_2, \ l_0^i \cos \theta_1)
\]

where \(l_0^i\) is the initial bond length; \(\theta_1\) and \(\theta_2\) are two random numbers between 0 and 2\(\pi\). If the placement is successful, then go to Step 4; otherwise, continue.

#### Step 3. Check if the number of placement attempts is larger than the preset limit or not. If yes, move both the current polymer bead and the bead most recently placed in the simulation box back to the queue, and return to Step 2; otherwise, return to Step 2 to conduct another placement attempt.

#### Step 4. Check if the chain has any polymer bead left for placement. If yes, return to Step 2; otherwise, continue.

#### Step 5. Check if any chain in the queue has not been placed or not. If yes, return to Step 1; otherwise, continue.

#### Step 6. Place all the individual polymer beads in the queue one by one to the feasible locations.

Note that all the bonds have the same initial length \((l_0^i)\), which can be set as the equilibrium length between any pair of bonded polymer beads. This setting, together with the application of the polymer chain backfolding restriction, will be necessary for the construction of an initial structure that is close to an equilibrium state; this should greatly help to reduce computational time for achieving a system equilibration.

### 3.4. System equilibration

There are three system equilibrations that the simulation system needs to reach during coating sample development. The first equilibration occurs after an initial configuration is generated, the second appears after the crosslinking reaction is accomplished, and the third is needed after the sample is cooled. These equilibration processes involve both the NVT and NPT ensembles, which can be accomplished by following a general procedure below:

#### Step 1. Initialize an equilibration process by setting the MC cycle index \((I)\) to 0, and enter system temperature \(T\), pressure \(P\), and volume \(V\).

#### Step 2. Start a new MC cycle by setting \(I=I+1\).

#### Step 3. Attempt to displace all entities by following the sub-steps below:

- **Step 3.1.** Initiate a new MC step and select randomly an entity that has not been selected in the current MC cycle. The position of the entity (the \(i\)-th) is \(\mathbf{r}_i\).

- **Step 3.2.** Determine a new position for entity \(i\) to move. The attempted new position is given by vector \(\mathbf{r}_i^\text{final}\)

\[
\mathbf{r}_i^\text{final} = \mathbf{r}_i + \Delta \mathbf{r}
\]

and

\[
\Delta \mathbf{r} = (l_{max}^i \sin \theta_1 \cos \theta_2, \ l_{max}^i \sin \theta_1 \sin \theta_2, \ l_{max}^i \cos \theta_1)
\]

where \(\xi\) is a random number between 0 and 1; \(l_{max}^i\) is a maximum displacement distance for entity \(i\) in an MC step.

- **Step 3.3.** Reject this move attempt and go to Step 3.5, if it violates either the minimum distance restriction or the bond length restriction; otherwise, continue.

- **Step 3.4.** Move the entity to the new position, if the attempt is accepted according to the Metropolis criterion in Eq. (5); otherwise, this move attempt must be discarded.

- **Step 3.5.** Check if all the entities have been attempted to displace once in the current MC cycle. If yes, go to Step 4; otherwise, return to Step 3.1.

#### Step 4. Attempt to change the volume of the simulation box by following the sub-steps below, if the system is in an NPT ensemble; otherwise, go to Step 5 directly.

**Step 4.1.** Determine the new volume of the simulation box according to

\[
V^\text{final} = \left(\sqrt{V^\text{initial}} + \frac{P^i_{max}(2\xi - 1)}{3}\right)^3
\]

where \(P^i_{max}\) is the maximum length change of each edge of the simulation box in an MC step.

**Step 4.2.** The trial positions of all the \(N^e\) entities are re-calculated as

\[
\mathbf{r}_i^\text{final} = \mathbf{r}_i \left( \frac{V^\text{final}}{V^\text{initial}} \right)^{1/3}, \ i = 1, 2, \ldots, N^e
\]
3.5. Crosslinking reaction

In the simulation system, crosslinking reactions are introduced to form 3D crosslinked polymer networks; this is essential for creating a TSNC coating sample. During the course of the network formation, interrelated physical and chemical phenomena (i.e., polymer and nanoparticle movement and crosslinking reaction) occur simultaneously, which are influenced by the dynamically changed curing environment. The phenomena should be properly characterized in order to have a reliable prediction on microstructure evolution. A detailed procedure below is designed for this purpose.

Step 1. Initialize the reaction simulation by setting the MC cycle index \(I\) and the crosslinking reaction conversion percentage \(z_t\) to 0.

Step 2. Start a new MC cycle by setting \(I=I+1\), and let \(T = T_t\) to update the system temperature.

Step 3. Attempt to displace a randomly selected entity by following the sub-steps below:

- Step 3.1. Select randomly an entity that has not been selected in the current MC cycle. The position vector of the entity (namely entity \(i\)) is \(r_i\).
- Step 3.2. Calculate a new position for entity \(i\); \(r_{i}^{\text{new}}\), using Eqs. (10) and (11). (Note that \(r_{i}^{\text{new}}\) is a function of the entities' current positions and the system temperature)
- Step 3.3. Reject the attempt and go to Step 4 if it violates the minimum distance restriction or the bond length restriction; otherwise, continue.
- Step 3.4. Move the entity to the new position, if the attempt is accepted according to the Metropolis criterion; otherwise, this move attempt must be discarded.

Step 4. Perform crosslinking reactions between the selected entity and other entities by following the sub-steps below:

- Step 4.1. Check if the selected entity \(i\) is a polymer bead or not. If yes, continue; otherwise, go to Step 5.
- Step 4.2. Check if there is a remaining functional group on this polymer bead or not. If yes, continue; otherwise, go to Step 5.
- Step 4.3. Check if there is such a neighboring polymer bead \(j\): (i) it has not been attempted to react with polymer bead \(i\) in the current run of Step 4, (ii) it is located within a reaction distance \(l_{\text{max}}\) from polymer bead \(i\), (iii) it has a different type of functional groups, and (iv) it has at least one remaining functional group for reaction. If all these conditions are met, continue; otherwise, go to Step 5.

Step 4.4. Create a bond between polymer beads \(i\) and \(j\) with a specified probability. This reaction probability, \(p'\), is a function of system temperature \(T\), i.e.,

\[
p' = \min\left\{1, \exp\left(\frac{-I^t}{k_B T}\right)\right\}
\]

where \(\eta\) and \(I^t\) are material dependent parameters (both positive).

Step 4.5. Return to Step 4.2 for another possible bond creation.

Note that \(l^t_{\text{max}}\) in Eq. (11) and \(l_{\text{max}}\) in Eq. (12) are automatically adjusted during the course of the simulation in order to keep the acceptance rates of the following attempts all at \(-50\%\): (i) the displacement attempts of effective monomers, crosslinkers, and nanoparticles and (ii) the simulation box volume change attempt. In this way, the algorithm can be more efficient, since neither large displacement (with a low acceptance rate) nor small displacement (with a high acceptance rate) is desirable (Chui and Boyce, 1999).

Step 5. Check if the number of MC cycles has reached the preset maximum number \((N_{\text{MC}})\). If yes, the equilibration process is finished; otherwise, return to Step 2.

Step 6. Calculate crosslinking conversion \(z_t\) using

\[
z_t = z_{t-1} + \frac{N_{\text{a}}^N - N_{\text{a}}^\text{NA}}{N_0^\text{NA}}
\]

where \(N_0^\text{NA}\) is the number of remaining Type A functional groups in the end of the \(I\)-th MC cycle. Thus, \(N_{\text{a}}^N - N_{\text{a}}^\text{NA}\) gives the number of bonds created in the \(I\)-th MC cycle.

Step 7. Check if \(z_t < z_{\text{max}}\), where \(z_{\text{max}}\) is the target crosslinking conversion. If yes, return to Step 2; otherwise, terminate the simulation as the network formation is accomplished.

Note that the system configuration and the potential energy will be changed due to bond creation. Whenever two non-bonded polymer beads become bonded, the FENE potential is added (see Eqs. (1) and (2)). The changes of configuration and energy will affect the succeeding entity movement, in turn the subsequent crosslinking reaction. This type of sophisticated interactions is effectively handled by the proposed procedure. Note that in order to satisfy the bond length restriction when creating new bonds, the reaction distance should be shorter than the maximum bond length, i.e., \(l^t_{\text{max}} < l_{\text{max}}\).

3.6. Cooling process

After the crosslinking reaction and the second-stage equilibration, the TSNC coating sample needs to be cooled down to a normal temperature. The cooling process is conducted at a constant pressure. Thus the volume change of the coating sample should be taken into account. This process can be accomplished by the following procedure:

Step 1. Initialize the cooling process simulation by setting the MC cycle index \(I\) to 0, and then enter an initial temperature \(T_0\), an external pressure \(P_{\text{ext}}\), and a desired cooling rate \(\Delta T\), and then set the system temperature \(T_t\) be \(T_0\).

Step 2. Start a new MC cycle by setting \(I=I+1\) and let \(T_t = T_{t-1} + \Delta T\).

Step 3. Attempt to displace each entity by following Sub-steps 3.1 to 3.5 of the System Equilibration Procedure introduced previously.

Note that the cooling process is conducted at a constant pressure. Thus the volume change of the coating sample should be taken into account. This process can be accomplished by the following procedure:
Step 4. Attempt a volume change of the simulation box by following Sub-steps 4.1 to 4.4 of the System Equilibration Procedure introduced previously.

Step 5. Check if $T_i \leq T_f$ or not. If yes, the cooling process is ended; otherwise, return to Step 2.

4. Characterization of TSNC coating microstructures

The information about the microstructural evolution in a coating sample is very valuable for gaining a deep understanding of the TSNC coating formation. An in-depth quantitative analysis of microstructures and dynamics can provide insights into the structural origin of material properties.

The microstructures can be characterized by quantifying the spatial distribution of the polymer beads surrounding the nanoparticles. The available methods are mostly limited to analyzing simple microstructures, where either a single nanoparticle is placed in the center of a simulation box or multiple nanoparticles are placed regularly in a simulation box (Starr et al., 2002; Zhang and Archer, 2004; Cho and Sun, 2007). The method introduced by Vacatello (2001, 2002) could be applied to the case where nanoparticles are randomly distributed; however, the method is very complicated and could generate misleading results. Most importantly, all known methods are not suitable for the study of TSNC coating microstructures where the polymer networks contain effective monomers as well as crosslinkers.

In the following section, three indicators and one characterization procedure are introduced. They are applicable to the microstructures with no restriction on the quantity and distribution of the nanoparticles in the system, and are capable of differentiating the effective monomer and crosslinker distributions and evaluating polymer network properties.

4.1. Microstructure indicators

**Polymer—bead number—density distribution.** The number density (ND) distribution of the effective monomers and that of the crosslinkers are defined below:

$$\rho^{\text{p}}(r_k) = \left( \frac{1}{N^\text{p}} \sum_{j=1}^{N^\text{p}} N^\text{p}(r_k, j) \right) \frac{1}{V(r_k)}, k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (16)

$$\rho^{\text{c}}(r_k) = \left( \frac{1}{N^\text{c}} \sum_{j=1}^{N^\text{c}} N^\text{c}(r_k, j) \right) \frac{1}{V(r_k)}, k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (17)

where $N^\text{p}(r_k, j)$ and $N^\text{c}(r_k, j)$ are, respectively, the number of effective monomers and that of crosslinkers, both within the $k$-th shell at distance $r_k$ from the center of the $j$-th nanoparticle. Fig. 2(a) gives an example involving three nanoparticles, where the $k$-th shell of each nanoparticle has the thickness of $\delta r$. The distance $r_k$ is given as

$$r_k = R^\text{c} + \left( \frac{2k - 1}{2} \right) \delta r, k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (18)

The terms in the parentheses of Eqs. (16) and (17) are, respectively, the average number of effective monomers and that of crosslinkers in the $k$-th shell of each nanoparticle. $V(r_k)$ is the volume of the $k$-th shell, which can be obtained by

$$V(r_k) = \frac{\pi \delta r}{3} (12 r_k^2 + \delta r^2), k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (19)

Note that the total number of shells, $k_{\text{max}}$, for each nanoparticle is

$$k_{\text{max}} = \text{int} \left( \frac{r_{\text{max}} - R^\text{c}}{\delta r} \right)$$  \hspace{1cm} (20)

and

$$r_{\text{max}} = \min \left( \frac{p, p, p, F}{2, 2, 2} \right)$$  \hspace{1cm} (21)

where $p, p$, and $F$ are, respectively, the edge length of the simulation box in the $x, y,$ and $z$ directions.

The polymer-bead ND distribution can be readily obtained by adding Eqs. (16) and (17), i.e.,

$$\rho^{\text{p}}(r_k) = \rho^{\text{p}}(r_k) + \rho^{\text{c}}(r_k)$$  \hspace{1cm} (22)

**Crosslink density distribution:** For thermoset polymers, an important structural property is the crosslink density or the concentration of elastically effective junction points (EEJs) in the infinite (INF) polymer network. Note that an EEJP is a polymer bead (either an effective monomer or a crosslinker) that has three or more arms leading out to the INF network (Miller and Macosko, 1976). Xiao and Huang (2009) introduced a method for EEJP identification, which is omitted here. An indicator, namely crosslink density (CD) distribution, is introduced to characterize the distribution of EEJs surrounding nanoparticles. It is defined as

$$\rho^{\text{c}}(r_k) = \left( \frac{1}{N^\text{c}} \sum_{j=1}^{N^\text{c}} N^\text{c}(r_k, j) \right) \frac{1}{V(r_k)}, k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (23)

where $N^\text{c}(r_k, j)$ is the number of EEJs within the $k$-th shell of the $j$-th nanoparticle.

**Polymer—bead cumulative-number-percentage distribution:** The cumulative number percentage (CNP) distributions of effective monomers and crosslinkers are, respectively, defined as

$$\psi^{\text{p}}(r_k) = \frac{1}{N^\text{p}} \sum_{i=1}^{k} N^\text{p}(r_i), k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (24)

$$\psi^{\text{c}}(r_k) = \frac{1}{N^\text{c}} \sum_{i=1}^{k} N^\text{c}(r_i), k = 1, 2, \ldots, k_{\text{max}}$$  \hspace{1cm} (25)

![Fig. 2. Illustration of the shells surrounding nanoparticles: (a) the $k$-th shells for three nanoparticles and (b) the $k$-th super-shell.](image-url)
where \( N^m(r_k) \) and \( N^c(r_k) \) are, respectively, the number of effective monomers and that of crosslinkers within a “super-shell” at distance \( r_k \) from the centers of all nanoparticles. Note that a super-shell has a complex geometry and it may contain more than one shell. Fig. 2(b) shows an example of a \( k \)-th super-shell (see the shaded area). \( \psi^m(r_k) \) and \( \psi^c(r_k) \) give, respectively, the number percentage of effective monomers and that of crosslinkers within a distance of \( r_k + \sigma_r / 2 \) from the centers of all nanoparticles. The polymer-bead CNP distribution is given by

\[
\psi^m(r_k) = \frac{1}{N^m + N^c} \sum_{i=1}^{n} (N^m(r_i) + N^c(r_i)), k = 1, 2, \ldots, k_{\text{max}}
\]

4.2. Evaluation procedure

The polymer-bead ND and CNP distributions and the CD distribution in any given microstructure can be obtained by following a general procedure below:

Step 1. Input all the entity positions, the entity numbers (\( N^m \), \( N^c \), and \( N^p \)), the nanoparticle radius (\( R^p \)), and the simulation box size (\( L_x \), \( L_y \), and \( L_z \)), and specify the shell thickness (\( \delta r \)) and calculate distance \( r_k \) using Eq. (18), and the total number of shells (\( k_{\text{max}} \)) using Eqs. (20) and (21).

Step 2. Initialize the calculation by setting \( N^m(r_{k,j}) \), \( N^c(r_{k,j}) \), \( N^p(r_k) \) and \( N^p(r_j) \) (\( j = 1, 2, \ldots, N^p; k = 1, 2, \ldots, k_{\text{max}} \)) to 0, and both polymer-bead index \( i \) and nanoparticle index \( j \) to 1.

Step 3. Read the position of the \( i \)-th polymer bead, \( r_i \).

Step 4. Read the position of the \( j \)-th nanoparticle, \( r_j \).

Step 5. Calculate and record the center-to-center distance between the \( i \)-th polymer bead and the \( j \)-th nanoparticle, \( r_{ij} \).

Step 6. Determine the index of the \( j \)-th nanoparticle’s shell where the \( i \)-th polymer bead resides. This shell index can be calculated as

\[
k = \left\lfloor \frac{r_{ij} - R^p}{\delta r} \right\rfloor
\]

where the symbol, \( \lfloor \cdot \rfloor \), gives the smallest integer not less than or equal to the number inside.

Step 7. Go to Step 8 if \( k > k_{\text{max}} \); otherwise, continue.

Step 8. Increase \( N^m(r_{k,j}) \) by 1 if the \( i \)-th polymer bead is an effective monomer, increase \( N^c(r_{k,j}) \) by 1 if the \( i \)-th polymer bead is a crosslinker, and increase \( N^p(r_{k,j}) \) by 1 if the \( i \)-th polymer bead is an EEP.

Step 9. Check if \( j < N^p \) or not. If yes, increase \( j \) by 1 and return to Step 4; otherwise, continue.

Step 10. Compare the distances between the \( i \)-th polymer bead and all the \( N^p \) nanoparticles, and then identify the minimum distance that is to be assigned to \( \rho_{\text{min}} \).

Step 11. Determine the index of the super-shell where the \( i \)-th polymer bead resides. The index \( k \) can be calculated by substituting \( \rho_{\text{min}} \) into Eq. (27) as \( r_{ij} \).

Step 12. Go to Step 14 if \( k > k_{\text{max}} \); otherwise, continue.

Step 13. Increase \( N^m(r_k) \) by 1 if the \( i \)-th polymer bead is an effective monomer, and increase \( N^c(r_k) \) by 1 if the \( i \)-th polymer bead is a crosslinker.

Step 14. Check if \( i < N^m + N^c \) or not. If yes, increase \( i \) by 1, reset \( j \) to 1 and return to Step 3; otherwise, continue.

Step 15. Calculate the ND distributions using Eqs. (16), (17) and (22), the CD distribution using Eq. (23), and the CNP distributions using Eqs. (24)–(26).

5. TSNC coating testing and quality evaluation

Fig. 1 shows that the evaluation of a cured TSNC coating sample requires prediction of mechanical, barrier, and rheological properties, etc. As the first step towards a thorough understanding eventually, this work focuses on a mechanical elastic property. This property is qualitatively correlated to the scratch resistance performance of a TSNC coating.

The elastic property or the stiffness of the coating can be determined by Young’s modulus. This modulus can be quantified based on a stress–strain curve, which can be obtained using either MD or MC based deformation simulation techniques. Note that MD techniques have been used to predict the elastic properties of TPNCs (Frankland et al., 2003; Cho and Sun, 2007; Adnan et al., 2007). The studies have shown some technical limitations, such as requiring a small system size and a huge unrealistic deformation rate. To simulate a relatively large system deformed under a relatively low deformation rates, MC techniques should be more desirable (Li et al., 2006; Mulder et al., 2007), as it has been proven a useful tool for simulating the deformation of polymers at low temperatures, which is inherently a non-equilibrium dynamic process (Chui and Boyce, 1999). Various lattice and off-lattice MC methods are available for the deformation simulation of a single polymer chain, polymer melts and crosslinked polymer networks (Wittkop et al., 1994; Holzl et al., 1997; Chui and Boyce, 1999; Li et al., 2006). The known methods for simulating pure polymers cannot be directly used for the polymer nanocomposite study. The limitations of the existing methods render a need to develop an MC-based deformation simulation method that can be used to reveal the stress–strain behavior of TSNCs.

5.1. Deformation simulation

The deformation of a TSNC coating sample is a nonequilibrium process. The simulation of such a process is accomplished by an off-lattice MC-based method in this work. According to Chui and Boyce (1999), MC-based deformation simulation can be considered as an energy minimization procedure, where the attainable lowest energy configuration is governed by the amount of available thermal energy and the number of MC cycles in simulation. For a highly crosslinked TSNC coating sample, the mobility of the polymer chains in it is highly restricted. This means the polymer structure is effectively trapped in a metastable state, which implies a system reaching a local minimum energy. This justifies the use of MC techniques to perform deformation simulation for a TSNC sample and the nonequilibrium mechanical behavior of the coating structure can be sampled feasibly.

Strain imposition: Tensile test simulation of a coating sample is performed by imposing a series of strain increments (\( \Delta \xi \)) on the simulation box along a preferred direction (e.g., the \( x \) direction) until the strain reaches the maximum (\( \xi_{\text{max}} \)). The box length increment for each strain increment should be

\[
\Delta L = \ell_0 \Delta \xi, \quad \ell_0, i = 1, 2, \ldots, l_{\text{max}}
\]

Fig. 3. Sketch of a simulation box: (a) before imposing the \( l \)-th strain increment, (b) after imposing the \( l \)-th strain increment, and (c) after the system relaxation.
where \( l_{x,i-1}^{l} \) and \( l_{x}^{l} \) are the box lengths in the x direction before and after imposing the \( l \)-th strain increment, respectively; \( I_{\text{max}} \) is the total number of strain increments to impose, which is

\[
I_{\text{max}} = \text{int} \left( \frac{\Delta \varepsilon_{\text{max}}}{A_{x}} \right) \tag{29}
\]

Fig. 3(a) and (b) show the simulation box before and after imposing the \( l \)-th strain increment in the \( x \) direction. Note that the box lengths in \( y \) and \( z \) directions are not changed at this stage. Due to the change of the simulation box, the positions of all entities should be changed accordingly. Affine motion is used as an initial guess for the entity positions (Chui and Boyce, 1999; Li et al., 2006), which gives

\[
r_{ij} = \left( \frac{I_{x}}{l_{x,i-1}^{l}} \right) x_{ij-1}, y_{ij-1}, z_{ij-1} \tag{30}
\]

System relaxation: Between two adjacent strain increments, the system must be relaxed in an extended ensemble in order to resemble a real material deformation process. Here, the selected ensemble has the total number of entities (\( N^{e} \)) fixed, and keeps the temperature and the transverse normal stresses (i.e., the normal stresses in the directions normal to the applied stress, \( \sigma_{T}^{l} \) and \( \sigma_{T}^{l} \)) constant. This extended ensemble, namely the \( N^{e}(l^{T}, \sigma_{T}^{l}, \sigma_{T}^{l})T \) ensemble, is the one similar to the NVT ensemble in the \( x \) direction and the NPT ensemble in the \( y \) and \( z \) directions (Yang et al., 1997).

In order to achieve a system relaxation in an \( N^{e}(l^{T}, \sigma_{T}^{l}, \sigma_{T}^{l})T \) ensemble, the procedure presented in the system equilibration section is adopted, where Step 4 (i.e., a method for changing the size of the simulation box) should be replaced by the following new step. The modification involves the box size changes in the \( y \) and \( z \) directions so that the stresses in these two directions can be maintained at the atmospheric pressure, \( p_{\text{atm}} \), which is close to zero as compared with the applied stress in the \( x \) direction. A simulation box after the system relaxation is shown in Fig. 3(c). The revised Step 4 is described below.

Step 4. Change the size of the simulation box by following the sub-steps below:

Step 4.1. Check if \( p_{\text{atm}} + \sigma_{T}^{l} \) is lower than the maximum allowable deviation \( (p_{\text{atm}}^{\text{max}}) \) or not. If yes, go to Step 5; otherwise, continue.

Step 4.2. Attempt to change the box size by calculating the new box lengths in the \( y \) and \( z \) directions, i.e.,

\[
p_{\text{now}} = p_{\text{now}} + p_{\text{max}}(Z_{c} - 1) \tag{31}
\]

Step 4.3. The trial positions of all the entities become

\[
r_{ij}^{\text{trial}} = \left( \begin{array}{c}
n_{ij}^{\text{now}} \left( \frac{p_{\text{trial}}}{p_{\text{now}}} \right) \left( \frac{p_{\text{trial}}}{p_{\text{now}}} \right) \left( \frac{p_{\text{trial}}}{p_{\text{now}}} \right) \end{array} \right) \tag{32}
\]

Step 4.4. Reject the attempt and return to Step 4.2, if it violates either the minimum distance restriction or the bond length restriction; otherwise, continue.

Step 4.5. Move all the entities to the new positions, and return to Step 4.1 if \( p_{\text{atm}}^{\text{trial}} < p_{\text{atm}}^{\text{now}} \); otherwise, return to Step 4.2.

Note that a major difference between the system equilibration in the coating formation and the system relaxation in the tensile test is the setting of the number of MC cycles (\( I_{\text{MC}} \)). For the former case, the number of MC cycles should be sufficiently large so that an equilibrium status can be reached. For the latter case, the number will be much smaller because the tensile test is essentially a non-equilibrium dynamic process. The number of MC cycles should be specified to ensure that the deformation is continuously applied before the system is allowed to fully equilibrate thermodynamically (Chui and Boyce, 1999). Also note that different strain rates can be studied by adjusting the magnitude of strain increment \( (\Delta \varepsilon) \) and the number of MC cycles after each strain increment (\( I_{\text{MC}}^{l} \)). The smaller the \( \Delta \varepsilon \) and the larger the \( I_{\text{MC}}^{l} \), the lower the strain rate.

Stress evaluation: For a unidirectional tensile test, only the normal stress needs to be evaluated. For a system containing equally sized entities, the normal stress can be calculated according to the Virial theorem (Allen and Tildesley, 1987), which is the sum of a kinetic stress (due to the thermal motion effect) and an inter-entity stress (due to the inter-entity interaction).

Since the cured coating sample is tested at a normal temperature, the kinetic stress contribution can be safely neglected (Cho and Sun, 2007), which gives

\[
\tau_{\beta i} = \frac{1}{V_{0}} \sum_{i=1}^{N_{e}} \sum_{j=1}^{N_{e}} \left( \frac{d_{ij}}{R_{i}} \right) \left( \frac{\sigma_{ij}^{T}}{R_{i}} \right), \beta = xx, yy, \text{or} zz \tag{34}
\]

where \( \tau_{\beta i} \) is the \( \beta \) component of the stress; \( V_{0} \) is the volume of the undeformed simulation box; \( r_{ij} \) and \( r_{ij}^{0} \) are the norm and the \( \beta \)-component (i.e., \( x, y, \text{or} z \)) of the vector separating entities \( i \) and \( j \), respectively.

Note that for the system of interest, the entities have two different sizes. Since the nanoparticle beads are much larger than the polymer beads, Eq. (34) must be modified through replacing \( r_{ij} \) by \( r_{ij} - \omega_{ij}R^{o} \) and \( r_{ij}^{0} \) by \( r_{ij}^{0}(1 - \omega_{ij}R^{o}/r_{ij}) \), which yields

\[
\tau_{\beta i} = \frac{1}{V_{0}} \sum_{i=1}^{N_{e}} \sum_{j=1}^{N_{e}} \left( \frac{d_{ij}}{R_{i}} \right) \left( \frac{\sigma_{ij}^{T}}{R_{i}} \right), \beta = xx, yy, \text{or} zz \tag{35}
\]

where \( \omega_{ij} \) is an integer determined by

\[
\omega_{ij} = \begin{cases} 0, & \text{if both are polymer beads} \\ 1, & \text{if one is a nanoparticle and one is a polymer bead} \\ 2, & \text{if both are nanoparticles} \end{cases} \tag{36}
\]

The total stress includes the contributions from four types of interactions: Type I—the polymer–polymer nonbonded interaction, Type II—the polymer–polymer bonded interaction, Type III—the polymer–nanoparticle interaction, and Type IV—the nanoparticle–nanoparticle interaction. That is

\[
\tau_{\beta i} = \tau_{\beta i}^{\text{I}} + \tau_{\beta i}^{\text{II}} + \tau_{\beta i}^{\text{III}} + \tau_{\beta i}^{\text{IV}}, \quad \beta = xx, yy, \text{or} zz \tag{37}
\]

According to Eqs. (1)–(4) where four types of potential energies are defined and using Eq. (35), the four types of stresses can be quantitatively evaluated as

\[
\tau_{\beta i}^{\text{I}} = \frac{24A_{\sigma}p_{\text{atm}}^{6}}{V_{0}} \sum_{i=1}^{N_{e}} \sum_{j=1}^{N_{e}} \left( \frac{d_{ij}}{R_{i}} \right) \left( \frac{\sigma_{ij}^{T}}{R_{i}} \right)^{2} \left( \frac{1}{R_{ij}} \right)^{6} - 2\sigma_{\varepsilon}^{6} \left( \frac{1}{R_{ij}} \right)^{12} \tag{38}
\]

\[
\tau_{\beta i}^{\text{II}} = \frac{24A_{\sigma}p_{\text{atm}}^{6}}{V_{0}} \sum_{i=1}^{N_{e}} \sum_{j=1}^{N_{e}} \left( \frac{d_{ij}}{R_{i}} \right) \left( \frac{\sigma_{ij}^{T}}{R_{i}} \right)^{2} \left( \frac{1}{R_{ij}} \right)^{6} - 2\sigma_{\varepsilon}^{6} \left( \frac{1}{R_{ij}} \right)^{12} \tag{39}
\]

\[
\tau_{\beta i}^{\text{III}} = \frac{24A_{\sigma}p_{\text{atm}}^{6}}{V_{0}} \sum_{i=1}^{N_{e}} \sum_{j=1}^{N_{e}} \left( \frac{d_{ij}}{R_{i}} \right) \left( \frac{\sigma_{ij}^{T}}{R_{i}} \right)^{2} \left( \frac{1}{R_{ij}} \right)^{6} - 2\sigma_{\varepsilon}^{6} \left( \frac{1}{R_{ij}} \right)^{12} \tag{39}
\]
The stress–strain behavior of a coating sample should be represented by an averaged stress–strain curve (Cho and Sun, 2007). A procedure is performed to obtain three stress–strain curves. The overall stress–strain behavior of a TSNC coating can be correlated to its elastic property and scratch resistance performance using

\[
\tau^\beta_{\text{cum}} = \left( \frac{24\rho \sigma \epsilon^0}{V_0} \right) \left( \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij} - R^2} \right)^{12} \left( \sum_{i=1}^{N_0} \sum_{j=1}^{N_0} \frac{1}{r_{ij} - R^2} \right)^{12} -2\sigma^0 \left( \frac{1}{r_{ij} - R^2} \right)^{12} \]

(40)

\[
\tau^\beta_{\text{IV}} = \left( \frac{24\rho \sigma \epsilon^0}{V_0} \right) \left( \sum_{i=1}^{N-1} \sum_{j=1}^{N} \frac{1}{r_{ij} - R^2} \right)^{12} -2\sigma^0 \left( \frac{1}{r_{ij} - R^2} \right)^{12} \]

(41)

Simulation procedure: It is known that molecular material models often show anisotropic mechanical properties, which is in contrast to the fact that bulk materials usually possess isotropic mechanical properties. In order to have a more reliable prediction, three independent tensile tests in x, y, and z directions should be performed to obtain three stress–strain curves. The overall stress–strain behavior of a coating sample should be represented by an averaged stress–strain curve (Cho and Sun, 2007). A procedure is introduced below for conducting tensile tests on a coating sample.

Step 1. Specify the maximum strain (\(\epsilon_{\text{max}}\)), the strain increment (\(\Delta \epsilon\)), and the number of MC cycles (\(N_{\text{MC}}\)) between two adjacent strain increments.

Step 2. Initialize a tensile test simulation in a coordinate direction \(\beta\) (i.e., x, y, or z) that has not been tested and set the strain increment index (\(I\)) and the initial strain (\(\epsilon_0\)) to 0. Then input the original simulation box size (\(V_0\)) and the undeformed coating microstructure, and subsequently calculate the stresses, \(\tau^\beta_0\), \(\tau^\beta_1\), \(\tau^\beta_{\text{II}}\), \(\tau^\beta_{\text{III}}\), and \(\tau^\beta_{\text{IV}}\) using Eqs. (37)–(41).

Step 3. Update the strain increment index (let \(I=I+1\)), increase the strain by \(\Delta \epsilon\) (thus, \(\epsilon_{I} = \epsilon_{I-1} + \Delta \epsilon\)), and increase the length of simulation box by \(\Delta l\) according to Eq. (28) (thus, \(l^\beta = l^\beta_{I-1} + \Delta l\)). Note that the positions of all the entities should be rescaled (see Eq. (30)) in order to fit all into the new simulation box.

Step 4. Relax the system in the extended ensemble for \(N_{\text{MC}}\) MC cycles.

Step 5. Evaluate stresses \(\tau^\beta_0\), \(\tau^\beta_1\), \(\tau^\beta_{\text{II}}\), \(\tau^\beta_{\text{III}}\), and \(\tau^\beta_{\text{IV}}\) using Eqs. (37)–(41).

Step 6. Check if \(\epsilon_I < \epsilon_{\text{max}}\) or not. If yes, return to Step 3; otherwise, the tensile test in one coordinate direction is finished, and thus record all the strain and stress data.

Step 7. Check if all three coordinate directions have been tested or not. If no, return to Step 2; otherwise, output the strain and stress data in the three directions, and the coating sample testing is accomplished.

5.2. Property and quality evaluation

The stress–strain behavior of a TSNC coating can be correlated to its elastic property and scratch resistance performance using the following methods:

Elastic property quantification: The elastic property (stiffness) of a TSNC coating is evaluated using Young’s modulus (\(E\)), which is quantified as the initial slope of the average stress–strain curve in the strain range up to \(\epsilon_{\text{max}}\) (about 1–2%). The quantification of \(E\) from the stress–strain data can be formulated as the following optimization problem

\[
\min_{\tau} \sum_{I=0}^{N_{\text{f}}} \left( E \epsilon^I - \tau^I \right)^2
\]

(42)

where

\[
\tau^I = \tau^x_I + \tau^y_I + \tau^z_I
\]

and

\[
\tau^I_{\text{max}} = \text{int} \left( \frac{\epsilon^I_{\text{max}}}{\Delta I} \right)
\]

(43)

(44)

Note that \(I_{\text{max}}\) is the number of strain increments imposed when the strain reaches \(\epsilon_{\text{max}}\).

Material property–scratch resistance correlation establishment: Scratch resistance is an important performance for coating systems in numerous applications. Various efforts have been devoted to correlating this performance to a wide variety of material properties, such as crosslink density, network homogeneity, glass transition temperature, modulus, toughness, hardness, and coefficient of friction (Kutscher and Sander, 2006; Ryntz and Britz, 2002; Shen et al., 1997). However, since no common benchmark or scale for scratch resistance is generally accepted (Kutscher and Sander, 2006), contradictory conclusions can be identified in different studies and the quantitative correlations are not available in the open literature.

In this work, the coating scratch resistance is correlated to the elastic modulus only and a qualitative correlation is adopted directly, i.e., an increment of the elastic modulus of a coating can improve the performance on scratch resistance. This relationship has been experimentally validated for various types of coating materials including the pure polymers and polymer nanocomposites (Garces et al., 2000; Kutscher and Sander, 2006; Misra et al., 2004).

6. Case study

The developed methodology can enable thorough investigations on the development of TSNC materials. It is particularly helpful for studying the correlations among the key material parameters, processing and testing conditions, and the final coating performance. The gained knowledge can be sufficiently valuable for experimentalists to develop superior TSNC materials with desired properties and at the lowest possible cost. In this section, the efficacy of the methodology is demonstrated through a detailed investigation on one type of TSNC coating material. For an understandable reason, the specifics of the material, including its type and key technical parameters, are omitted. To ensure the generality of the design methodology and that of the obtained conclusions, all the parameter values are expressed in a reduced form (i.e., dimensionless) (Allen and Tildesley, 1987). In the following text, all the quantities will be in the reduced form; the term “reduced” will be omitted for convenience, unless otherwise stated.

6.1. Material specification

Polymeric material: The thermoset material of interest is a resin with a polymer number average molecular weight (\(M_n\)) ranging from 2.78 to 16.68. The weight of the resin per mole of Type A functional group (\(M_{\text{N}^A}\)) is 1.81. The crosslinker has the molecular weight (\(M^*\)) of 1.08 and the functionality (\(f^*\)) of 6. The number ratio of Type B to Type A functional groups (\(r_{\text{BA}}\)) is 1.5. These parameters can be used to characterize a wide range of resin materials, one of which is a high solid acrylic-melamine resin, where the polymer is a hydroxyl-functional acrylic copolymer and the crosslinker is hexamethoxy-methylmelamine (Xiao and Huang, 2009).

Nanoparticle: Spherical nanoparticles are studied with a size (\(R^*\)) ranging from 2.33 to 7.00. Varying the settings of energy...
parameters (i.e., $\varphi^{m}$ and $\varphi^{r}$) allows investigation of different organomodified nanoparticles, such as alumina, silicate, and ceramic. In this work, $\varphi^{m}$ is set to 10.0, and $\varphi^{r}$ can be selected from 0.4 to 16.0.

6.2. Base case analysis

In the base case (Case 1), the polymer number average molecular weight ($\bar{M}_{n}$) and the nanoparticle size ($R^{n}$) are, respectively, set to 8.34 and 7.00. A relatively strong polymer–nanoparticle interaction is imposed, which gives $\varphi^{m}$ a value of 8.0. The volume fraction of nanoparticles ($\varphi^{r}$) is 10.39% and the number density of polymeric materials is 79.89% ($\rho^{p}$) (see Table 1). With these settings, a simulation system is created, which contains 8510 effective monomers, 1386 crosslinkers and one nanoparticle allocated in a simulation box ($24.0 \times 24.0 \times 24.0$). The values of other parameters used in the model and simulation are listed in Table 2.

Coating formation. A TSNC coating sample is prepared by following the procedure introduced before. The system is first equilibrated in the NVT ensemble at a temperature of 0.75 for 2000 MC cycles. The equilibrated system is then cured under a constant rate of $/C_{0}$ pressure of 0 for 5000 MC cycles. The equilibrated system is then cooled down from the temperature of 1 to 0.75 at a specified temperature profile to reach 80% of conversion. The curing process consists of a heating-up stage specified temperature profile and a second-stage isothermal stage at a temperature of 1. After that, a second-stage equilibration is conducted for 2000 MC cycles. The TSNC coating sample is then cooled down from the temperature of 1 to 0.75 at a constant rate of $-2.5 \times 10^{-4}$ MCC$^{-1}$ and the succeeding isothermal stage at a temperature of 1. Finally, the system is equilibrated in the NPT ensemble at a temperature of 0.75 and a pressure of 0 for 5000 MC cycles.

Initial configuration and first-stage equilibration: Fig. 4(a) demonstrates a snapshot of the initial system structure. As a note, all the 3D structures shown in this work are plotted using the visual molecular dynamics (VMD) software (Humphrey et al., 1996). The silver, green, and red beads represent the nanoparticles, the effective monomers, and the crosslinkers, respectively. The bonds connecting the polymer beads are displayed by cylindrical rods. In this structure, one nanoparticle is embedded in a polymer matrix containing 1038 precursor polymer chains with 44 different lengths and 1386 individual crosslinker molecules. Due to the imposed PBC 492 bonds (out of 7472) cross the simulation box boundary. These bonds are not shown explicitly and the effective monomers connected by these bonds are shown as the blue beads. Note that if one nanoparticle is involved in the simulation system, it is initially placed at the center of the simulation box in Fig. 4(a). The nanoparticle is not visible in the figure as it is covered completely by the polymer beads.

During the first-stage equilibration, the entities move around randomly to find their energetically favorable positions, which can give the lowest system potential energy. It is shown that the percentages of the accepted movements of the effective monomers, crosslinkers, and nanoparticles are all ~50%; and their maximum allowable displacements in one MC step are, respectively, 0.1488, 0.2999, and 0.0385. Since a higher value of the maximum allowable displacement indicates a higher mobility, the crosslinkers have the highest mobility during the first-stage equilibration, which is twice more than the mobility of effective monomers. This is understandable because all the crosslinkers are individual beads, while most effective monomers are bonded beads and thus with a poor mobility. The nanoparticle has the lowest mobility due to its size. A small position perturbation of a

### Table 1

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Study type</th>
<th>Material parameters$^{a}$</th>
<th>Product performance (scratch resistance)</th>
<th>Process performance (energy efficiency)</th>
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$^{a}$ For all cases, $\varphi^{r}$=10.39% and $\rho^{p}$=79.89%.

### Table 2

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nanoparticle could cause a violation of the minimum distance restriction and/or a large increase of system potential energy.

A sufficiently equilibrated system can be obtained using the introduced algorithm, which is evidenced by the system potential energy curve in Fig. 5(a). The equilibrated structure is shown in Fig. 4(b). The difference between Fig. 4(a) and (b) in terms of the polymer bead distribution cannot be visually identified. However, it will be shown later that the polymer bead distribution actually has a considerable difference. On the other hand, due to the low mobility, the position change of the nanoparticle is negligible, since the displaced distance of the nanoparticle during equilibration is 0.0285, which is only 0.2% of the nanoparticle diameter.

Crosslinking reaction and second-stage equilibration: The conversion dynamics of the curing process is shown in Fig. 5(b), where the curing temperature profile is also plotted. In the initial stage of reaction (i.e., about the first 1000 MC cycles), the reaction takes place very slowly because the temperature is relatively low. The reaction is then accelerated as the result of curing temperature increment. The reaction slows down in the final stage of the reaction due to the decrease of the mobility of crosslinkers and effective monomers and the reduction of the number of unreacted functional groups. Compared to those known athermal approaches for simulating polymer network formation (Gina et al., 2000), the introduced algorithm can successfully take into account the temperature effect on curing dynamics. Thus, it promotes a more realistic and reliable prediction of microstructure evolution.

In the second-stage equilibration, the maximum allowable displacements of the effective monomers, crosslinkers, and nanoparticles are, respectively, 0.1213, 0.0948, and 0.0169. All types of entities demonstrate decreased mobility as compared with the situation in the first-stage equilibration. The most significant decrease is for the crosslinkers, since they are originally individual beads, but then become connected, which restricts significantly their mobility. Also note that the mobility of crosslinkers becomes lower than that of the effective monomers, which is not the case in the first-stage equilibration. This can be attributed to the high functionality of crosslinkers. In this work, a crosslinker is allowed to connect six other polymer beads. But an effective monomer can be connected to no more than three other polymer beads (i.e., two neighboring effective monomers in the same precursor polymer chain and one crosslinker). A polymer bead having more connections shows a lower mobility.

The system structure after curing and reaching the second-stage equilibration is given in Fig. 4(c). In this structure, there are 4436 bonds newly created that connect effective monomers and crosslinkers. Note that some crosslinkers are connected to other polymer beads beyond the simulation box boundary by bonds, which are not shown in the figure; those crosslinkers are displayed as pink beads.

Cooling and third-stage equilibration: Cooling the coating sample leads to its shrinkage. This is revealed in Fig. 5(c), where the simulation box volume is decreased by 8% (from 13,824 to 12,635). The volume decrease causes an increment of the polymer number density. Note that the cooling process also causes a reduction of system potential energy by ~4% (see Fig. 5(d)).

In the third-stage equilibration, the system volume and energy are decreased further, but at a much lower speed (see Fig. 5(c) and (d)). The mobility of the entities is further reduced as compared to that in the second-stage equilibration. This is mainly due to the
decrease of system temperature and volume. Note that a lower temperature leads to a lower acceptance rate for a move attempt (see Eq. (5)). A smaller system volume makes the space less vacant for entities to move around. The more compact system structure after the third-stage equilibration is displayed in Fig. 4(d).

Microstructure analysis. Four structures shown in Fig. 4 possess a common feature: $\rho_r^p$ or $\psi_p^p$ begins to rise from 0 at a certain distance away from the nanoparticle surface. It means that there exists a vacant layer next to the nanoparticle surface. Beyond this vacant layer, the effective monomers and crosslinkers distribute differently in the four structures.

In the initial structure, the distribution of polymer beads is relatively uniform. As shown in Fig. 6(a), $\rho_r^p$ is slightly fluctuated around a bulk density of 0.7989 (i.e., the initial setting for the polymer-bead ND presented in Table 1). The uniform distribution is also confirmed in Fig. 7(a), where $\psi_p^p$ increases nearly linearly with the distance.

After the first-stage equilibration, the shape of the distribution curves changes dramatically. Fig. 6(b) shows that a high-polymer-density layer forms next to the vacant layer. This layer starts at the distance of 0.95 from the nanoparticle surface and has a width of 0.5. A prominent peak occurs at the distance of 1.15 to the nanoparticle surface, where both the effective monomer and the crosslinkers reach their highest number densities. The maximum value of $\rho_r^p$ reaches 5.535, which is 6.9 times greater than the bulk density of 0.7989. The formation of this high-density layer is due to the aggregation of a noticeable number of effective monomers and crosslinkers during equilibration. As shown in Fig. 7(b), this layer accumulates 7.2% of the polymer beads with the distance range of 0.95–1.45 to the surface of the nanoparticle. On the other hand, only 5.5% of the polymer beads are initially allocated within the same distance range to the nanoparticle surface (see Fig. 7(a)). In detail, the effective monomers in the layer are increased from 5.2% by 1.5%, while the crosslinkers are increased from 7.5% by 2.8%. It shows that the crosslinkers have a higher propensity to aggregate towards the nanoparticle surface.

As shown in Fig. 6(b) and (c), the polymer-bead number density distribution patterns after the first and the second equilibration are very similar, but the maximum number density of the effective monomers ($\rho_r^m$) and that of the crosslinkers ($\rho_r^c$) are decreased by 9.5% and 14.1%, respectively, after the second equilibration. On the other hand, the effective monomers and the crosslinkers in the high-density layer are slightly increased from 6.67% to 7.03% and from 10.32% to 10.53%, respectively (see Fig. 7(b) and (c)). These findings evidently show that during curing, more effective monomers than the crosslinkers, percentage wise move into the high-density layer, which means a moderate redistribution of the polymer beads. These help to achieve a high crosslinking conversion.

It is interesting to note that the high-density layer in Fig. 6(c) is a highly crosslinked layer shown in Fig. 8(a), and it possesses a high number density of EEJPs. Also note that the third-stage equilibration (after cooling) makes the heavily crosslinked layer even more concentrated. The maximum number density and the number percentage of the effective monomers and those of the crosslinkers in the layer are all slightly increased (see Figs. 6(d) and 7(d)). The same trend is found for the crosslink density (see Fig. 8(b)). The volume shrinkage of the coating after cooling contributes to the increase of the polymer bead number density and crosslink density.

Coating testing and quality evaluation. The tensile test is conducted at the temperature of 0.75 and the pressure of 0. The coating sample is stretched in the required directions at a constant strain rate until reaching the maximum strain of 5%. The constant strain increment of 0.05% is applied once every 10 MC cycles, which indicates a strain rate of 0.005% MCC$^{-1}$. According to Papakonstantopoulos et al. (2005), polymer nanocomposites have glass transition temperature $T_g$ of around 0.4, at
which the number density of polymer beads is ~1.01. In this case study, the TSNC coating sample to be tested is at the temperature of 0.75, which is above $T_g$ at which the polymer bead number density is 0.944. It indicates that this sample is in a rubbery state.

Stress–strain behavior: Stress evolution during tensile tests is critical for mechanical property quantification. To obtain insights into the origin of the stress and to have a deep and comprehensive understanding on the deformation behavior of a TSNC material, stress partitioning should be studied to differentiate the contributions by different types of stresses. The known studies on stress partitioning are only for studying the deformation behavior of amorphous polymers (Chui and Boyce, 1999; Li et al., 2006; Mulder et al., 2007), but not for polymer nanocomposites.

The average normal stress in the tensile direction ($\tau^\nu$) is given by Eq. (43), while the average transverse normal stress ($\tau^\nu_x$) is shown by Fig. 6. Stress–strain behavior: Stress evolution during tensile tests is critical for mechanical property quantification. To obtain insights into the origin of the stress and to have a deep and comprehensive understanding on the deformation behavior of a TSNC material, stress partitioning should be studied to differentiate the contributions by different types of stresses. The known studies on stress partitioning are only for studying the deformation behavior of amorphous polymers (Chui and Boyce, 1999; Li et al., 2006; Mulder et al., 2007), but not for polymer nanocomposites.

The average normal stress in the tensile direction ($\tau^\nu$) is given by Eq. (43), while the average transverse normal stress ($\tau^\nu_x$) is defined as

$$\tau^\nu = \frac{1}{3} (\tau^\nu_{yy} + \tau^\nu_{xx} + \tau^\nu_{zz})$$

Fig. 9(a) plots two types of reduced stresses ($\tau^{\nu'}$ and $\tau^{\nu''}$) as a function of strain ($\xi$). It is shown that $\tau^{\nu'}$ increases nearly linearly before $\xi$ reaches ~0.025, and its further increment becomes low, but $\tau^{\nu''}$ fluctuates around zero, which is at the pre-specified pressure. This means that the simulation is under excellent control over the transverse stress in the tensile test. Fig. 9(b) gives the behavior of the partitioned stresses against strain. As a note, a positive stress value indicates an attractive stress, while a negative one is a repulsive stress. This figure provides the following important information:

(i) Type I stress—$\tau^{\nu'}$ (between the nonbonded polymer beads) is always attractive. This means that the average distance between any pair of nonbonded polymer beads during a tensile test is always greater than the minimum-energy distance (i.e., 1.12).

(ii) Type II stress—$\tau^{\nu''}$ (between the bonded polymers) is always repulsive, but its magnitude ($|\tau^{\nu''}|$) is decreased along the strain. This indicates that the bond is stretched. When two bonded polymer beads are repulsive to each other, increasing the distance between them (i.e., the bond length) will decrease the magnitude of the repulsive stress.

(iii) Type III stress—$\tau^{\nu''}$ (between the polymer beads and the nanoparticle) is always attractive, but its magnitude is increased only slightly along the strain. It indicates that the average polymer–nanoparticle interaction distance is always larger than 1.12 (i.e., the minimum-energy distance in a polymer–nanoparticle potential). The increase of the stress is a result of the increase of average polymer–nanoparticle distance, i.e., the polymer beads are pulled away from the nanoparticle surface during a tensile test.

(iv) Type IV stress—$\tau^{\nu'''}$ (between the nanoparticles) is always zero, because only one nanoparticle is involved in this case.

Overall, Type II stress causes the most significant stress fluctuation as compared to the others.
Tensile property quantification and coating quality evaluation: For this base case, Young’s modulus ($E$) of the TSNC coating sample is 50.94, which is obtained by solving the optimization problem formulated in Eq. (42). For comparison, a pure thermoset material is also simulated, which has the same polymer number density and the number average molecular weight as the base case material. The polymeric coating is prepared and tested using the processing condition for the base case. Its Young’s modulus ($E_C$) is only 39.67, which is 22.12% smaller than that for the base case TSNC coating. This indicates that the TSNC coating has a much better scratch resistance performance.

6.3. Parametric analysis

To investigate the impact of material parameters on product and process performance, additional 16 cases (Cases 2–17 in Table 1) are designed. This allows to assess the effect of polymer–nanoparticle interaction strength ($\epsilon_{pn}$), nanoparticle size ($R_n$), and polymer number average molecular weight ($M_n$) on coating scratch resistance and curing energy efficiency. To ensure a reliable prediction, each case has four independent simulation runs, and comparisons are made based on the average results.
Based on the distributions of the polymer-bead number density, the stress–strain behavior below are only for Case 1. For simplicity, the analysis of microstructure and samples are prepared and tested under the condition the same as for Case 1. For Case 1, are designed to have different polymer–nanoparticle interaction strengths, which is reflected by the value of the energy parameter \( \varepsilon_p^n \) in [0.4–16.0] (see Table 1). The TSNC coating samples are prepared and tested under the condition the same as that for Case 1. For simplicity, the analysis of microstructure and stress–strain behavior below are only for Case 1 (\( \varepsilon_p^n = 8.0 \)), Case 2 (\( \varepsilon_p^n = 0.4 \)), and Case 4 (\( \varepsilon_p^n = 4.0 \)).

Coating microstructure: The microstructures of the undeformed coating samples in Cases 1, 2 and 4 are characterized based on the distributions of the polymer-bead number density \( \rho^c \), the cumulative number percentage \( \psi \), and the crosslink density \( \rho^c \). As shown in Fig. 10(a), the microstructure in Case 1 contains a prominent high-density layer, and the crosslinkers show a higher propensity to aggregate towards the nanoparticle surface than the effective monomers. In that layer, \( \psi^c \) reaches 11.18%, and \( \psi^m \) is only 7.45%. In Case 4 (see Fig. 10(b)), the high-density layer becomes less prominent, with the maximum \( \rho^c \) of 4.30 (29% lower than that in Case 1). The crosslinkers do not have a clear higher propensity to aggregate towards the nanoparticle surface than the effective monomers. Note that Case 2 shows a completely different distribution (see Fig. 10(c)), as there is no high-density layer and the polymer beads are more or less uniformly distributed. Note that the difference of the \( \rho^c \) distributions in three cases is also clear. The maximum \( \rho^c \) are 1.246 for Case 1 and 0.935 for Case 4; all appear in the highly crosslinked layer. But this is not the case for Case 2 as there is no such a layer.

The above analysis reveals that decreasing the polymer–nanoparticle interaction strength can give rise to: (i) a less prominent high-density layer, (ii) a reduction of the number of...
polymer beads in the high-density layer, (iii) a less prominent highly crosslinked layer, and eventually (iv) a uniform distribution of polymer beads and EEJPs.

Stress-strain behavior: It is found that the polymer–nanoparticle stress ($\tau^{\text{PN}}$) in Case 1 is greater than the other two cases. This indicates that in order to have more contributions from the polymer–nanoparticle stress, a greater polymer–nanoparticle interaction strength ($\rho^{\text{PN}}$) should be imposed.

Tensile property quantification and quality evaluation: The correlation between $E'/E_p$ and $\rho^{\text{PN}}$ is presented by a regression curve based on the results of Cases 1–6 (see Fig. 11). The detailed data of $E'/E_p$ with the mean value and standard deviation for all six cases are listed in Table 1. It shows clearly that when $\rho^{\text{PN}}$ is increased (i.e., the polymer–nanoparticle interaction strength is enhanced), $E'$ is increased as well and thus the tensile property/scratch resistance performance is improved. Fig. 11 also shows that adding nanoparticles into a conventional thermoset material does not guarantee enhancement of coating performance. A key to achieving performance improvement is to ensure that the polymer–nanoparticle interaction strength ($\rho^{\text{PN}}$) is greater than a critical value (1.2 in this case, see Fig. 11).

Effect of $R^n$ on product performance: Six new cases (Case 7–12) are designed to explore the quantitative correlation between nanoparticle size and coating performance, as compared to Case 1. As shown in Table 1, the only material parameter different from each other is the radius of nanoparticles ($R^n$). Note that the same-size simulation box is used for all cases. In order to achieve the same nanoparticle volume fraction ($\phi^{\text{PN}}=10.39\%$) and polymer number density ($\rho^{\text{F}}=79.89\%$), the numbers of nanoparticles involved in Cases 1 and 7–12 are, respectively, 1, 27, 12, 8, 4, and 2. The coating samples are prepared and tested under the same condition as that for the base case. For simplicity, Case 1 ($R^n=7.00$), Case 7 ($R^n=2.33$), and Case 10 ($R^n=3.50$) are selected for analysis below.

Coating microstructure: As shown in Fig. 12, in each case, the crosslinkers have a higher propensity than the effective monomers to move towards the nanoparticle surface (see the $\psi$ curves in Fig. 12, where the dotted line is above the dashed line in each high-density layer). The number percentages of the polymer beads within the high-density layers are, respectively, 7.97%, 19.93%, and 35.31% for Cases 1, 10, and 7.

The study shows that the nanoparticle size has a minor influence on the polymer-bead $\rho^*$ distribution and $\rho^c$ distribution, but it plays a major role on the $\psi$ distribution. Decreasing the nanoparticle radius can cause a significant increase in the number percentage of polymer beads within the high-density layer. One
reason is the difference of the total surface areas of nanoparticles. For the systems having the nanoparticle radii of 7.00, 3.50, and 2.33, the total surface areas of the nanoparticles are 616, 1,232, and 1,847, respectively.

Stress–strain behavior: It is found that the nanoparticle size has a very small influence on the polymer–polymer bonded stress ($\tau^b$) and the nanoparticle–nanoparticle stress ($\tau^{nn}$). The difference of the total stresses ($\tau^t$) in the three cases is mainly due to the difference of the polymer–nanoparticle stresses ($\tau^{p\star}$) and the polymer–polymer nonbonded stresses ($\tau^{pp}$). Decreasing nanoparticle size makes $\tau^t$ increased in the whole range of strain under study. This can be understood by checking the $\psi$ distributions in these cases (see Fig. 12). In the high-density layer, the $\psi$ value for Case 7 (using the smallest nanoparticles) is larger than that for the other two cases; this causes a greater polymer–nanoparticle stress. It is also noticed that when smaller nanoparticles are used, the stress between the nonbonded polymer beads ($\tau^t$) becomes smaller throughout the range of the strain studied. The reason for this phenomenon is yet to be investigated.

Tensile property quantification and quality evaluation: Fig. 13 provides the relationship between $E'/E_p$ and $R^m$. It shows that using smaller nanoparticles can improve the tensile property of the TSNC coating and thereby scratch resistance performance. The improvement will be more significant when the nanoparticles are much smaller. This is difficult to be explained using the continuum mechanics theory, but can be readily understood when examining the microstructures and the stress partitioning.

Effect of $M_n$ on product performance: The performance of a TSNC coating heavily depends on the type of polymeric material used.

**Fig. 13.** The effect of nanoparticle size on Young’s modulus of the TSNC coating.

**Fig. 14.** Distributions of the polymer-bead number density ($\rho^b$), cumulative number percentage ($\psi$), and crosslink density ($\rho^c$) as a function of the polymer number average molecular weight for (a) Case 17 ($M_n = 16.68$), (b) Case 1 ($M_n = 8.34$), and (c) Case 13 ($M_n = 2.78$).

**Fig. 15.** Effect of the polymer number average molecular weight on Young’s modulus of the TSNC coating.
In this regard, five new cases (Cases 13–17) are designed, where the polymer number average molecular weights are different from each other as well as Case 1 (see Table 1). In the following, Case 1 ($\overline{M}_n = 8.34$), Case 13 ($\overline{M}_n = 2.78$), and Case 17 ($\overline{M}_n = 16.68$) are selected for a more detailed investigation.

Coating microstructure: The $\rho^*$ and $\psi$ distributions for Cases 17, 1, and 13 are plotted in Fig. 14, where no major difference can be observed. However, this is not the case for the $\rho^*$ distribution; the $\rho^*$ always has a greater value when $\overline{M}_n$ is greater. This suggests that $\overline{M}_n$ has a negligible effect on the distributions of effective monomers and crosslinkers, but has a pronounced influence on the distribution of EEJPs. The crosslink density, or the number density of EEJPs, increases along $\overline{M}_n$. This is because for the same conversion the chance for a polymer bead to be an EEJP in a higher $\overline{M}_n$ system is much greater than that in a lower $\overline{M}_n$ system.

![Graph showing curing time dependence on polymer-nanoparticle interaction strength, nanoparticle radius, and polymer number average molecular weight.](image)

**Fig. 16.** Curing time dependence on (a) the polymer–nanoparticle interaction strength, (b) the nanoparticle radius, and (c) the polymer number average molecular weight.

Stress–strain behavior, tensile property, and quality evaluation: Simulation shows that the selection of $\overline{M}_n$ has almost no effect on the polymer–nanoparticle stress ($τ^{p\text{-}n}$) and the nanoparticle–nanoparticle stress ($τ^{n\text{-}n}$), but is relatively sensitive to the slope of the polymer–polymer bonded stress ($τ^{p\text{-}p}$) when the strain is < 2%. This makes the overall stress curves ($τ^*$) different, particularly for a smaller $\overline{M}_n$. Fig. 15 shows how Young’s modulus ($E^*$) behaves as the polymer number average molecular weight ($\overline{M}_n$) changes. Clearly, the TSNC coating scratch resistance is more robust when $\overline{M}_n$ is larger, and thus that the crosslink density in the system is greater (see Fig. 14).

Effect on process performance. Another uniqueness of the introduced methodology is its capability of identifying opportunities for improving processing efficiency. The processing efficiency considered in this work is evaluated by the time needed for curing the TSNC coating to a specific crosslinking conversion percentage. If the pattern of the curing temperature profile (or the heating policy) is given (see Fig. 5(b)), and the time duration for curing at temperature $T^*$ is adjustable, it is certain that the longer the time duration, the higher the energy consumption.

Note that in MC simulation, the curing time elapsed can be reflected by the MC cycles used. Their exact correlation, however, is difficult to derive, because for any specific MC cycle, its equivalence of real curing time varies. But it is certain that more MC cycles imply a longer curing time and thus more energy required. Fig. 16 demonstrates how the ratio of $N^\text{MCC}$ to $N^\text{MCC}_p$ changes for a material that is characterized by $\varepsilon^{p\text{-}n}$, $R^*$, or $\overline{M}_n$; where $N^\text{MCC}$ and $N^\text{MCC}_p$ are, respectively, the needed number of MC cycles for the TSNC coating and that for the pure-polymer coating to reach 80% of crosslinking conversion. It is shown that to reduce energy consumption for coating curing, the nanomaterial should have a smaller $\varepsilon^{p\text{-}n}$ and $\overline{M}_n$, but a larger $R^*$. However, according to the discussion in the previous sections, such a type of material can lead to a less or even much less superior performance on scratch resistance (see the summarized data in Table 1). Consequently, material designers should be prepared to make trade-offs between product performance and processing efficiency. This introduced methodology can provide detailed, quantitative information for the purpose.

7. Conclusions and future work

Thermoset nanocomposites (TSNCs) are the polymer composite materials that can significantly improve appealing properties and offer new functionalities in the resulting coatings. However, how to effectively and efficiently design TSNCs to achieve anticipated coating properties and performance as well as material processing efficiency is an extremely challenging task. The computational methodology introduced in this work is probably among the first of this kinds for TSNC material design. The 3D simulation and structural and parametric analysis techniques can provide material designers with various types of insightful information, and help gain a comprehensive and deep understanding on how the TSNCs formulation can influence coating property and energy efficiency. This is also among the earliest efforts on stress partitioning when studying the deformation of TSNCs. Through examining the contributions by different stresses, the deformation behavior of the material can be clearly visualized.

The developed methodology builds a solid basis for the future study on optimal TSNC coating design. Undoubtedly, more comprehensive and sophisticated studies are needed. The methodology is currently being extended for characterizing TSNCs using different shapes of nanoparticles. In analyzing the stress–strain behavior, a large strain will be imposed so that other
properties, e.g., yield strength and yield strain, can be quantified. Furthermore, quantitative correlations between the scratch resistance and various properties need to be developed. Other coating performance, such as corrosion prevention, appearance, and inter-coat adhesion, should also be investigated. Needless to say, all the correlations and design improvement strategies identified through simulation must be experimentally validated.

Acknowledgments

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References


