



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

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ABSTRACT

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 thermoset 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,

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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, Halphin-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 i and j , designated Γ_{ij}^I , can be evaluated by the Lennard–Jones (LJ) potential as follows:

$$\Gamma_{ij}^I = 4\varepsilon^{pp} \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right), r_{\min}^{pp} \leq r_{ij} \leq r_{\max}^{pp} \quad (1)$$

where r_{ij} is the distance between beads i and j ; ε^{pp} is an energy parameter; σ is a distance parameter; r_{\min}^{pp} and r_{\max}^{pp} are, respectively, the minimum distance and the cutoff distance between any two polymer beads. Note that the potential energy is set to zero when $r_{ij} > r_{\max}^{pp}$.

The potential energy between each pair of bonded beads i and j , denoted Γ_{ij}^{II} , can be evaluated by both the finite extension nonlinear elastic (FENE) potential and the LJ potential (Kremer and Grest, 1990), i.e.,

$$\Gamma_{ij}^{II} = -\frac{\mu \varepsilon^{pp}}{2 \sigma^2} (l_{\max}^b)^2 \ln \left(1 - \left(\frac{r_{ij}}{l_{\max}^b} \right)^2 \right) + 4\varepsilon^{pp} \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right), r_{\min}^{pp} \leq r_{ij} \leq l_{\max}^b \quad (2)$$

where μ is a spring constant; l_{\max}^b 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):

$$\Gamma_{ij}^{III} = 4\varepsilon^{pn} \left(\left(\frac{\sigma}{r_{ij} - R^n} \right)^{12} - \left(\frac{\sigma}{r_{ij} - R^n} \right)^6 \right), r_{\min}^{pn} \leq r_{ij} \leq r_{\max}^{pn} \quad (3)$$

where Γ_{ij}^{III} is the potential energy shared by polymer bead i and nanoparticle bead j ; ε^{pn} is an energy parameter, whose value is related to the size ratio of a nanoparticle bead to a polymer bead; R^n is the nanoparticle radius; r_{\min}^{pn} and r_{\max}^{pn} are, respectively, the minimum distance and the cutoff distance between a nanoparticle bead and a polymer bead.

The interaction potential between two nanoparticle beads can be evaluated as

$$\Gamma_{ij}^{IV} = 4\varepsilon^{nn} \left(\left(\frac{\sigma}{r_{ij} - 2R^n} \right)^{12} - \left(\frac{\sigma}{r_{ij} - 2R^n} \right)^6 \right), r_{\min}^{nn} \leq r_{ij} \leq r_{\max}^{nn} \quad (4)$$

where Γ_{ij}^{IV} is the potential energy shared by nanoparticle beads i and j ; ε^{nn} is an energy parameter; r_{\min}^{nn} and r_{\max}^{nn} are, respectively, the minimum distance and the cutoff distance between two nanoparticle beads.

Note that the values of the minimum distance and the cutoff distance in Eqs. (1)–(4) are determined based on the potential energy. At the minimum distance, the potential energy should be larger than $50\varepsilon^{pp}$. At the cut-off distance, the absolute value of the potential energy should be smaller than $0.017\varepsilon^{pp}$. 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.

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