Multiscale Modeling and Optimization of Nanoclearcoat Curing for Energy Efficient and Quality Assured Coating Manufacturing†

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Abstract

Nanopaint is a new type of coating material that could offer significantly improved coating performance and/or a number of new functionalities, such as super scratch resistance, self-healing, surface texture alteration control, and toxic chemical/acid/corrosive agent repelling. However, how to ensure the achievement of the anticipated nanocoating performance and functionalities in coating manufacturing is a great challenge. In this paper, we introduce a multiscale modeling and analysis methodology for characterizing nanoclearcoat curing in a multi-stage manufacturing system. The methodology provides an opportunity to gain a deep understanding of the nanocoating formation process, which involves solvent evaporation, cross-linking reaction, and film thickness change at the presence of nanoparticles in the coating layer. The information provided by the integrated model facilitates the analysis of nanocoating quality the development of optimal operation strategies for energy efficient coating manufacturing. Methodological efficacy is demonstrated through a comprehensive case study.

† For publication in Industrial and Engineering Chemistry Research (Special Issue on Sustainable Chemical Manufacturing).
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1 INTRODUCTION

Clearcoat is a top layer of coating on vehicle surface. It protects the underlying coating layers from chemical corrosion, UV degradation, and mechanical damage.\(^1\) Owing to the increasing demand on high-performance coatings, nanopaint-based clearcoat has drawn great attention. Nanopaint is a type of nanocomposite material that incorporates organo-modified inorganic nanoparticles into a conventional thermoset polymeric resin. This type of coating material, if applied properly, can provide superior coating performance, such as anti-scratch, self-cleaning, self-healing, etc.\(^2\)\(^-\)\(^4\) A significant improvement of barrier properties compared to conventional polymeric coatings was also reported.\(^5\) Nanopaint could become a dominant automotive coating material in the near future.

Application of nanoclearcoat encounters a number of manufacturing challenges in spite of the promising coating features. Clearcoat curing is a critical manufacturing step in achieving expected high coating performance. This renders a need to investigate in depth nanoclearcoat curing fundamentals. A key technical concern is the curing environment that determines product quality. In curing, the presence of nanoparticles in paint could slow down solvent evaporation from the surface of a thin wet film, as the dissolved solvent in paint takes a tortuous path to reach the film surface. Cross-linking reactions taken place in the film is also affected by the nanoparticles both at the microscale and macroscale. Zhou et al. stated that inappropriate addition of nanoparticles could lead to an adverse impact on polymer network evolution.\(^6\) A natural question is whether a conventional coating drying system can be used to cure nanoclearcoat to achieve its anticipated quality performance, and if so, how to adjust curing operational settings, especially when the size, shape, and volume fraction of nanoparticles in paint vary.
A number of theoretical studies on the drying of polymer solution have been reported, which demand various types of physico-chemical property information for modeling. Lou and Huang introduced an integrated macroscale modeling approach to investigate the dynamics of conventional clearcoat curing. Xiao et al. described a Monte Carlo simulation method to study polymer network formation at microscale. Zhou et al. studied product formation processes, which improved the understanding of the correlation between material dynamics and product and process performance. It is known that coating defects could occur during curing if the operational setting is inappropriate. Price and Cairncross discovered that solvent residual in coating may lead to the generation of blisters if the coating temperature exceeds the bubble point. Domnick et al. introduced a statistical model to study the relationship between the pinhole density and the operational settings (such as oven temperature gradient and convection air velocity). Integration of macroscopic process dynamics with product realization at the finer scales can deepen the understanding of nanocoating formation and thus help identify the most suitable strategy for nanocoating curing.

In this work, we introduce an integrated multiscale modeling and dynamic analysis method to study nanoclearcoat curing. It aims at establishing quantitative correlation among coating material parameters, product quality, and process energy consumption. A general product quality and process efficiency analysis method will be also introduced. An optimization approach is then presented for deriving an optimal operational setting to minimize energy consumption while ensuring process and product quality. A comprehensive case study will demonstrate the methodological efficacy.
Clearcoat curing is a sophisticated, energy intensive operation in the automotive coating manufacturing industry. It becomes more challenging when the clearcoat is nanoparticles incorporated, as it is not fully understood how the nanoparticles and the polymer matrix interact in the coating layer during curing in a coating manufacturing. Curing oven is a usual manufacturing facility that is designed to have a number of operational zones, with the first one or two zones for radiation and convection based drying, and the rest four to five zones for convection based curing where polymeric reactions take place. In production, vehicle bodies covered by a wet topcoat layer are moved by a conveyor one by one through a curing oven at a constant speed. In operation, four types of phenomena occur simultaneously, which are depicted in Fig. 1. These include: (i) heat transfer within the coating film and with the drying environment, (ii) mass transfer of solvent within the film and its evaporation at the film surface, (iii) cross-linking reaction that leads to the formation of a nanoparticle-incorporated polymeric network, and (iv) film thickness change mainly due to solvent removal. In study, a macroscopic process model is needed to characterize the heating environment; at the meso-scale, solvent removal associated with film thickness change should be characterized; the cross-linking reaction and polymer network formation can be described by microscale models.

2.1 Drying of Wet Coating Film

As stated, a curing oven usually is divided into a number of zones where heating mechanisms and operational settings are set differently. It is known that the amount of energy
consumed for drying a nanoclearcoat on vehicle panels is significantly less than that for heating the substrate. It can be safely assumed that the temperature difference between the substrate and the coating layer is negligible throughout the curing process, as the Biot number in the heat transfer process is very small.\textsuperscript{13} Lou and Huang introduced a coating heating model for convention paint drying.\textsuperscript{10} It can be used to characterize nanocoating drying. The lumped parameter model is presented below.

\[
\frac{dT(t)}{dt} = \begin{cases} \frac{\sigma \varepsilon}{\rho_m C_p Z_m} \left( T_w^4 - T(t)^4 \right) + \frac{h_v}{\rho_m C_p Z_m} (T_a - T(t)), & \text{Radiation / convection zone} \\ \frac{h_v}{\rho_m C_p Z_m} (T_a - T(t)), & \text{Convection only zone} \end{cases}
\]  

(1) 

where \( T(t) \) is the temperature of the nanocoating film; \( T_w \) and \( T_a \) are the temperature of the oven wall and that of the convection air, respectively; \( \rho_m, C_p, \) and \( Z_m \) are the density, the heat capacity and the thickness of vehicle panels, respectively; \( \sigma \) and \( \varepsilon \) are the Stefen Boltzman constant and the emissivity, respectively; \( h_v \) is the heat transfer coefficient of the convection air, which is a function of the convection air velocity (\( v_a \)), i.e.,

\[
h_v = \beta v_a^{0.7},
\]  

(2)

The energy consumed during coating curing in the oven is the sum of the energy consumed in different zones of the oven from two different energy sources. The wall radiation consumes electricity, while the hot convection air is provided by natural gas combustion. The energy consumption can be expressed as follows:

\[
Q_t = \sum_{i=1}^{N_e} Q_{e,i} + \sum_{j=1}^{N_{ng}} Q_{ng,j},
\]  

(3)
where $N_r$ and $N_a$ are the number of radiation heating zones and that of the convection zones respectively; $Q_{e,i}$ and $Q_{ng,i}$ are the electricity and natural gas consumed in the $i$-th radiation zones and the $j$-th convection air zones, respectively.

Fundamental modeling of energy consumption in a curing process is challenging. However, empirical regression models that correlates the consumption of energy (electricity and natural gas) with curing over design (in terms of the length of each zone in the oven) and oven operating temperature of each zone can be readily derived.\textsuperscript{14-16} In this work, the models for electricity consumption ($Q_{e,i}$) and natural gas consumption ($Q_{ng,i}$) during curing are as follows:

$$Q_{e,i} = 2.45L_i \exp \left( \frac{T_{w,j}}{688.2} \right) - 3.80L_i; \quad i = 1, 2, \ldots, N_r$$

$$Q_{ng,j} = 0.0017(T_{a,j} - 294.11)L_j^2; \quad j = 1, 2, \ldots, N_a$$

where $L$ is the length of a specific drying zone; $T_{w,j}$ and $T_{a,j}$ are the temperature of the oven wall and that of the convection air in each zone, respectively. Detailed derivations of these two models have been listed in the Appendix.

### 2.2 Solvent Removal from the Wet Film

Solvent is uniformly distributed within the wet coating layer on substrate. During drying, solvent in different locations within the film moves towards the coating surface and then evaporate. Along solvent removal, the thickness of the coating layer decreases. Typically, solvent removal rate is controlled by solvent evaporation from the coating surface and solvent diffusion within the coating film. Known studies on drying coatings show that the rate of diffusion and evaporation are related with solvent concentration and temperature.\textsuperscript{17-20} Lou and Huang proposed a Fick’s
second law based solvent removal model for conventional clearcoat.\textsuperscript{10} Note that the presence of nanoparticles within a coating layer forces solvent to change diffusion pathways, which affects the solvent removal process to some extent. Therefore, the solvent removal model by Lou and Huang needs to be modified.\textsuperscript{10}

According to Falla \textit{et al.} and Swannack \textit{et al.},\textsuperscript{21,22} the solvent diffusivity for a nanocomposite \(D_n(t)\) is related to that for a conventional paint \(D_o(t)\) in the following way:

\[
D_n(t) = \frac{1 - \phi_n}{1 + 0.5\phi_n} D_o(t),
\]

where \(\phi_n\) is the volume fraction of nanoparticles in a dry film (usually less than 10\%). This equation is applicable to the case where the nanoparticles are spherical with no size limit. The solvent diffusivity in conventional paint \(D_o(t)\) is expressed as:\textsuperscript{10,17,20}

\[
D_o(t) = \eta \exp \left( \frac{\gamma}{T} - \frac{E_d}{RT(t)} \right),
\]

where \(\eta\) is a pre-exponential constant for diffusivity; \(\gamma\) is a constant; \(E_d\) is the activation energy for diffusion; \(R\) is the ideal gas constant.

By using the diffusivity for nano-film \(D_n(t)\), the solvent diffusion dynamics within the film can be expressed as:

\[
\frac{\partial C(z,t)}{\partial t} = \frac{\partial}{\partial z} \left( D_n(t) \frac{\partial C(z,t)}{\partial z} \right),
\]

where \(C(z,t)\) is the mass concentration of solvent within the film; \(z\) is the thickness of the film.

The change of solvent content at the coating surface results from the solvent loss due to evaporation and solvent gain from the underlying film. Thus, the mass-transfer process at the coating surface and the solvent evaporation process can be modeled as:\textsuperscript{23,24}
\[
\frac{\partial C(z,t)}{\partial t} = \frac{D_s(t)}{Z_s} \frac{\partial C(z,t)}{\partial z} - \frac{K(p_s(t) - p_{lb})}{\rho_s Z_s},
\]

(9)

where \(\rho_s\) is the density of irreducible components in the film; \(Z_s\) is the thickness of irreducible components in the film; \(K\) is the mass transfer coefficient; \(p_s(t)\) and \(p_{lb}\) are, respectively, the solvent partial pressure at the coating-air interface and its partial pressure in the bulk gas phase.

The solvent partial pressure at the coating-air interface \(p_s(t)\) can be calculated as the vapor pressure of pure solvent at the current temperature multiplied by the activity of the solvent at the current polymer phase solvent concentration.\(^9\) We assume that the Flory–Huggins equation describes the solvent activity. Therefore,

\[
p_s(t) = P_l(t) \phi_l \exp \left( (1 - \phi_l) + \chi(1 - \phi_l)^2 \right),
\]

(10)

where \(\chi\) is the Flory–Huggins interaction parameter; \(\phi_l\) is the volume fraction of solvent; \(P_l(t)\) is the vapor pressure of pure solvent at temperature \(T(t)\). For the solvent contained in the nanoclearcoat layer, the vapor pressure of pure solvent at the solid-air interface can be obtained based on the Antoine equation:\(^{25}\)

\[
\ln P_l(t) = a - \frac{b}{c + T(t)},
\]

(11)

Note that solvent evaporation at a wet film surface is modeled as a moving boundary problem, as the thickness of the wet film decreases along the time. The initial and boundary conditions are expressed below:

\[
C(z,0) = C_0,
\]

(12)

\[
\frac{\partial C(0,t)}{\partial t} = 0,
\]

(13)

In modeling, the coating film is vertically divided into \(N\) very thin slices, each of which
has a same initial thickness ($\Delta z_0$). The solvent concentration in $i$-th slice $C(z_i, t)$ can be readily obtained through process dynamic simulation.

### 2.3 Film Thickness Modeling

The film thickness change occurs mainly due to solvent removal. Note that the average mass concentration of solvent, $\bar{C}(t)$, is defined as:

$$\bar{C}(t) = \frac{1}{N} \sum_{i=1}^{N} C(z_i, t),$$

Thus, the film thickness, $(Z(t))$, can be estimated using the following formula:

$$Z(t) = \frac{\rho_l (V_s + V_n) (1 - \bar{C}(t)) + (\rho_s V_s + \rho_n V_n) \bar{C}(t)}{A \rho_l (1 - \bar{C}(t))},$$

where $A$ is the surface area of the substrate covered by the film; $V_l(t)$, $V_s$ and $V_n$ are the volumes of solvent, polymeric materials, and nanoparticles contained in the film, respectively.

Note that the final film thickness, $(Z(\infty))$, after the solvent is completely removed, is:

$$Z(\infty) = \frac{V_s + V_n}{A},$$

This is the same as Eq. (15) when $V_l$ reaches zero. In practice, however, the cured film will still contain a few percent of solvent residue. Thus, the average coating thickness is slightly greater than that evaluated using Eq. (15).

### 2.4 Monte Carlo Modeling for Cross-linking Reaction Characterization
Xiao et al. developed an off-lattice Monte Carlo (MC) modeling method to study the dynamic features of the nanocoating microstructure during curing.\textsuperscript{11} That method can be used to predict coating quality, i.e., mechanical properties. It is known that in curing operation, polymer and nanoparticle interacts and cross-linking reactions occur. The polymer network formation is simulated in multiple stages including system creation, curing condition application, cross-linking chemical reaction, and multiple system relaxations. In this study, only spherical nanoparticles are incorporated in the polymer solution.

In simulation, the first step is to set up a simulation box in which the polymer beads representing monomers and cross-linkers, as well as a large number of nanoparticles, are randomly distributed to generate an initial system configuration. In the simulation system, the size and volume fraction of nanoparticles, the total number of effective monomers and that of cross-linkers, and the number density of polymeric materials should be specified. Such information is used to identify the total number of nanoparticles as follows:

\[
N_n = \text{int} \left( \frac{6 \phi_n (N_b + N_c)}{\rho_p \left(1 - \phi_n \right) \pi d_n^3} \right),
\]  

(17)

where \( \rho_p \) is the density of polymeric materials; \( N_b \) and \( N_c \) are the total number of effective monomers and that of cross-linkers, respectively; \( d_n \) and \( \phi_n \) are the size and the volume fraction of nanoparticles, respectively.

The cubic simulation box can then be defined by calculating the initial edge length as:

\[
l_0 = d_n \left( \frac{\pi N_n}{6 \phi_n} \right)^{1/3},
\]  

(18)

In simulation, there are three equilibrium states 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 cross-linking reaction is accomplished; and the third is needed after the sample is cooled. The model takes into account the interaction among polymer beads and that between polymer beads and nanoparticles.

Cross-linking reaction takes place in the simulation system after the system reaches the first-stage equilibrium state. During the network formation, interrelated physical and chemical phenomena (i.e., polymer and nanoparticle movement and cross-linking reaction) occur simultaneously, which are influenced by the dynamically changed curing environment. The thermal profile is obtained from the macroscopic oven heating dynamic model in Eqs. (1) and (2). The profile must be imposed in simulation to ensure a full realization of the required curing environment. Existing studies show that the reaction kinetics in a coating curing process can be characterized by an autocatalytic mechanism.\(^{26}\) Zhou et al. studied the curing process of thermosetting nanocoating materials, and showed that autocatalytic model could also be used to characterize the curing process.\(^{6}\) However, nanoparticles added into the polymer matrix have a negative effect on polymer network formation.\(^{27,28}\) Thus, the autocatalytic mechanism is used to model the reaction kinetics with the existence of nanoparticles in the polymer matrix. The chemical conversion rate can be calculated as

\[
\frac{d\alpha(t)}{dt} = \zeta \exp\left(-\frac{E}{RT(t)}\right)\alpha(t)^m(1-\alpha(t))^n,
\]

(19)

where \(\alpha(t)\) is the conversion of cross-linking reaction; \(\zeta\) is a polymerization reaction frequency factor; \(E\) is the activation energy; \(m\) and \(n\) are constants.

After the cross-linking reaction reaches its target conversion rate, the nanocoating sample will be cooled down to a normal temperature, which is followed by the second-stage equilibration. The cooling process is operated at a constant pressure.
3 PRODUCT QUALITY ANALYSIS AND SIMULATION PROCEDURE

To ensure achievement of the anticipated functionalities in the final nanoclearcoat product, the curing process should meet the following standards: (i) the solvent residual is reduced to no more than 2% in the dried film; (ii) the conversion of cross-linking reaction reaches 95%; and (iii) the scratch resistance performance should be improved at least 45% over that offered by the conventional clearcoat.

3.1 Product Performance Evaluation

Before introducing a product quality analysis procedure, we describe a simulation method for product performance analysis. Note that the developed multiscale models can be used to generate a variety of valuable information about the macroscopic reactive drying operation and the meso- to micro-scale coating structural formation process. Correlating the structure with the product quality is a critical task. In this work, we focus on the coating scratch resistance performance which is qualitatively correlated with its elastic property quantified by Young’s modulus. The change of Young’s modulus is directly used to represent the change of coating scratch resistance performance. A deformation simulation that is a non-equilibrium deformation process is accomplished by an off-lattice mc-based method to establish a stress-strain relationship for modulus calculation.\(^{11}\)

In order to acquire a comprehensive and accurate simulation result, the deformation tensile tests are carried out in x, y, and z directions of the cubic simulation box. During a tensile test simulation, a series of strain increments are applied on the simulation system along a specific direction. The strain increment must be small enough in order to reveal practical deformation
behavior. The corresponding normal stress of each strain increment is evaluated by adopting Virial theorem.\textsuperscript{29} It must be pointed out that a relaxation process must be included between two adjacent strain increments to approximate a real material deformation process. An averaged stress-strain curve obtained from three independent tensile tests in x, y, and z directions can be used to investigate the stress-strain behavior of the cured product. Through examining the contributions from different stresses, the deformation behavior of the material can be clearly analyzed. Such behavior is capable of providing accurate evaluation of Young's modulus of the cured product.

Ideally, MC simulation and subsequent analysis of product performance should be conducted when the temperature profile of curing environment changes. However, the microscale simulation is time consuming, which makes design optimization extremely inefficient. Model to predict the mechanical properties of cured nanocomposite coating material has not been developed yet. Thus, it is of great importance to derive quantitative correlations between the overall coating mechanical performance and key material parameters based on the developed modeling and simulation method. The conversion rate of cross-linking reaction also plays a key role in evaluating coating mechanical property.\textsuperscript{28} An empirical regression model that represents the relationship among the improvement of coating scratch resistance performance ($S$) compared with cured conventional clearcoat, final reaction conversion ($\alpha(t^*)$), and the size ($d_n$) and volume fraction ($\phi_n$) of nanoparticles can be generally expressed as:

$$S = f(\alpha(t^*), d_n, \phi_n),$$  \hspace{1cm} (20)

In this work, the target clearcoat contains 5% of 20 nm nanoparticles. A series of tests based on the microscale MC simulation have been conducted to explore the relationship shown in Eq. (20). In simulation, a simplified temperature profile is used: the oven temperature which is initially set at 300K increases to 400K after 2000 Monte Carlo simulation cycles and then remains
constant at 400 K until the cured coating material reaches the preset final conversion percentage ($\alpha(t_e)$) of polymer network, that is, 80%, 83%, 86%, 89%, 92%, 95%, and 98% respectively. Each simulation is repeated three times to obtain accurate results. The seven groups of simulation results lead to a specific form of Eq. (20):

$$S = 8.27 \exp \left( 1.01 \alpha(t_e)^{3.44} - 3.06 \right),$$  \hspace{1cm} (21)

Note that this simplified relationship can only be applied to the cured coating material with final conversion percentage ($\alpha(t_e)$) greater than 80%. Having the above model, the mechanical improvement of a cured nanocoating with any proper combination of material parameter values can be readily calculated.

### 3.2 Energy Efficient Curing

Coating curing operation in a multi-zone oven is energy intensive. However, how to optimize oven operational settings to achieve most energy efficient curing has not been well studied, even for the curing of conventional clearcoat. In this work, we propose a curing optimization framework, where energy minimization is targeted and various produce and process constrains are imposed. The optimization model is presented below.

$$T_{w,1}, T_{w,2}, T_{a,1}, T_{a,2}, T_{a,3}, T_{a,4}, T_{a,5}, T_{a,6} \quad \min Q_t = \sum_{i=1}^{N} Q_{e,i} + \sum_{i=1}^{N_g} Q_{ng,i}$$  \hspace{1cm} (22)

Subject to:
\[
\frac{dT(t)}{dt} = \begin{cases} 
\frac{cE}{\rho_m c_p Z_m} \left( T_w^4 - T(t)^4 \right) + \frac{h_v}{\rho_m c_p Z_m} (T_a - T(t)), & \text{Radiation / convection zone} \\
\frac{h_v}{\rho_m c_p Z_m} (T_a - T(t)), & \text{Convection only zone}
\end{cases}
\]

(1)

\[
\frac{dT(t)}{dt} \leq 22.2 
\]

(23)

\[
C(t^e) \leq 0.02 
\]

(24)

\[
\frac{d\alpha(t)}{dt} = \zeta \exp \left( -\frac{E}{RT(t)} \right) \alpha(t)^m (1 - \alpha(t))^n 
\]

(19)

\[
\alpha(t^e) \geq 0.95 
\]

(25)

\[
Q_{e,i} = 2.45L_e \exp \left( \frac{T_{w,i}}{688.2} \right) - 3.80L_e; \quad i = 1, 2, \ldots, N_r 
\]

(4)

\[
Q_{ng,j} = 0.0017(T_{a,j} - 294.11)L_j v_{a,j}; \quad j = 1, 2, \ldots, N_a 
\]

(5)

\[
S = 8.27 \exp \left( 1.01 \alpha(t^e)^{3.44} - 3.06 \right) 
\]

(21)

\[
S \geq 0.45 
\]

(26)

\[
T_{w,i} \in [400, 500] 
\]

(27)

\[
T_{a,j} \in [400, 480] 
\]

(28)

where the decision variables in the objective function, \( T_{w,i} \)'s and \( T_{a,j} \)'s, are the wall temperatures and convection air temperatures in different operational zones of the oven; \( t^e \) denotes the ending time of curing process. Note that the achievement of reaction conversion constraint in Eq. (25) could lead to a \( S \) value greater than 0.45 in Eq. (26). It will affect the optimization results only if Eq. (21) changes with respect to different coating composition.
3.3 System Simulation Procedure

The developed product, process, and optimization models are incorporated in a five-step simulation procedure that is described below.

**Step 1.** Input process design and operational parameters (e.g., the oven design with zone partition and heating types, operational restrictions, vehicle moving speed on conveyor, etc.), coating material parameters (i.e., solvent properties, paint properties including the size and volume fraction of nanoparticles), product quality specifications (i.e., solvent residual, cross-linking reaction conversion rate, and Young's modulus of cured product).

**Step 2.** Identify the optimal temperature settings for all the radiation and convection zones (i.e., $T_{w,i}$’s and $T_{a,j}$’s) through running the optimization model in Eq. (22) associated with the listed equality and inequality constraints.

**Step 3.** Use the identified temperature settings to calculate the following: (a) the coating temperature profile using Eqs. (1) – (2), (b) the solvent removal dynamics using Eqs. (6) – (13), (c) the coating thickness change using Eqs. (14) - (15), (d) the cross-linking conversion rate dynamics using Eq. (19), and (e) the coating scratch resistance performance using the method described in the above Product Performance Evaluation section.

**Step 4.** Plot the results obtained in Step 3. Although all of them have already met the process and product quality requirement, there could be some need for further exploration of opportunities of more significant improvement of product quality and process performance, after reviewing the plots. For instance, one may want to investigate how a further reduction of the solvent residue in the cured coating will impact the cross-linking conversion and/or scratch resistance performance, then the constraint, $\bar{C}(t') \leq 0.02$, in Eq. (24) can be adjust to a value
smaller than 0.02. If any equality and/or inequality expressions in the optimization model are changed, then go to Step 2; otherwise, proceed to the next step.

Step 5. Output a complete set of system input information, including the process specifications, nanomaterial data, and product quality requirement, as well as a complete set of optimization results, including the derived oven temperature settings, the achieved product quality data, and process energy consumption data.

4 CASE STUDY

The developed modeling and optimization methodology has been used to study the optimal curing strategy for a given nanocoating material.

**System specification.** The thermoset coating material is a hydroxyl-functional acrylic copolymer with a number average molecular weight of 2,880; the cross-linker is hexamethoxy-methylmelamine, of which the molecular weight is 390. The nanoparticle component is nanosilica, which is of the size and the volume fraction at 20 nm and 5%, respectively. The initial solvent concentration of the wet clearcoat is 18% and the file thickness is 60 μm. The densities of the solvent, the polymeric material, and the nanoparticle are 0.81 g/cm³, 1.2 g/cm³, and 2.4 g/cm³, respectively. The curing oven is 124.2 m long, which is divided into seven zones of different lengths (see Column 3 in Table 1). The line speed of vehicle moving through the oven is 0.069 m/s. The convection air velocity from the nozzles in the radiation heating zones is 0.18 m/s and that in the convection heating zones is 1.8 m/s. In simulation, parameters β, η, r, K, χ, a, b, c, and $E_d$ are 22, 9.38×10⁻⁶ cm²/s, 0.19, 9.49×10⁻¹¹ g/cm²·atm·s, 0.93, 2.60, 472.92, -94.43, and 32.7×10³ J/mol, respectively. To simplify the simulation process, the solvent vapor partial pressure at the
bulk air is assumed to be 0. The reaction kinetics data for simulating the cross-linking reaction, $\zeta$, $E$, $m$, and $n$, are $9.72 \times 10^6$, $7.266 \times 10^3 \text{ J/mol}$, 0.71, and 1.23, respectively.

**Solution identification and coating dynamics.** The optimization model was used to identify an optimal oven operational strategy, i.e., the optimal setting of the radiation and convection air temperatures in the seven operational zones. The derived temperature settings in different zones are shown in Table 1 (see the two columns under the heading, “Optimal”). The energy consumption data in each operational zone of the oven is listed in Table 2 (see the two columns also under the heading, “Optimal”). As shown, the total amount of energy consumed is 63.25 kWh per vehicle.

Using the oven temperature settings, the coating layer heating profile, the solvent residue dynamics, the coating thickness change, and the cross-linking reaction rate dynamics can be obtained, which are plotted in Fig. 2 (see the solid curves). It is shown in Fig. 2(a) that the curing operation takes 1,800 sec. In drying, the coating temperature increases quickly due to the strong radiation in zones 1 and 2. As the drying proceeds, the coating temperature increment becomes slower in zones 3 and 4, and stable at around 417 K in zones 5 and 6. Figure 2(b) shows that the solvent in the film is mostly removed in the first two zones. But in the end of zone 7, there is still 2% of solvent remained in the dry film; at that time the coating thickness is reduced to 48.29 μm (see Fig. 2(c)). The cross-linking reaction rate dynamics in Fig. 2(d) indicates that the reaction takes place quickly in zones 3 and 4, and reaches 95.0% in the end of zone 7. Figure 3 demonstrates the micro-structure of the nanocoating after curing. The tensile property of the nanocoating is quantified using Young’s modulus. It shows that the cured nanocoating layer can achieve 46.50% of improvement of scratch resistance ($S$) over the conventional coating layer.
Performance comparison using an industrial setting. One task of this work is to study if the known industrial oven design and operational setting used for curing the conventional paint based clearcoat is appropriate for curing nanoclearcoat. The industrial setting (i.e., the wall and convection air temperatures in the seven zones of the same oven) is listed in Table 1 (see the columns under the heading, “Industrial”). Using this setting, which is lower than the optimal except for one convection air temperature, the coating temperature dynamics is obtained, which plotted in Fig. 2(a) (see the dotted line). It is shown that the coating temperature is always lower than that using the optimal setting, with the maximum difference of about 8K in zone ②. This means the nanocoating layer does not receive enough energy for drying and curing.

Consequently, the solvent removal becomes slower; in the end of the process, the solvent residue in the coating is 3.1% (see the dotted line in Fig. 2(b)). This is understandable because in the nanoclearcoat, the presence of nanoparticles makes the solvent diffusion within the film more difficult, and the energy provided for solvent evaporation using the industrial setting is not that sufficient. Because of this slower solvent diffusion and removal, the film thickness reduction process becomes slower accordingly, giving the final thickness of 48.94 μm (see the dotted line Fig. 2(c)), which is slightly thicker than the one drying using the optimal setting (48.29 μm). Note that Fig. 3(d) shows that the cross-linking reaction conversion can reach only 92.26%, which is below the minimum requirement of 95%. Using the industrial setting, the estimated scratch resistance improvement can reach only 42.57%; this is below the minimum requirement of 45%. Energy consumption, however, is 2.70% lower than the one using the optimal operational setting, which is shown in Table 2 (under the heading of “Industrial”). Apparently, the nanocoating using the known industrial setting cannot achieve the anticipated product quality performance.
**Product quality satisfactory region using different nanopaint.** Note that the nanopaint used in the case study has the nanoparticle size and volume fraction of 20 nm and 5%, respectively. It is known that the nanoparticle size and volume fraction of commercial nanopaint are in the range of 10 to 40 nm and 2 to 10%, respectively. Thus, it is worthwhile to investigate whether the identified optimal oven operational setting can ensure the nanoclearcoat quality through the curing operation when the coating material composition changes.

By applying the identified optimal oven operational setting, a series of modeling and simulation are conducted on the nanoclearcoat material with the nanoparticle size and volume fraction of commercial nanopaint from 10 to 40 nm and from 2 to 10%, respectively. Figure 4(a) depicts the correlation between the cross-linking conversion rate verses the nanoparticle size and the volume fraction of the nanoparticles in the nanopaint, while Fig. 4(b) demonstrates how the scratch resistance performance changes along the change of nanoparticle size and the volume fraction of nanoparticles in nanopaint; both are derived using the previously optimized settings for the oven wall temperatures and the convection air temperatures. For the minimum requirement of the cross-linking conversion rate set to 95%, Fig. 4(a) marks a quality satisfactory region in the plane of nanoparticle size verses volume fraction. For the minimum requirement of the scratch resistance improvement of 45%, Fig. 4(b) shows a quality satisfactory region also in the plane of nanoparticle size verses volume fraction. Figure 5 combines the quality satisfactory regions in Fig’s. 4(a) and (b). As shown, the darker area, which is the overlap of the two regions, provides a guideline for choosing nanoparticle size and volume fraction in order to meet the quality requirement of both the cross-linking conversion rate and the improvement of scratch resistance.

5. **CONCLUDING REMARKS**
Nanopaint becomes a very promising coating material in manufacturing industries. Nanopaint based clearcoat is an excellent example in automotive coating. However, there is a lack of fundamental study on cost-effective and quality assured nanoclearcoat curing. It is of great importance to dynamically characterize nanocoating curing under industrial oven operational settings. In this work, a multiscale modeling and simulation methodology is introduced, which can be used to characterize various chemical and physical phenomena in curing operation, which is a critical stage in coating manufacturing. The developed integrated models allow the formulation of an optimization model, targeting minimum energy cost, while all process performance and product quality specifications are considered. The comprehensive case study demonstrates the methodological efficacy. The methodology is general; it can be applied to the study on nanocoating curing using different nanopaint materials in various coating manufacturing operations.

Supporting Information

Detailed description of the derivation of the energy consumption models (Eq’s. (4) and (5)) can be found in the supporting material. This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENT

This work is supported in part by NSF (Grant No. 1421191 and 1140000).
NOMENCLATURE

\( C \)  \( \text{Solvent concentration in film (g solvent/g solid)} \)

\( \overline{C} \)  \( \text{Average solvent concentration in film (g solvent/g solid)} \)

\( C_p \)  \( \text{Heat capacity (J/kg-K)} \)

\( D \)  \( \text{Diffusivity (m}^2/\text{s)} \)

\( d \)  \( \text{Size of nanoparticle} \)

\( E \)  \( \text{Activation energy (J/mol)} \)

\( F \)  \( \text{Volumetric flow rate (m}^3/\text{s)} \)

\( h \)  \( \text{Heat transfer coefficient (W/m}^2\cdot\text{K)} \)

\( K \)  \( \text{Mass transfer coefficient (g/cm}^2\cdot\text{atm} \cdot \text{s)} \)

\( L \)  \( \text{Length of heating zones in curing oven (m)} \)

\( l \)  \( \text{Length of simulation box (m)} \)

\( M \)  \( \text{Vehicle production rate (vehicle/hour)} \)

\( m \)  \( \text{Cross-linking reaction constant} \)

\( n \)  \( \text{Cross-linking reaction constant} \)

\( P \)  \( \text{Pressure (Pa)} \)

\( Q \)  \( \text{Energy consumption (kWh/vehicle)} \)

\( R \)  \( \text{Gas constant (8.314 Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K)} \)

\( t \)  \( \text{Time (s)} \)

\( T \)  \( \text{Temperature (K)} \)

\( v \)  \( \text{Velocity (m/s)} \)

\( U \)  \( \text{Heat density of wall heating materials (Watt/m}^2\)
\begin{align*}
V & \quad \text{Volume (m}^3\text{)} \\
W & \quad \text{Oven radiation heating power (kW)} \\
Z & \quad \text{Thickness (m)} \\
\end{align*}

**Greek**

\begin{align*}
\alpha & \quad \text{Conversion of cross-linking reaction} \\
\beta & \quad \text{Constant} \\
\gamma & \quad \text{Constant} \\
\sigma & \quad \text{Stefen-Boltzman constant (5.67} \times 10^{-8} \text{W/m}^2\cdot\text{K}^4) \\
\varepsilon & \quad \text{Emissivity} \\
\mu & \quad \text{Coefficient of effective radiation surface area} \\
\zeta & \quad \text{Polymerization reaction frequency factor (1/s)} \\
\eta & \quad \text{Pre-exponential constant for diffusion (cm}^2\text{/s)} \\
\rho & \quad \text{Density (g/cm}^3\text{)} \\
\omega & \quad \text{Energy coefficient (kWh} \cdot \text{s/K} \cdot \text{m}^2\cdot\text{-vehicle)} \\
\chi & \quad \text{Flory-Huggins interaction parameter} \\
\phi & \quad \text{Volume fraction} \\
\end{align*}

**Subscript**

\begin{align*}
0 & \quad \text{Initial status} \\
a & \quad \text{Convection air} \\
b & \quad \text{Monomer} \\
c & \quad \text{Cross-linker} \\
\end{align*}
\( d \)  Diffusion

\( e \)  Electricity

\( l \)  Solvent in paint

\( ls \)  Solvent partial vapor pressure at the coating-air interface

\( lb \)  Solvent partial vapor pressure in bulk gas phase

\( m \)  Metal substrate

\( n \)  Nanoparticle or nanopaint

\( ng \)  Natural gas

\( o \)  Conventional clearcoat

\( p \)  Polymeric material

\( r \)  Radiation

\( s \)  Solids in paint

\( v \)  Convection air

\( w \)  Oven wall

*Superscript*

\( e \)  Ending point
REFERENCES


Table 1. Oven temperature setting for a conventional clearcoat system

<table>
<thead>
<tr>
<th>Zone No.</th>
<th>Heating mechanism</th>
<th>Zone length (m)</th>
<th>Radiation wall temperature (K)</th>
<th>Convection air temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Optimal</td>
<td>Industrial</td>
</tr>
<tr>
<td>1</td>
<td>Radiation/Convection</td>
<td>20.73</td>
<td>474</td>
<td>473</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>13.41</td>
<td>483</td>
<td>478</td>
</tr>
<tr>
<td>3</td>
<td>Convection</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>23.67</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>23.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>10.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Air cooling</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Zone number</td>
<td>Energy consumption (kWh/vehicle)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>Industrial</td>
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</tr>
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<td></td>
<td>Electricity</td>
<td>Natural gas</td>
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<td>Natural gas</td>
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<td>22.36</td>
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<td>0.69</td>
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</tr>
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<td>N/A</td>
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<tr>
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<td>9.41</td>
<td>N/A</td>
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<tr>
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<td>8.97</td>
<td>8.97</td>
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<tr>
<td>6</td>
<td>4.00</td>
<td>4.00</td>
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<tr>
<td>Total</td>
<td>71.89</td>
<td>70.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Transport phenomena and reaction occurred in the coating film during curing.
Figure 2. Coating performance under new oven operational setting: (a) coating temperature profile; (b) concentration of solvent residual in nanoclearcoat; (c) thickness of nanoclearcoat; (d) conversion rate of cross-linking reaction in nanoclearcoat.
Figure 3. Micro-structure of the cross-linked nanocoating layer.
Figure 4. Coating quality performance using different nanopaint compositions: (a) conversion rate of cross-linking reaction, and (b) improvement of scratch resistance.
Figure 5. Quality satisfactory zones with respect to different nanopaint compositions.
SUPPORTING INFORMATION

Derivation of Energy Consumption Models

Detailed derivation procedures for the energy consumption models (Eq’s. (4) and (5)) have been listed in this section.

1. Estimation of electricity energy consumption by ceramic heating

In general, the energy consumption per vehicle $Q_e$ (kW•h/vehicle) is a function of heating power $W$ (kW) and the production rate $M$ (vehicles/hr).

$$Q_e = \frac{W}{M}.$$  \hspace{1cm} (S1)

Heat power $W$ is a function of material heat density ($U$) and the amount of heat material used:

$$W = \mu AU ,$$ \hspace{1cm} (S2)

where $\mu$ is the coefficient for the calculation of effective radiation area; $N_r$ denotes the total number of radiation zones.

The total surface area of radiation wall $A$ can be calculated as

$$A = 2HL + WL.$$ \hspace{1cm} (S3)

Heating material heat density ($U$) is a function of heating material output temperature:

$$U = f(T).$$ \hspace{1cm} (S4)

In this work, it is assumed that the wall in a radiation zone is covered by strip band ceramic heating material. Detailed information about a relationship between $U$ and $T$ for this type of
material can be obtained from a manufacturer of ceramic heating material.\textsuperscript{14} Thus, the correlation shown in Eq. (S4) can be calculated as:

\[
U = 19.74 \exp \left( \frac{T}{688.2} \right) - 30.67 .
\] (S5)

Note that the units of temperature and heat density in Eq. (S5) have been converted to K and kW/m\textsuperscript{2} respectively.

Thus, the electric heating power of the \( i \)-th radiation zone can be calculated as:

\[
U_i = 19.74 \mu A_i \exp \left( \frac{T_{w,i}}{688.2} \right) - 30.67 \mu A_i , \quad i = 1, 2, \cdots, N_r
\] (S6)

The electric energy consumption of each vehicle in the \( i \)-th zone can then be calculated by plugging Eq. (S6) into Eq. (S1):

\[
Q_{\text{e},i} = \frac{\eta A_i}{M} \left( 19.74 \exp \left( \frac{T_{w,i}}{688.2} \right) - 30.67 \right) .
\] (S7)

For the specific case investigated in this work, the production rate is assumed to be 46 vehicles/hour; the cross section area of the radiation zone is 2.4 m high and 2.8 m wide; 75\% of the wall surface is covered by ceramic heating materials. With these settings, Eq. (S7) for the \( i \)-th radiation zone becomes:

\[
Q_{\text{e},i} = 2.45L_i \exp \left( \frac{T_{w,i}}{688.2} \right) - 3.80L_i .
\] (S8)

The above equation is Eq. (4) in the main text.

2. Estimation of energy consumption from natural gas combustion
According to Papasavva et al.,\textsuperscript{15} the natural gas consumption (ft$^3$/vehicle) for simultaneous curing of three different layers in all eight heating zones is

$$V_{ng} = \frac{65 \times (T_a - 70) \times L}{0.85 \times 1000},$$  \hspace{1cm} (S9)

where the unit of energy, temperature and length are BTU, F, and ft respectively.

In order to be consistent with the electric energy consumption, the volume of natural gas consumption is converted to energy in kWh. Thus, Eq. (S9) is modified as:

$$Q_{ng} = 0.1311L(T_a - 294.11),$$  \hspace{1cm} (S10)

where the unit of energy, temperature and length are kWh/vehicle, K, and m respectively.

It is essential to characterize the energy consumption in individual heating zone with respect to the air temperature setting and air flow rate. The total energy consumption of natural gas combustion for curing one vehicle shown in Eq. (S10) is:

$$Q_{ng} = \sum_{j=1}^{N_a} Q_{ng,j} , \hspace{0.5cm} j = 1, 2, \cdots, N_a,$$  \hspace{1cm} (S11)

where $Q_{ng,j}$ denotes the energy consumption from natural gas combustion in the $j$-th heating zone for each vehicle.

However, this model (Eq. S9) may not take into account the energy conservation of hot convection air. According to Roelant et al.,\textsuperscript{16} 58% energy in convection air can be conserved. The total energy consumption is estimated 70 kWh/vehicle. In this work, seven heating zones are used to cure the clearcoat layer only. Thus, Eq. (S9) needs to be modified in order to accurately analyze the natural gas consumption.

Note that each heating zone has different length, hot air flow rate and operational temperature setting. In order to characterize the energy consumption in each heating zone, the
oven length, convection air flow rate, and the operational temperature must be taken into consideration. The energy consumption of hot air in the \( j \)-th heating zone \( Q_{ng,j} \) is calculated as:

\[
Q_{ng,j} = F_j C_p \Delta T_{a,j},
\]

(S12)

where \( F \) denotes the volumetric flow rate of hot air, \( C_p \) is the heat capacity of hot air, and \( \Delta T \) is the change of hot air temperature.

It is very challenging to calculate \( Q_{ng,j} \) based on Eq. (S12) due to the insufficient information. The energy consumption of hot air in the \( j \)-th heating zone \( Q_{ng,j} \) shown in Eq. (S12) is obtained based on analogy of Eq. (S9) with the account of hot air flow rate:

\[
Q_{ng,j} = \omega L_j v_j \left( T_{a,j} - 294.11 \right),
\]

(S13)

where \( \omega \) represents an energy coefficient. Its unit is kWh·s/(K·m²·vehicle).

In the main manuscript, the total energy consumption for curing one vehicle is:

\[
Q = \sum_{i=1}^{N_i} Q_{c,i} + \sum_{j=1}^{N_v} Q_{ng,j}.
\]

(S14)

The total energy consumption \( Q \) to cure conventional clearcoat is set at 70 kWh/vehicle based on Roelant and coworkers’ study.\(^{16} \) Based on the industrial oven operational temperature settings shown in Table 1 in the main manuscript, coefficient \( \omega \) can be calculated as 0.0017 based on Eq. (S9), (S11), (S13), and (S14). Thus, Eq. (S13) is obtained as:

\[
Q_{ng,j} = 0.0017 L_j v_j \left( T_{a,j} - 294.11 \right).
\]

(S15)

The above equation is Eq. (5) in the main text.
Nanocoating curing process

 Radiation/convection  |  Zone 1  |  Zone 2  |  Zone 3  |  Zone N

 Mass Transfer

 Crosslinking Reaction

 Basecoat/Powder/E-coat/Phosphate and Metal Substrate

 Heat Transfer

 Clearcoat

 Time-variant microstructure of nanoparticle-incorporated polymer matrix