Cure-Window-Based Proactive Quality Control in Topcoat Curing

Jie Xiao,[†] Jia Li,[†] Helen H. Lou,[‡] and Yinlun Huang*,[†]

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, and Department of Chemical Engineering, Lamar University, Beaumont, Texas 77710

Automotive topcoat curing is critical to the quality of the final coating. In production, topcoat curing quality is commonly judged through the evaluation of sample panel temperature−time series data from the finished product directly against the cure window that is specified for the polymeric coating material used. This inspection-based post-process quality control (QC) is not only methodologically passive, but also is very likely to be erroneous in its conclusions on coating quality. It can hardly generate effective guidance for quality improvement. This paper introduces a novel cure-window-based proactive QC methodology. Using this methodology, dynamic process-product models are deployed to predict the key indicators of film curing quality, according to a given cure window. A dynamic optimization method is then used to search for the optimal operational settings for film curing. The methodology can be used for the development of on-line optimal QC strategies, and it is also applicable for improving traditional inspection-based reactive QC practice. The efficacy of this methodology is demonstrated with a case study on the curing of a topcoat.

Introduction

Automotive coating involves multiple layers of polymeric thin films that are developed over the metal or plastic substrates in automotive paint application processes. Each coating layer, with certain physical and chemical properties, is expected to provide specific functions for improving surface appearance and protection. In production, operational optimality has a key role in achieving superior coating performance. Topcoat curing is the last and possibly the most critical step of polymeric material applications.[1]

Generally speaking, there are two classes of coating quality control (QC) approaches: inspection-based post-process approaches and prevention-oriented in-process approaches. The first class focuses on examination of the coating performance.[2−5] Various experimental techniques, such as confocal Raman microscopy or atomic force microscopy, nanoscratch measurement, and dynamic mechanical thermal analysis, are used to quantify certain key parameters (e.g., cross-linking density, microhardness, extent of conversion) and coating performance (e.g., chemical resistance, scratch resistance, mar resistance, weathering resistance, and adhesion). Paint-specific cure windows, which have traditionally been used as a simple technique for quality assessment,[6] display various curing time−panel temperature ranges over which satisfactory coating quality is assumed to be achievable. In practice, cure windows are used to examine the history data of oven curing, i.e., the durations of film curing at different temperatures. Note that a simple check of panel heating profiles against the cure window may generate erroneous conclusions on coating quality. This type of QC is methodologically passive, because it is performed on the manufactured products, and it can hardly generate effective guidance for quality improvement.

The second class of QC approaches takes advantage of the methods of process systems engineering. It focuses on quality prediction by modeling the topcoat curing processes and then taking prevention-oriented measures for quality assurance. In this direction, several modeling attempts, with relatively ideal experimental validation, have been made.[6−10] However, the resulting models are mostly highly nonlinear and are too detailed for on-line application.

More recently, Lou and Huang[11] introduced a first-principles-based, integrated process-product modeling approach for characterizing topcoat curing operations. Through their approach, intrinsic relationships between a set of process (operational) variables and a set of product (performance) variables can be established in the dynamic domain. The resulting model has been used to describe the following key processing information: (i) panel heating, (ii) solvent removal, (iii) film thickness change, and (iv) cross-linking conversion. These types of information are most valuable for answering the following question: How will an ongoing operation affect coating quality? Using the model by Lou and Huang,[11] Xiao et al.[12] solved a class of quality-constrained oven energy minimization problems, in which an effective optimization method was introduced for solution identification. The proactive coating QC in that work was intended to identify an optimal oven temperature profile, so that the energy consumption of the oven could be minimized, subject to a group of quality constraints. While their work paves the way for prevention-oriented in-process QC, the prediction of a key coating quality parameter, e.g., cross-linking conversion, cannot be directly validated in production, thus hindering its methodological application in a real plant setting.

The gap between theoretical advancement and industrial practice can be bridged by utilizing a commonly adopted quality evaluation tool, i.e., cure windows, as well as dynamic modeling and optimization methods in a seamless way. By concerning the achievement of the best coating quality through curing, the use of the cure window is the most widely acceptable method and is practiced in the industry. Note that the cure window (as well as the nominal cure condition within the window) is a reflection of the curing requirement by considering a variety of coating quality requirements, including DOC, adhesion, scratch resistance, prevention/reduction of many other defects (e.g., crater and orange peel), as well as paint properties, including viscosity, solid level, resin and solvent. Thus, it is desirable to use the cure-window-based nominal-cure-centered curing tem-

* To whom correspondence should be addressed. Tel.: 313-577-3771. Fax: 313-577-3810. E-mail: yhuang@wayne.edu.
† Department of Chemical Engineering and Materials Science, Wayne State University.
‡ Department of Chemical Engineering, Lamar University.

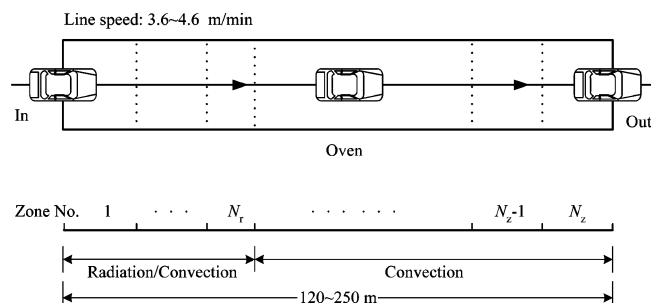**Figure 1.** Sketch of a typical topcoat oven-curing process.
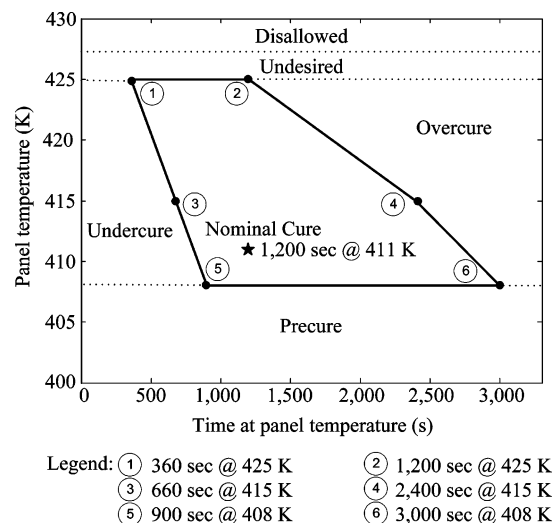

Figure 2. Topcoat cure window with the indicated nominal cure conditions.

perature uniformity among all the panels as an objective. A novel optimal product QC methodology is introduced. In this methodology, dynamic process-product modeling is pursued for predicting the key indicators of curing quality, according to a given cure window. Dynamic optimization is then performed to identify the optimal settings for film curing. The methodology can be used toward developing on-line optimal QC strategies and is also applicable for improving traditional inspection-based reactive QC practice. The efficacy of this methodology is demonstrated by a case study on the curing of a topcoat.

Cure-Window-Assisted Reactive Quality Control

Automotive topcoat curing occurs in an oven that could be as long as 250 m (see Figure 1). In production, the wet-coated vehicle bodies on a conveyor move at a constant speed, sequentially through the oven. The oven is typically divided into many zones of different lengths, heating mechanisms, and operational settings. As always, the first few zones use convection/radiation heating, the last is a cooling zone, and those between are convection-only zones. It can be anticipated that, for a given vehicle geometry, paint material, and wet coating formation on vehicle surface, there must exist an optimal curing policy that can result in superior coating quality at the highest possible energy efficiency.

As stated, cure windows have been used for the assessment of curing quality. Figure 2 is a sample cure window, which displays the various restricted curing time ranges at different panel temperatures. It is accepted that, by following the time–temperature specifications shown in the cure window, an acceptable coating quality can be achieved. For example, a panel temperature of 408 K need be maintained for at least 900 s, but no more than 3000 s. Similarly, at 425 K, the panel should have

a shorter heating period (360–1200 s). In addition, this particular cure window suggests that the panel temperature not exceed 425 K. The cure window also provides an optimum cure condition (called the nominal cure condition). In this case, the nominal cure condition is 1200 s at 411 K. The temperature ranges associated with the curing times are defined based on the physical and chemical properties of the polymeric coating material. Panel heating may also obey other restrictions for quality assurance, such as limitations on the panel temperature gradient (or bring-up rate) to avoid the occurrence of certain surface defects.

Typical automotive production facilities only sample a small percentage of wet-coated vehicle bodies (<1%) for temperature-based curing quality checking. The time-series data that is collected for each panel of a vehicle is then analyzed, and operational appropriateness is judged according to an applicable cure window. If the curing operation has deviated from a permissible heating policy, the operational settings, such as wall temperatures, air temperatures, and air velocities in relevant zones, will be adjusted almost exclusively based on experience. Note that because data analysis is always performed after the completion of curing, this type of quality checking is an inspection-based open-loop approach. Although it may provide guides for improving future operation, the processing effectiveness after adopting improvement guides can only be assessed in the next round of post-process inspection. This type of QC and process improvement procedure could conceivably take a long time, during which coating quality may be continuously questionable. Needless to say, this situation should be modified.

Cure windows can, in fact, be used more effectively, even for inspection-based post-process QC. For prevention-oriented in-process QC, panel-curing strategies can be developed to achieve the ultimate goal, i.e., the nominal cure condition. Clearly, these results cannot be attained through simple, intuitive time-series data checking, which has been traditional industry practice. Indeed, cure-window potentials for proactive coating QC should be fully explored.

A panel temperature profile of interest contains complete panel temperature-time series data sets throughout the curing process. In current industrial practice, each panel temperature profile is converted to a transformed temperature profile suitable for representation in a cure window. Figure 3 shows three hypothetical examples of transforming the panel temperature profiles in Figure 3a to the transformed panel temperature profiles in Figure 3b. Each transformation can be accomplished by performing the following steps:

(1) To identify the maximum temperatures (T^{max}) of a known panel temperature profile (e.g., 422 K for profile No. 1 in Figure 3a) and the lowest panel temperature in the cure window (T^{low}) (e.g., 400 K in Figure 3b). Note that the panel temperature will not exceed T^{max}, and T^{low} is the lowest panel temperature in the cure window (which is the lower limit value of the y-axis in the cure window; panel temperatures lower than this value cannot be shown in the cure window).

(2) To select a set of discrete temperatures between T^{low} and T^{max} with an interval of ΔT (e.g., 1 °C).

(3) To determine the time duration in which the panel is kept at and above each temperature in the discrete temperature set. This step will be repeated until all the time durations are obtained.

(4) To plot each panel temperature–time duration pair as a point in the cure window. This step will be repeated until all the temperature–time duration pairs are located in the cure window.
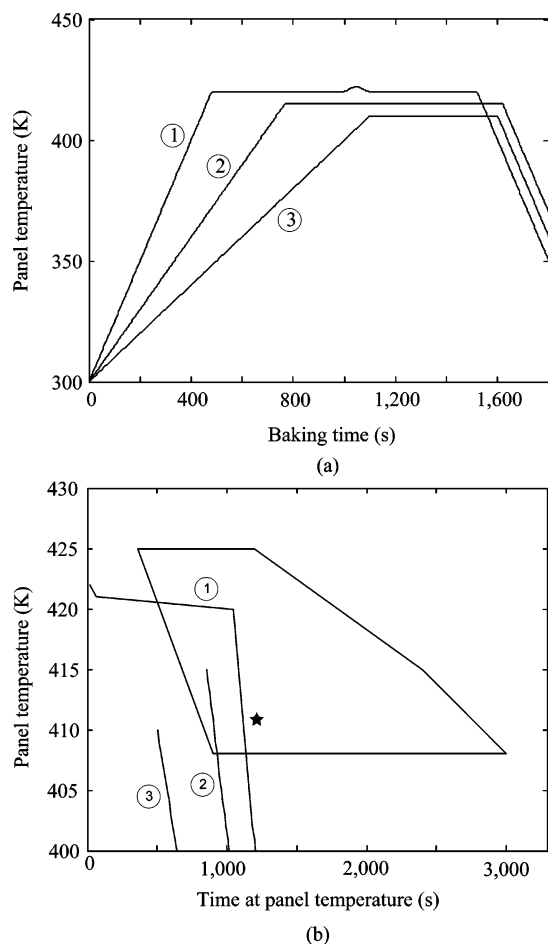
Figure 3. Panel temperature profile transformation: (a) temperature profiles and (b) transformed temperature profiles in the cure window.

(5) To link all the marked points to generate a transformed panel temperature profile in the cure window (e.g., profile No. 1 in Figure 3b).

Traditional coating quality checking is to directly examine the location of the transformed panel temperature profiles, with respect to a cure window. In Figure 3b, the transformed panel temperature profile No. 1 has a point, 1150 s at 408 K, which is located on the right side of the lowest cure condition (900 s at 408 K) defined by the cure window. Thus, the panel heating is judged to be a satisfactory curing. Nevertheless, this type of quality checking has a major deficiency, i.e., it does not tell the degree of satisfaction, as compared to the nominal cure condition in the given cure window (symbolized by a star symbol ("★") in Figure 3b). Furthermore, the quality checking may be erroneous. As shown in Figure 3b, the transformed panel temperature profile No. 3 is completely located on the left side of the cure window. According to the traditional coating quality checking approach, this would be judged as unsatisfactory curing. However, this could be an incorrect conclusion. The curing represented by profile No. 3 could be better than that by profile No. 1. A detailed example of this will be illustrated in the later section of the case study.

Cure-Window-Based Proactive Quality Control

A proactive QC approach should provide answers to two areas of concern: (i) how will the panel temperatures change with time in an oven? and (ii) how can a heating policy be adjusted effectively so that coating quality can be assured? The first

question refers to *process prediction,* which requires a dynamic model that can reveal panel heating behavior throughout the entire curing process. The second refers to *process optimization,* which suggests the use of a dynamic optimization method for solution search.

1. Predictive Modeling for Film Curing. In an oven curing process, the panel temperature is the only parameter, which is practically measurable on the vehicle body. It can be reasonably assumed that the panel temperature is the same as the temperature of the thin polymeric films covering it. Therefore, a panel temperature model is sufficient as the process-product model for cure-window-based coating quality assessment. The oven film curing model by Lou and Huang[11] can be used to predict panel temperature, solvent removal, film thickness, and cross-linking conversion along time. With a cure window available, the panel-temperature dynamic model alone is sufficient for curing quality prediction. This approach is close to the real application and will greatly ease computations in the process optimization step. The panel-temperature-based process-product model by Lou and Huang[11] is as follows:

$$
\rho_m C_{p_m} Z_m \frac{dT}{dt} =
\begin{cases}
\mathcal{F}\sigma\epsilon((T_i^w)^4 - T^4) + \beta V_i^{0.7}(T_i^a - T) & \text{(for } i = 1, ..., N_{rc}) \\
\beta V_i^{0.7}(T_i^a - T) & \text{(for } i = (N_{rc} + 1), ..., N)
\end{cases}
\tag{1}
$$

where T is the panel temperature; T_i^w and T_i^a are, respectively, the wall temperature and the convection air temperature in the ith zone; ρ_m, C_{p_m}, and Z_m are the density, heat capacity, and the thickness of the metal substrate, respectively (it is assumed that the mass of coating is negligible, when compared with the panel); $\mathcal{F}$ is the viewing factor for radiation; σ is the Stefan−Boltzmann constant; ϵ is the emissivity; V_i is the convection air velocity in the ith zone; β is a constant that is related to the distance between the panel and the convection air nozzles, etc.; N_{rc} is the number of zones with both radiation and convection; and N is the total number of zones.

The above model is applicable to the prediction of the temperature change of any panel on a vehicle body in any zone of the oven curing process, except that certain model parameters may be adjusted based on the panel location and its surrounding condition. A model validation approach using industrial data is described in Lou and Huang.[11]

2. Cure Window Interpretation. Cure windows are obtained from the experimental measurements of the physical and chemical properties of coatings under various isothermal curing conditions. A mechanistic interpretation of cure windows can provide real insight into the critical parameters that represent major coating properties.

Figure 4 provides a conceptual understanding of how a cure window can be used toward coating quality evaluation. As shown, there are three curves of cross-linking conversions, x_1-x_3, within the cure window. The curve for x_1 (the lowest conversion percentage) is located on the left-hand side of the nominal cure condition (marked by a star, "★"), while the two other curves for x_2 and x_3 are on the right-hand side. When a curve moves toward the upper right direction, the degree of cure (DOC) will increase, and the energy consumption for the curing also will increase.

There are several quality criteria for topcoats, including, most importantly, the resistance against scratches and environmental fallouts (e.g., acid rain). The scratch resistance seems to be proportional to the cross-link density, which is directly deter-
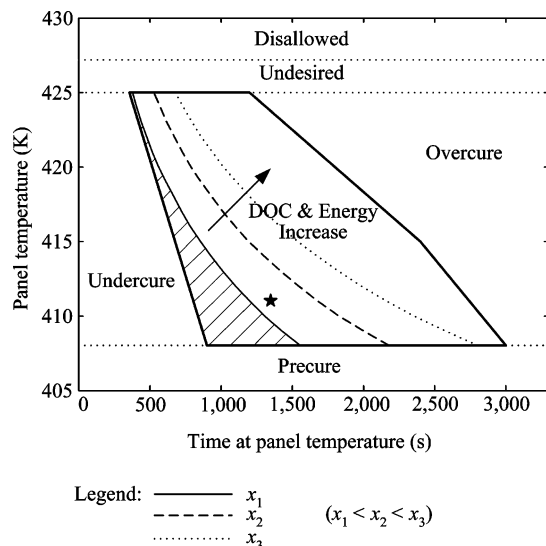
Figure 4. Cure window interpretation, in terms of degree of cure (DOC).

mined by the extent of cross-linking conversion.[4] On the other hand, adhesion and chip resistance are also affected by the cure state.

A solid experimental and theoretical background has been established for research in curing kinetics, which offers simple, yet satisfactory, models for conversion dynamics.[13–15] For these reasons, the extent of conversion (or DOC) has been chosen as a critical parameter. The nominal cure condition within a cure window represents the optimal DOC value. As long as a panel temperature profile is mapped into an isothermal cure condition in the cure window, direct quality evaluation and further optimization can be conducted. Before proceeding further, two terms must be defined: *cure condition* and *equivalent cure condition*.

A cure condition refers to the time of curing at a specific temperature. It is represented as a point in a cure window (e.g., 900 s at 408 K, i.e., point No. 5 in Figure 2), which means that the panel must be kept at 408 K isothermally for 900 s). A nominal cure condition is a suggested optimal cure condition (e.g., 1200 s at 411 K, i.e., the point identified by the star, "★", in Figure 2).

An equivalent cure condition refers to an isothermal cure condition converted from a nonisothermal cure history (e.g., a panel temperature profile). A detailed approach for this conversion will be introduced in the next section.

3. Quality Prediction and Evaluation. The kinetic analysis of a curing reaction is usually performed via differential scanning calorimetry (DSC).[13] A DSC thermograph is a measure of an instantaneous flow of heat (H) over time, which is assumed to be proportional to the rate of reaction. The extent of conversion (fractional conversion, x) is also assumed to be proportional to the heat of reaction evolved in a time interval (ΔH) over the total heat of reaction (ΔH_{tot}). This gives

$$x = \frac{\Delta H}{\Delta H_{tot}} \qquad (2)$$

Generally, the rate of reaction can be expressed as follows:

$$\frac{dx}{dt} = K(T) f(x) \qquad (3)$$

where $K(T)$ is the temperature-dependent rate constant and $f(x)$ is the reaction model. These two can have the following forms:

$$K(T) = A \exp\left(\frac{-E}{RT}\right) \qquad (4)$$

$$f(x) = (1 - x)^n \qquad (5)$$

where A is the frequency factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature of reaction.

For an isothermal reaction with constant frequency factor and activation energy, eqs 3–5 can be rearranged to have the following integral form:

$$\int_0^x \frac{1}{(1 - \zeta)^n} d\zeta = A \exp\left(\frac{-E}{RT}\right) \int_0^t d\tau \qquad (6)$$

Integrating the above equation gives

$$t = \begin{cases} -\dfrac{\ln(1 - x)}{A} \exp\left(\dfrac{E}{RT}\right) & \text{(for } n = 1) \\[3mm] -\dfrac{1 - (1 - x)^{-(n-1)}}{A(n - 1)} \exp\left(\dfrac{E}{RT}\right) & n > 1 \end{cases} \qquad (7)$$

According to eq 7, a different curing time (t) can be obtained at a different isothermal reaction temperature (T). By considering two curing cases that achieve the same final conversion—(i) curing time t_1 at temperature T_1, and (ii) curing time t_2 at temperature T_2—the following relationship can be derived, regardless of the order of reaction:

$$\frac{t_2}{t_1} = \exp\left[\frac{E}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)\right] \qquad (8)$$

The aforementioned relationship was used by Turi[13] to develop a so-called equivalent isothermal time (EIt) method. EIt is a hypothetical isothermal time at a specific reference temperature, which yields a DOC, identical to that of a nonisothermal curing operation. The temperature at the nominal cure condition is treated as the reference temperature, T_r (e.g., 411 K in Figure 2). To obtain the EIt value, the nonisothermal temperature profile is discretized to generate a set of temperature data in many equally spaced time intervals. Each time interval is denoted as Δt, and the temperature in the ith interval is $T(i)$. According to eq 8, the equivalent isothermal time at a reference temperature T_r for each time interval can be obtained. For example, the equivalent time for the ith interval is

$$EIt(i)|_{T_r} = \exp\left[\frac{E}{R}\left(\frac{T(i) - T_r}{T(i) T_r}\right)\right]\Delta t \qquad (9)$$

The equivalent isothermal time at the reference temperature T_r for the complete temperature profile then is

$$EIt|_{T_r} = \sum_i EIt(i)|_{T_r} = \sum_i \exp\left[\frac{E}{R}\left(\frac{T(i) - T_r}{T(i) T_r}\right)\right]\Delta t \qquad (10)$$

For $\Delta t \to 0$,

$$EIt|_{T_r} = \int_0^{t_e} \exp\left[\frac{E}{R}\left(\frac{T(\tau) - T_r}{T(\tau) T_r}\right)\right] d\tau \qquad (11)$$

where $T(\tau)$ is the panel temperature at time τ and t_e is the total curing time for a vehicle body in the oven. The EIt value at T_r

can then be compared with the nominal cure time (e.g., 1200 s in Figure 2) for quality evaluation. A reasonable criterion for the evaluation could be

$$\frac{1}{N_p \times \max[(t^u - t_r),(t_r - t^l)]}\sum_{j=1}^{N_p}|(\mathrm{EIt}_j|_{T_r}) - t_r| < \psi \quad (12)$$

where t_r is the nominal cure time; t^u and t^l are, respectively, the longest and shortest permissible curing time at T_r specified by the cure window; N_p is the total number of panels of a vehicle; ψ is a small number (between 0 and 1) that is selected as the maximum acceptable total deviation of the panel curing condition from the nominal cure condition. The summed absolute differences between each panel's equivalent isothermal time at the nominal temperature ($\mathrm{EIt}_j|_{T_r}$, for $j = 1, 2, ..., N_p$) and the nominal time (t_r) are divided by $N_p \times \max[(t^u - t_r), (t_r - t^l)]$ to make the result a value between 0 and 1.

4. Optimal Curing through Dynamic Optimization. Proactive coating QC requires an on-line development of an optimal curing policy. Such a policy should result in the optimal settings for the operational parameters, such as the wall temperature, the air temperature, and the air velocity of each zone of an oven. This is a very challenging dynamic optimization task, because of its inherent nonlinearity and operational interactions between each pair of adjacent zones. As the first step toward the goal of on-line application, this work is restricted to the construction of an effective dynamic optimization procedure and the cross-linking conversion is adopted as the only quality indicator.

4.1. Optimization Formulation. Cure windows, provided by paint manufacturers, are developed through a large number of experiments and tests under different operating conditions and are based on paint properties and coating quality requirements. Thus, they are used as a standard for wet-paint curing, and the nominal cure of a cure window is considered the target in production. Therefore, the optimization objective in this work is restricted to uniformly curing the films on the panels and the curing conditions for the panels are to be as close to the nominal cure conditions as possible. It becomes the essential part of the proposed cure-window-based proactive QC framework. Because the nominal temperature has been chosen as the reference temperature, quality evaluation can be readily evaluated through comparison of EIt and the nominal time. Mathematically, the objective can be expressed as the minimization of the normalized summation of the absolute differences between each panel's equivalent isothermal time at the nominal temperature ($\mathrm{EIt}_j|_{T_r}$, for $j = 1, 2, ..., N_p$) and the nominal time (t_r). This gives

$$\min J = \frac{1}{N_p \times \max[(t^u - t_r),(t_r - t^l)]}\sum_{j=1}^{N_p}|(\mathrm{EIt}_j|_{T_r}) - t_r| \quad (13)$$

This optimization is subject to the following main constraints: (a) the panel heating temperature model that is already listed in eq 1; and (b) the equivalent isothermal time for each panel (EIt_j, for $j = 1, 2, ..., N_p$) that should be in the ranges defined by the cure window, i.e.,

$$t^l < \mathrm{EIt}_j < t^u \quad (14)$$

where t^l and t^u are, respectively, the shortest and longest curing times specified by the cure window; (c) the panel temperatures

(T_j, for $j = 1, 2, ..., N_p$) that should not exceed the upper limit anytime, i.e.,

$$T_j < T_{\max} \quad (15)$$

(d) the panel temperature gradient in heating, or simply the bring-up rate (dT_j/dt, for $j = 1, 2, ..., N_p$) that must not exceed the upper limit (μ^u) specified based on the coating material, i.e.,

$$\frac{dT_j}{dt} \leq \mu^u \quad (16)$$

(e) the panel temperature gradient between two adjacent zones that should be under a limit, i.e.,

$$\left|\frac{dT_j(t^e)|_i}{dt} - \frac{dT_j(t^0)|_{i+1}}{dt}\right| \leq \Delta\mu^u \quad (17)$$

where t^0 and t^e are, respectively, the starting and ending times of curing (the subscripts i and j refer to the zone and the panel number; $\Delta\mu^u$ is the upper limit of temperature change rate between the two adjacent zones. When the vehicle moves into the last zone (i.e., the cooling zone), this constraint does not apply); (f) the wall temperature setting that must be restricted to avoid the loss of control of panel heating. This leads to

$$(T_i^w)^l \leq (T_i^w) \leq (T_i^w)^u \quad (18)$$

where $(T_i^w)^l$ and $(T_i^w)^u$ are the lower and upper bounds of the wall temperature in the ith zone, respectively. (g) the convection air temperature and air velocity that should be in specific ranges. The air velocity limits may be different among the zones. In the convection-only zones, the maximum permissible air velocity is much higher than those in the radiation/convection zones. These suggest

$$(T_i^a)^l \leq (T_i^a) \leq (T_i^a)^u \quad (19)$$

$$V_i^l \leq V_i \leq V_i^u \quad (20)$$

where $(T_i^a)^l$ and $(T_i^a)^u$ are the lower and upper bounds of the air temperature in the ith zone, respectively; V_i^l and V_i^u are the lower and upper limits of the air velocity in the ith zone, respectively. Note that the upper limits of air velocity in the first two radiation zones will be much lower than those in the succeeding zones, because the dust contamination should be controlled properly.

4.2. Procedure. The proposed proactive QC approach involves five major tasks: (i) panel temperature prediction based on given oven operational settings; (ii) panel temperature profile mapping with an applicable cure window; (iii) coating quality assessment; (iv) identification of an optimal set of oven operational settings, if the current one is not optimal; and (v) the newly derived operational setting can be adopted for improving production. These tasks are conceptually depicted in Figure 5. A computational procedure for implementing these tasks is listed below; each of the following steps matches a specific step in Figure 5.

Step 1. Use eq 1 to generate a set of temperature profiles of all the panels of a vehicle, or collect panel temperature profiles, if it is for inspection-based post-process QC rather than prevention-oriented in-process QC.
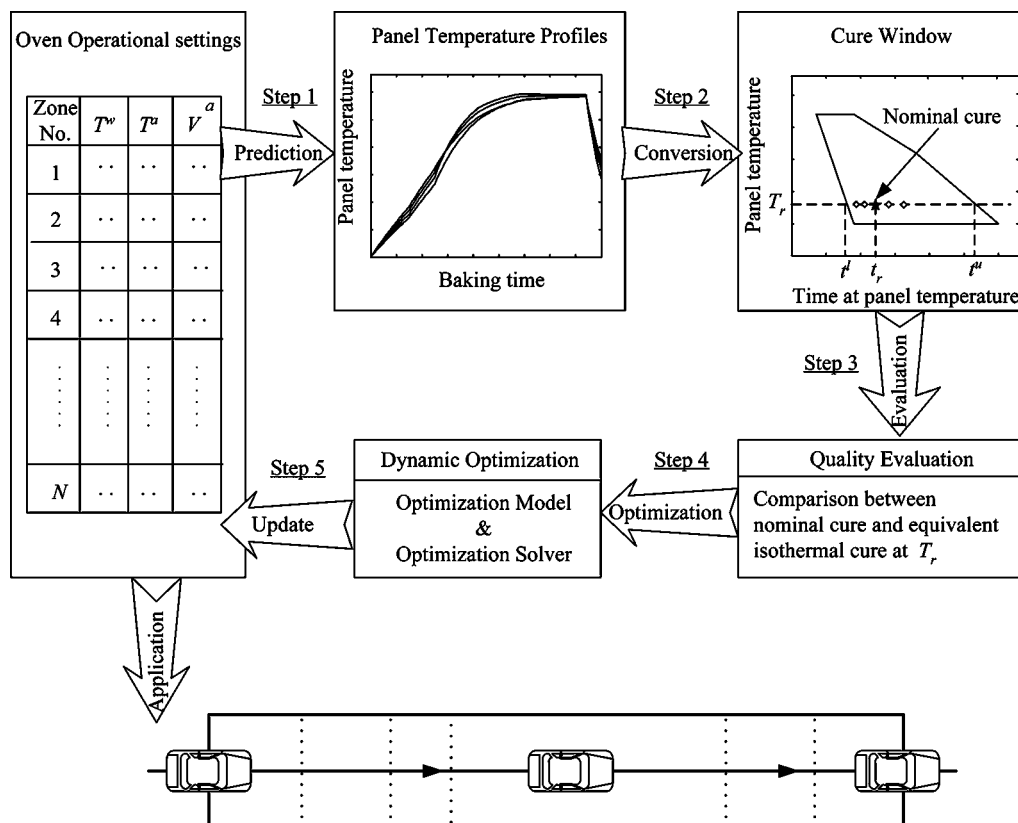
Figure 5. Cure-window-based product quality control procedure.

Table 1. Oven Design and Operational Specification

zone number	heating mechanism	zone length (m)	Radiation Wall Temperature, T^v (K)		Convection air Properties			
					Temperature, T^a (K)		Velocity, V^a (m/s)	
			Orig.	Opt.	Orig.	Opt.	Orig.	Opt.
1	IR/convection	20.73	473	476	403	434	0.18	0.07
2	IR/convection	13.41	478	484	478	483	0.18	0.07
3	convection	23.67	N/A	N/A	428	418	1.8	1.56
4	convection	23.67	N/A	N/A	423	418	1.8	2.27
5	convection	23.67	N/A	N/A	418	412	1.8	2.20
6	convection	10.54	N/A	N/A	418	391	1.8	1.78
7	air cooling	9.14	N/A	N/A	300	300	3.5	3.5

Step 2. Use eq 11 to convert the nonisothermal panel temperature profiles one by one to a set of equivalent (isothermal) cure conditions and plot them in the cure window.

Step 3. Use the inequality presented in eq 12 to evaluate the coating curing quality by comparing the equivalent cure conditions with the nominal cure conditions. If the quality is acceptable, then conclude the evaluation; otherwise, proceed to the next step.

Step 4. Identify a set of optimal operational settings by solving the optimization problem formulated in eqs 13–20. In this step, steps 1–3 will be repeatedly applied for coating quality evaluation. The optimization methodology used in this step is the so-called ant colony system (ACS)-based dynamic optimization methodology[12] (see a brief introduction of its methodology in the Appendix).

Step 5. Generate a list of the suggested operational settings for the next-step production.

Case Study

The proactive coating QC approach has been successfully used to study several industrial case study problems. One of these is illustrated below to demonstrate the methodology's applicability in solving practical problems.

1. Process/Product Specification. The oven under investigation is ~125 m long and is divided into seven zones. The zone definition and the original settings of the wall temperature for radiation, and the air temperature and air velocity for convection in all relevant zones, are listed in Table 1 (see the columns with the heading of "Orig."). Vehicle bodies, initially at 300 K, move through the seven zones in sequence at a constant speed of 0.069 m/s. Each vehicle body has seven coated panels: the hood, deck, roof, left and right sides, and left and right sills. The surface areas and the viewing factors for radiation ($\mathcal{F}$) are panel-dependent, whereas the emissivity is set to $\epsilon = 0.4$ for all. Because of geometric symmetry, the left door (denoted P3) and the right door (P4) are assumed to have the same curing experience. The same is also assumed for the hood (P1) and the deck (P5), and the left sill (P6) and the right sill (P7).

In this case, the cure window in Figure 2 is used, where the nominal cure condition of curing for 1200 s at 411 K is indicated. The maximum panel temperature bring-up rate is 0.23 K/s. A first-order reaction is assumed (i.e., to set n to a value of 1 in eq 5).[6] Note that, in the cure-window-based proactive quality control methodology, the transformed equivalent cure conditions are independent of values of n (see, eq 11). This means that in optimization, the value of n does not affect the
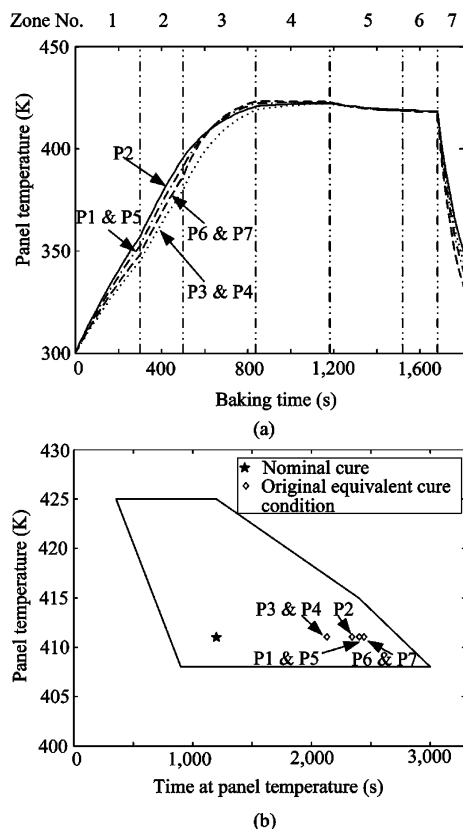
Figure 6. Equivalent cure conditions converted from panel temperature profiles for the original case: (a) panel temperature profiles and (b) equivalent cure conditions in the cure window.

final optimization solution. After obtaining a final solution, the first-order reaction is assumed for conversion comparison between the original curing case and the optimized curing case. The frequency factor A and the activation energy E in eq 4 are 3.2×10^{12} s^{-1} and 1.2×10^5 J/mol, respectively. These parameters are inherent properties of the paint material. DSC experiments can be performed to generate a set of conversion data during the curing process, which will be used to obtain values for n, A, and E through data fitting.

2. Solution Identification. The proposed proactive QC procedure was used to analyze the curing process. The following summarizes the results by executing each of the five steps in the procedure.

Step 1. With original operational settings listed in Table 1 (see the columns with the heading of "Orig."), eq 1 was used to generate the panel temperature profiles, as shown in Figure 6a.

Step 2. Equation 11 was used to convert the temperature profiles in Figure 6a one by one to a set of equivalent isothermal cure conditions (shown in Figure 6b). It shows that the curing in the original production is satisfactory, because all the points that represent the equivalent cure conditions of the panels are within the cure window.

Step 3. The inequality depicted by eq 12 was used to evaluate the curing quality. Parameter ψ is set to 0.1 as the maximum acceptable total deviation of the panel curing condition from
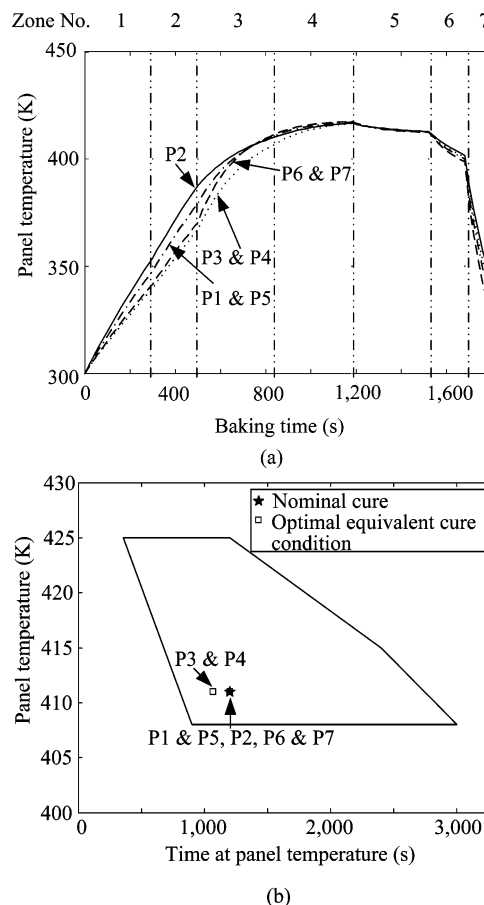
the nominal cure condition. The evaluation shows that the term on the left-hand side of the inequality is equal to 0.73, which is much greater than 0.1. Table 2 lists the detailed evaluation information (see the row labeled "original"). This evaluation suggests the need for optimization.

Step 4. Using the ACS-based dynamic optimization methodology,[12] a set of optimal operational settings were identified and listed in Table 1 (see the columns with the heading of "Opt."). This optimization gives the objective function value of 0.025. Table 2 lists the detailed evaluation information and the values of the objective function in the original case and in the optimal case. These results were obtained within 6 min on a single desktop computer (2.39 GHz).

Step 5. The optimal settings were used to generate a set of new panel temperature profiles (see Figure 7a) and equivalent isothermal cure conditions (see Figure 7b).

3. Solution Analysis. The application clearly demonstrates the superiority of the optimized production to the original one in the following aspects.

(a) The optimized production shows that the equivalent cure condition of each panel is much closer to the nominal cure condition than any panel in the original production. Figure 8 combines the results in Figures 6b and 7b, which gives a much easier comparison.

Figure 7. Equivalent cure conditions converted from panel temperature profiles for the optimal case: (a) panel temperature profiles and (b) equivalent cure conditions in the cure window.

Table 2. Panel-Based and Overall Comparison of the Objective Function Value[a]

operation	hood P1 and deck P5	roof P2	left door P3 and right door P4	left sill P5 and right sill P6	overall J
original	0.111	0.106	0.086	0.115	0.730
optimal	0	2.7×10^{-4}	1.2×10^{-2}	1.8×10^{-4}	0.025

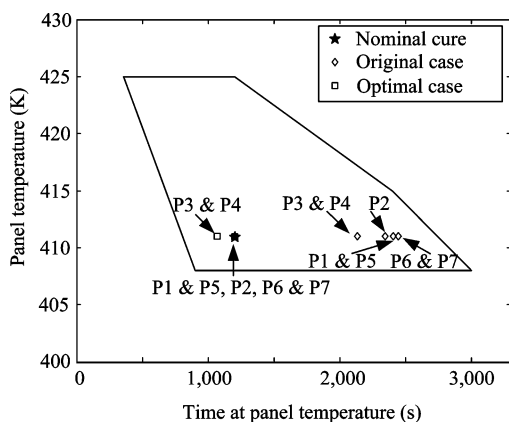[a] Nominal cure conditions: curing for 1200 s at a temperature of 411 K.

Figure 8. Comparison of the equivalent cure conditions between the original cases and the optimal cases.
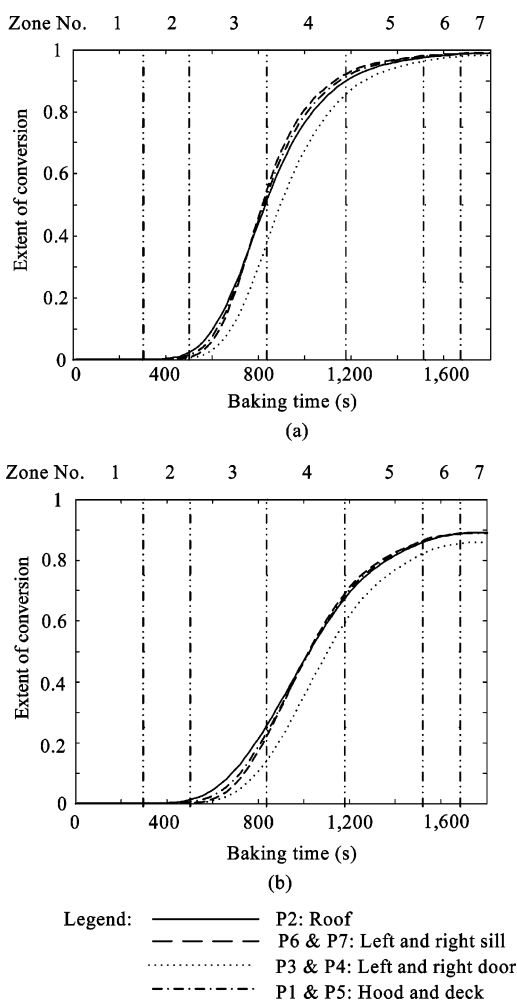

Figure 9. Comparison of the extent of cross-linking conversion: (a) original case and (b) optimal case.

(b) The optimized production gives a lower cross-linking conversion percentage (85%–90%), as compared to the original case (98%–99%) (see Figure 9). This means that the optimized production also requires a lower energy requirement. This can also be confirmed through the panel temperature profiles in Figures 6a and 7a, where the panel temperatures in Figure 7a are relatively lower than those in Figure 6a. Table 1 shows that the wall temperatures and air temperatures of the first two oven zones are increased but the air velocities are decreased. This helps decrease the contamination of dust on the wet film surface in the initial curing stage. In the succeeding zones, the air temperatures are lower than the original settings, which
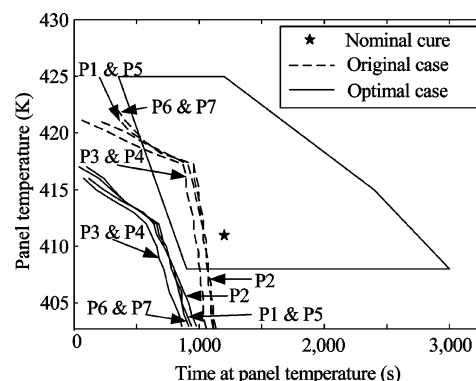

Figure 10. Comparison of the transformed panel temperature profiles between the original case and the optimal case.

contribute to an energy reduction. On the other hand, a lower conversion percentage in the optimized production may prevent some undesired changes in property, e.g., reduction in adhesion, that might be a concern in the original production.

(c) The proposed methodology may also prevent erroneous judgment of coating quality through simple, intuitive panel temperature profile checking against a given cure window in traditional practice. Figure 10 is an excellent example of this, where the transformed panel temperature profiles for both the original production and optimized production are plotted. According to the traditional QC technique, the original production would be determined to be better than the optimized production, because those transformed panel temperature profiles of the original production are all on the right side of the lowest cure condition (curing 900 s at 408 K), whereas all the transformed panel temperature profiles of the optimized production are on the left-hand side of the lowest cure condition. Apparently, this conclusion is not correct.

Discussion

The main purpose of this work is to introduce a cure-window-based proactive QC framework. For simplicity, therefore, cross-linking conversion is the only quality indicator chosen in this work. However, the framework allows integration of any other additional quality indicators as well as product and/or process constraints in formulation. In this section, a viscosity-related quality concern is briefly discussed as a possible additional consideration.

Note that numerous equivalent conversion cure conditions (isothermal temperature versus curing time) exist in the cure window, which can be readily obtained using eq 7. Figure 4 illustrates three examples of equivalent conversion ($x_1–x_3$). However, the recommended nominal cure condition is just a single point (see point marked by a star, "★", in Figure 4). This suggests that additional quality indicators, which control the final coating properties, together with cross-linking conversion, must be identified.

In the study of curing polymeric thick film, viscosity kinetics are frequently investigated.[13,16] For isothermal curing, a predominant empirical model has the following form:[16]

$$\ln\frac{\eta(t,T)}{\eta(0,T)} = A \exp\left(\frac{-E}{RT}\right)t \qquad (21)$$

where $\eta(t,T)$ is the viscosity at temperature T and t is the elapsed cure time; A is the frequency factor; E is the activation energy; and $\eta(0,T)$ is the viscosity of the uncured material (no elapsed cure time) at temperature T.
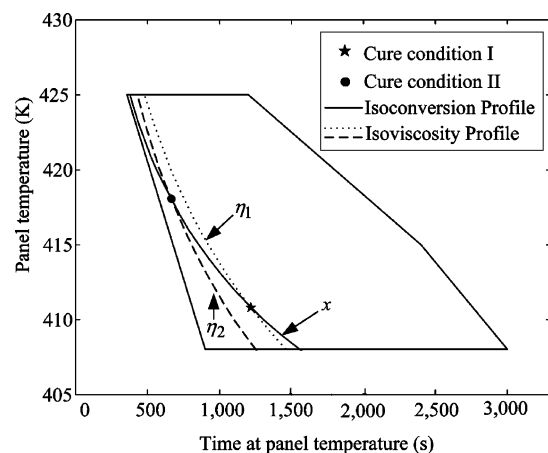
Figure 11. Further interpretation of the cure window by integrating the viscosity.

Figure A1. Search tree representation for the optimization algorithm.

The above equation allows generation of various equivalent viscosity profiles in a cure window. Figure 11 illustrates two of such profiles, η_1 and η_2, where the equivalent conversion profile, x, passing through the nominal cure condition (see the point marked by a star, "★") is also plotted. This figure shows two cure conditions: (i) cure condition I, where the nominal cure condition is realized with the viscosity of the film at η_1, and (ii) cure condition II, where the nominal cure condition is not followed, but a new viscosity (η_2) is reached. In either of these two conditions, the cross-linking conversion (x) is the same. Note that although they possess the same DOC, different viscosities are obtained at last, which may result in different coating properties. This can provide a different view on coating quality selection.

Concluding Remarks

The curing of polymeric coatings is a key operation in automotive coating systems. The optimality of the curing will largely determine coating performance in terms of surface appearance and durability. Traditionally, coating quality control (QC) is passively pursued through the inspection of scarcely sampled products using given cure windows. This is a post-process reactive QC approach. It has been found that cure windows are always used incorrectly, mainly because of the lack of deep understanding of the cure windows that are generated under isothermal cure conditions, while the oven curing of films is always under a nonisothermal condition.

This paper has introduced a proactive QC methodology, which is established based on (i) deep understanding of the cure window development and application conditions, (ii) simple, yet effective, process-product modeling for prediction of key system parameter, and (iii) dynamic optimization for identifying solutions for optimal production. The developed QC procedure can be used to predict coating performance, quantify eventual coating quality against cure windows, and derive operational strategies for quality assurance. In addition, this methodology can be used for improving traditional QC approaches through the correct use of cure windows. The case study has demonstrated its technical effectiveness in applications.

The developed methodology is, in principle, applicable to a variety of polymeric coating curing operations. The problem formulation shows an effective framework that can be enhanced by integrating more technical concerns into it, which may lead to a more comprehensive proactive QC with satisfaction of multiple theoretical and practical objectives.
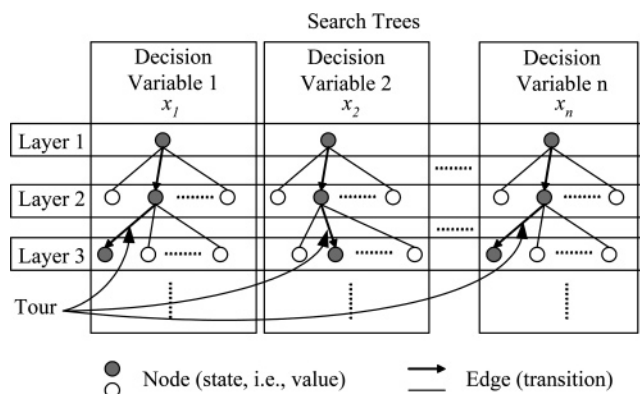
Appendix: Ant Colony System (ACS)-Based Dynamic Optimization Methodology

The ant colony system (ACS)-based dynamic optimization method by Xiao et al.[12] is adopted in this work and it is briefly presented below. More-detailed information about the methodology can be found in Xiao et al.[12]

The goal of the optimization is to minimize the objective function, J, through optimizing the decision variable set, $X \in R^N$, while all constraints should be satisfied. The optimal values of X form the vector, $\tilde{X}^{\text{opt}}$.

A solution identification process can be expressed by a set of search trees (see Figure A1). Each tree corresponds with one variable; it contains a number of nodes that are distributed in layers and a number of edges each of which connects two nodes in two adjacent layers. All the artificial ants work in this set of search trees cooperatively. Each node represents a state (i.e., a value) of a variable. The change of its state from one to the other is called state transition, or the transition between two nodes. Note that a "node" represents each initial or candidate value for each decision variable, an "edge" refers to a transition from the initial value to a candidate value for one decision variable, and a "tour" is defined as a set of edges traversed by one ant for all variables from the initial points (not random, but a feasible solution) to the new settings (a new feasible solution).

The search approach is iterative (see Figure A2) and contains the following major steps.

Step 1. Initiate a new computation outer iteration. Evaluate the sensitivity of each element x_i in X and rearrange the sequence of decision variables according to their sensitivities.

Step 2. Optimize variables in X in the rearranged sequence. An accomplishment of optimizing all variables in X once accounts for the completion of an inner iteration. Note that each outer iteration consists of two or more inner iterations. Each inner iteration will be accomplished by executing the following four substeps.

Step 2-1. For the selected x_i, ant a_j starts at its current value $\tilde{x}_i^c(a_j)$ to search for an optimal value $\tilde{x}_i(a_j)$ using the state transition (ST) rule. Then, ant a_j updates the pheromone on the edge he traversed using the Pheromone Updating (LPU) rule.

Step 2-2. Repeat step 2-1 m times so that each ant can identify its optimal value for x_i (a new node) and update the pheromone of the relevant edge.

Step 2-3. For variable x_i, m ants generate m optimal values (they could be all same, or all different, as two extremes). And they will remember their own choices for that variable.

Step 2-4. After finishing all the variables, each ant finds an optimal solution $\tilde{X}(a_j)$ for the problem. The solution by one ant
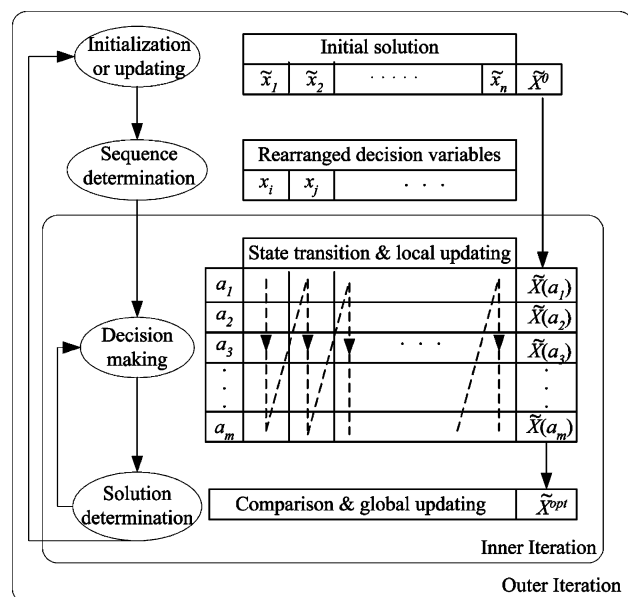
Figure A2. Ant colony system (ACS)-based optimization procedure.

giving the smallest value of J is the best and if this solution is better than the existing solution, this newly identified set, $\tilde{X}^{opt}$ is selected as the optimal. Moreover, in this layer, the pheromone of each edge of each tree will be re-evaluated by the global pheromone updating (GPU) rule. Then, begin another inner iteration from step 2-1 in this outer iteration.

Step 3. Determine if the identified $\tilde{X}^{opt}$ is acceptable or not, after finishing all inner iterations in one outer iteration. The acceptance criterion can be convergence-based, the number of iterations based, etc. If acceptable, $\tilde{X}^{opt}$ is considered the final solution of X, and the corresponding objective function value, $J(\tilde{X}^{opt})$, is the minimum value. The optimization process can be terminated in this outer iteration. If the identified $\tilde{X}^{opt}$ is not acceptable, then this $\tilde{X}^{opt}$ will be the initial value for the next outer iteration starting from step 1 again.

The search uses a sensitivity sequence determination method and three rules repeatedly, i.e., the state transition (ST) rule, the local pheromone updating (LPU) rule, and the GPU rule. These have been described in detail by Xiao et al.[12]

Literature Cited

(1) Cohen, E. D.; Gutoff, E. B. *Modern Coating and Drying Technology*; VCH Publishers: New York, 1992.

(2) Jurgetz, A. Automotive Paint Performance. *Met. Finish.* **1995**, *93*, 53.

(3) Osterhold, M.; Wagner, G. Methods for Characterizing the Mar Resistance. *Prog. Org. Coat.* **2002**, *45*, 365.

(4) Seubert, C. M.; Nichols, M. E. Alternative Curing Methods of UV Curable Automotive Clearcoats. *Prog. Org. Coat.* **2004**, *49*, 218.

(5) Tahmassebi, N.; Moradian, S. Predicting the Performances of Basecoat/Clearcoat Automotive Paint Systems by the Use of Adhesion, Scratch and Mar Resistance Measurements. *Polym. Degrad. Stab.* **2004**, *83*, 405.

(6) Dickie, R. A.; Bauer, D. R.; Ward, S. M.; Wagner, D. A. Modeling Paint and Adhesive Cure in Automotive Applications. *Prog. Org. Coat.* **1997**, *31*, 209.

(7) Navarri, P.; Andrieu, J. High-Intensity Infrared Drying Study. Part II. Case of Thin Coated Films. *Chem. Eng. Process.* **1993**, *32*, 319.

(8) Blanc, D.; Vessort, S.; Laurfnt, P.; Gerard, J. F.; Andrieu, J. Study and Modeling of Coated Car Painting Film by Infrared or Convective Drying. *Drying Technol.* **1997**, *15*, 2303.

(9) Howison, S. D.; Moriarty, J. A.; Ockendon, J. R.; Terrill, E. L.; Wilson, S. K. A Mathematical Model for Drying Paint Layers. *J. Eng. Math.* **1997**, *32*, 377.

(10) Hugget, A.; Sebastian, P.; Nadeau, J. P. Global Optimization of a Dryer by Using Neural Networks and Genetic Algorithms. *AIChE J.* **1999**, *45*, 1227.

(11) Lou, H. H.; Huang, Y. L. Integrated Modeling and Simulation for Improved Reactive Drying of Clearcoat. *Ind. Eng. Chem. Res.* **2000**, *39*, 500.

(12) Xiao, J.; Li, J.; Xu, Q.; Huang, Y. L.; Lou, H. H. ACS-based dynamic optimization for curing of polymeric coating. *AIChE J.* **2006**, in press.

(13) Turi, E. A.; *Thermal Characterization of Polymeric Materials*; Academic Press: New York, 1997.

(14) Kessler, M. R.; White, S. R. Cure kinetics of Ring-opening Metathesis Polymerization of Dicyclopentadiene. *J. Polym. Sci., Part A* **2002**, *40*, 2373.

(15) Kosar, V.; Gomzi, Z. In-Depth Analysis of the Mathematical Model of Polyester Thermosets Curing. *Eur. Polym. J.* **2004**, *40*, 2793.

(16) Kiuna, N.; Lawrence, C. J.; Fontana, Q. P. V.; Lee, P. D.; Selerland, T.; Spelt, P. D. M. A Model for Resin Viscosity During Cure in the Resin Transfer Moulding Process. *Composites: Part A* **2002**, *33*, 1497.