High Throughput Workflow for the Development of Coatings

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Organic coating formulations are complex mixtures of ingredients including resins, crosslinkers, catalysts, pigments, pigment dispersants, solvents, and other additives. In order to prepare a robust, commercially successful coating, all of these ingredients must be carefully optimized.

Evaluation of all of the possible variables involved in developing a coating system is a daunting task for the coating formulator. Consider the example of a solventborne, two-component polyurethane clear coating. A typical composition will include one or more polyols, a polyisocyanate, catalyst, potlife extender, several solvents, and flow, rheology, and weathering additives. If no assumptions are made regarding the performance of the possible ingredients, formulating a system like this could involve the exploration of as many as 25 variables. Evaluating all of the possible combinations of these variables would require the preparation of tens of thousands of formulations.

Fortunately, the coating formulator does not have to start from scratch in formulating a new coating. There is an abundance of information available that will help eliminate large classes of materials from consideration. For example, if a weatherable coating is required, aromatic isocyanate crosslinkers can be eliminated from the formulations. Commonly, starting point formulations are used as a basis for developing a new formulation and a series of iterative experiments are conducted to develop the desired coating. More adventurous formulators may employ statistical experimental design techniques to study a particular variable space in detail.

For more than a decade, the pharmaceutical industry has been practicing methods for the simultaneous synthesis and analysis of tens to thousands of compounds in a single experiment. This approach has been motivated by the need to accelerate the process of identification of drug candidates and the recognition that conducting candidate synthesis one at a time in the laboratory was an inefficient approach to carry out experiments.

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More recently, the combinatorial and high throughput concept has been applied to the development of materials, including polymers and coatings.[1-11] Since coatings are highly complex formulated materials, the use of a high throughput approach is extremely attractive. Given that a large number of compositions and formulations can be explored in a short period of time, the process of identifying compositions having targeted properties is significantly accelerated. In addition, many compositions and formulations can be explored systematically, the data collected, and correlations drawn between composition and performance. Thus, deeper insight on the relationship between composition and properties can be obtained.

COMBINATORIAL SYSTEM FOR COATING DEVELOPMENT

Coating formulation requires a large number of steps and activities. Breaking the process down into its individual steps and then determining which steps are critical and require automation generates the coating workflow. An overall view of the coating workflow is shown in *Figure* 1. This involves the steps of experimental design, polymer synthesis, polymer analysis, coating formulation, coating film formation, and coating analysis.

To get started, NDSU collaborated with Symyx Technologies, Inc., to identify and implement the key components of the workflow that would enable us to generate materials and begin rapid testing of these materials. The components are a simple batch polymer synthesis system, a coating formulation system including viscosity measurement, a coating application (film formation) system to apply the coatings to a substrate, and a coating surface energy measuring system. This is all tied together with a robust suite of software tools for library design, experiment execution, data storage, and data mining.

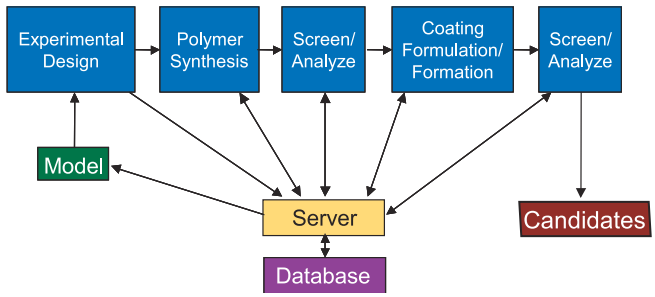
From this initial system we are able to easily add components such as the parallel dynamic mechanical analysis system, coating adhesion system, and rapid GPC system to further enhance our capabilities and fill any remaining gaps in the overall workflow.

Synthesis System

The synthesis system is composed of a robotic reaction system that is housed in a triple glovebox to provide an oxygen- and moisture-free environment. A photo of the glovebox in the laboratory is in *Figure* 2.

The reactor system consists of a platform with an array of nine wells for receiving standard size blocks of reaction vessels. The center three sections are heated and magnetically stirred. Two liquid handling robot arms are used to transfer stock solutions into the individual reactor vessels. Each liquid handling robot has two syringes, 5.0 ml and 500 µl, for delivering low viscosity reagents. Reactor arrays ranging in volume from 1 ml (96 reactors) to 20 ml (6 reactors) are available. Larger sized containers are used for holding stock solutions and monomers while the 6 × 4 and 8 × 12 arrays are used for synthesis of polymers and oligomers. A photo of some of the vessel sizes used is in *Figure* 3.

Figure 1—Workflow for combinatorial and high throughput coating development.



The glovebox system is used to maintain an oxygen- and moisture-free environment for the reagents used in the reactions. Unlike using a simple round-bottom flask, the individual reactors cannot be purged with nitrogen and the reagents are handled in the open during transfer operations. Thus the entire environment has to be an inert atmosphere. The glovebox also has a built in freezer/refrigerator for storage of raw materials.

This system is optimized for those reactions where the reactants can be charged to the reactor vessel, sealed, and then the temperature raised and held to effect the reaction. Polymerization reactions that can be conducted using this system include thermally initiated free radical polymerizations, ring opening polymerizations, and polysiloxane polymerizations.[11] In addition, simple organic reactions or functionalization reactions can also be carried out.

Figure 2—Triple glovebox housing the synthesis system.

Figure 3—Various sample array configurations for the synthesis system.

Coating Formulation System

Following polymer synthesis and characterization, coating formulation is the next step in the workflow.[10] Coatings formulation involves the dispensing and mixing of resins, crosslinkers, catalysts, solvents, pigment, and other additives to create a coating formulation. The system consists of a two-arm robot with a platform very similar to that of the synthesis unit (see *Figure* 4). Thus, there are three center wells having heating and magnetic stirring. Since this system will be used to dispense higher viscosity liquids than the synthesis system, a pipette with disposable tips is used. Using disposable tips minimizes the possibility of cross contamination of the reagents and eliminates the need for cleaning of the tip between reagents, speeding up the dispensing process.

This system is optimized for preparing 6 × 4 arrays of coating formulations. This size vial provides 3–6 ml of solution to use for preparation of multiple sets of coatings in a variety of formats.

The second robot arm holds a unique viscometer that is used to measure the viscosity of the coating formulations (*Figure* 5).[12] The viscometer measuring tips are interchangeable: that is, a new measuring tip is used to measure the viscosity in each coating formulation. A tip rack holds 24 tips in a 6 × 4 arrangement. The viscometer is calibrated using viscosity standards. After a tip is used, it is ejected into a beaker containing solvent. Then the tips are cleaned and returned to use.

The system is programmed with a software routine to reduce the viscosity of the coating array to a target value. This process involves repeated additions of solvent, mixing, and viscosity measurement. This gives us the option of preparing libraries of coating formulations that have either the same volume solids or the same viscosity.

The automated viscometer correlates extremely well with a standard method such as Brookfield viscosity. *Figure* 6 shows a plot of the viscosity measured using the combinatorial viscometer compared to a conventional Brookfield viscometer for a commercial polyester resin diluted with methyl amyl ketone.

Coating Film Formation System

Coating film formation is the next step in the workflow. A versatile system was developed for automatically depositing coating films on standard coating substrates using a drawdown blade. A pipette on one robot arm is used to deposit the coating formulation in a bead on the substrate. A doctor blade mounted on the other robot arm then spreads the bead into a coating. When the doctor blade is finished, it then is given a solvent wash in a three-chambered ultrasonic bath, and dried with an air knife (*Figure* 7).

The coating substrate holders were designed to hold standard 4 × 8 in. coating substrates, which are available from several suppliers. Two 4 × 8 in. substrates are required for a complete library of 24 coatings. There are two substrate holders so that the library can be duplicated on two sets of substrates at one time. The drawdown blade can be adjusted to compensate for substrates of varying thickness. Thus, in addition to standard steel and aluminum substrates, the system can also accommodate thicker glass and plastic substrates. (*Figure* 8).

The doctor blade can also be adjusted to provide a range of wet film thicknesses. The drawdown approach is also more flexible and forgiving than a spray or spin coating approach. Since drawdowns are used extensively in the coatings industry for initial development work, it is also easier for a typical coatings scientist to relate to this method of coating.

Another benefit we have found in the way this system is designed is that rela-

Figure 4—Coating Formulation System.

Figure 5—Close up photo of the rapid viscometer.

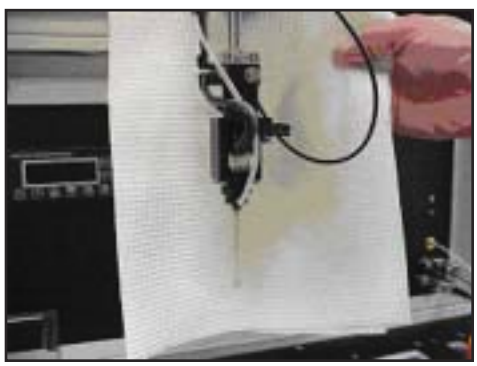
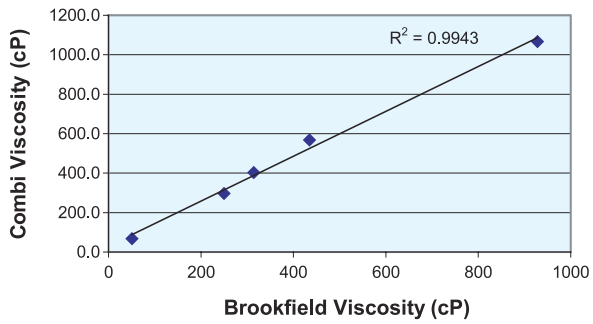


Figure 6—Correlation of Brookfield and combi viscosity measurements.



tively large areas of coating are produced. We believe that this approach has several distinct advantages. The area of the coating spots is large enough that off-the-shelf equipment for measuring gloss, color, or film thickness can be used. Many of these instruments now come with computer interfaces so the data can be captured and stored. Using the standard substrates also means that we can use these test panels in standard test equipment, such as accelerated weathering or corrosion testing (of course, bare areas between the coatings have to be protected).

Coating Surface Energy System

Coating surface energy is an important property and can be used to follow coating aging as well as be correlated with the ability of marine organisms to adhere to coatings. It uses the coating array format that is prepared with the film formation system. Droplets of liquid are placed on the coating, a CCD camera takes a picture of the droplet, and then image analysis is used to determine the contact angle. If liquid droplets of differing surface tension are used, the coating surface energy can be calculated. Currently the system is configured to deposit three droplets of water and three droplets of methylene iodide on the coating surface. A photo of the system is shown in *Figure* 9.

Software: Software tools known collectively as Renaissance® were also developed by Symyx. The core of the software is the Renaissance Application Server (RAS).[12] The RAS is the central component that interacts with all of the systems and stores library designs as well as screening results in the central Oracle® database.

Library Studio® is used to design libraries of materials that are prepared in the Synthesis System or Coating Formulation System.[13] Library designs can be carried out either in mass, mole, or volume units. Composition gradients can be established and special rules can also be used to design material libraries. Statistical designs prepared using software such as Design-Expert® can also be imported into Library Studio.

Impressionist® is used to operate the robots used in the Polymer Synthesis, Coating Formulation and Coating Film Formation systems.[14] Impressionist also interacts with Epoch™, which is the software program that collects data from measurement devices.[12]

Polyview® is used to query the database for library designs and experimental results. Data extracted using Polyview can be viewed in the program or it can be exported to another software package such as Spotfire®.

The importance of the software system cannot be underestimated. Capturing the compositions of each experiment, as well as all of the data associated with the experiment, is crucial in deriving the maximum benefit from this approach. It is in querying the database and looking for correlations, trends, and relationships among thousands of data points that important discoveries are identified.

EXAMPLES

Free Radical Polymerization

To illustrate the power of this method for studying polymer compositions, we carried out a statistically designed free radical polymerization experiment using

Figure 7—Coating Film Formation System.

Figure 8—Closeup of doctor blade and substrate holder.

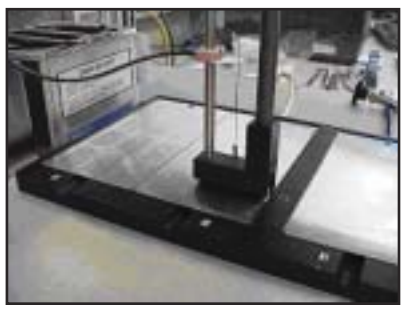


Figure 9—Coating surface energy system.

Figure 10—Response surface for M_n.

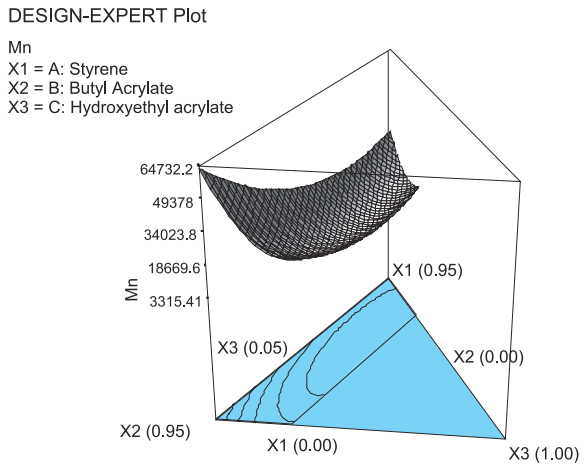


Figure 11—Response surface for T_g.

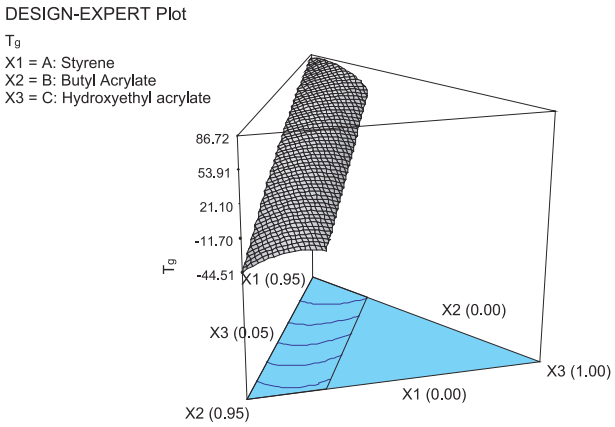
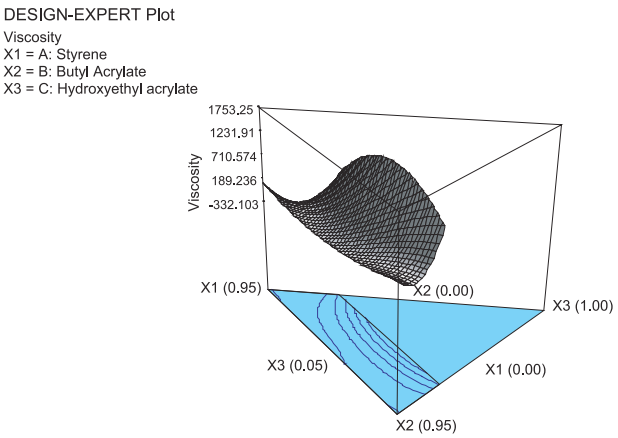


Figure 12—Response surface for viscosity.



three simple monomers. Hydroxyethyl acrylate was varied from 5–30% and the other two monomers (styrene, butyl acrylate) covered the balance of the compositional range. Initiator (Vazo 67), initiator level, solvent (toluene), concentration (50%), and reaction temperature (90°C) were held constant. Inhibitors were not removed from the monomers before polymerization. Twenty-four polymerizations were carried out in parallel using the synthesis unit.

GPC was used to characterize the molecular weight. Differential scanning calorimetry (DSC) was used to measure the polymer T_g. The viscosity of the polymer solutions was measured using the combinatorial viscometer. The data was then used by Design-Expert to develop models that fit the data and are statistically significant.

The response surface map for number average molecular weight is shown in *Figure* 10. The best fit to the data was a quadratic equation, which results in the curvature shown. These results are confounded, however, by the fact that different compositions will have different hydrodynamic volume in solution, thus have different apparent molecular weight in the GPC experiment. As mentioned above, the inhibitor was not removed from the monomers in this experiment. Since different inhibitors are used for the different monomers, this molecular weight variation could be a result of the inhibitor type and concentration in each composition. However, manufacturers of acrylic polymers for coatings usually do not remove the inhibitors before conducting free radical polymerizations. So, this suggests additional experiments to explore the effect of inhibitors on molecular weight of copolymers.

The T_g response surface is shown in *Figure* 11. Note that while there is a linear relationship between the T_g of the copolymers and the styrene-butyl acrylate composition, there is some curvature as the hydroxyethyl acrylate composition is varied. Relationships such as the Fox equation for predicting T_g do not take factors such as molecular weight or hydrogen bonding into account. Conducting multiple series of experiments like this could generate models for the T_g contribution of a wide variety of monomers as a function of polymer molecular weight and include the effect of polar monomers such as hydroxyethyl acrylate.

The viscosity response surface of the polymer solutions is plotted in *Figure* 12. Note the extremely complex relationship between viscosity and composition for this experiment. Viscosity is a function of polymer molecular weight, T_g, and polarity. These effects are difficult to model from first principles for the complex compositions that are usually used for coatings polymers. Note, too, that the minimum in the viscosity response surface is not at the composition that one might expect. However, with the combinatorial approach, we

can simply conduct the polymerizations and determine these relationships experimentally.

Silicone-Urethane Coatings

Another example system consists of a series of silicone polyurethane coatings. These coatings are being explored as low surface energy coatings for ship hulls. A series of coatings were formulated using varying levels of reactive silicone oligomer as well as additional solvent in the formulation. Isocyanate crosslinker, pot life extender, and catalyst were all held constant. Coating formulations were prepared and coated on aluminum test panels and allowed to cure. Since it is important that these hydrophobic coatings stay hydrophobic on exposure to seawater, water contact angle measurements were made on the coatings initially and after exposure to artificial seawater for one week. The change in contact angle is illustrated in *Figure* 13.

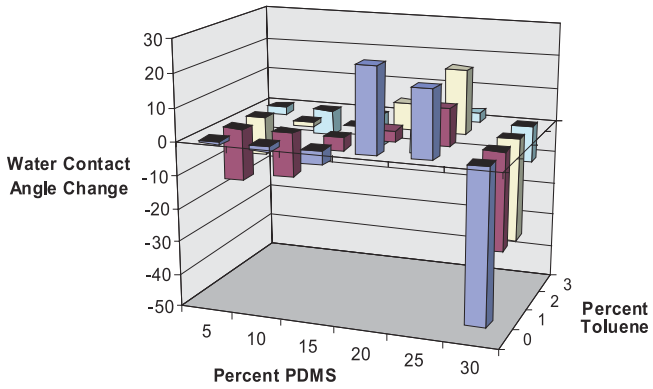
Note that all of the coatings with 30% PDMS had a drastic decrease in contact angle while many other coatings were much more stable and several became more hydrophobic. Thus, in this one experiment we have found that some coatings are not stable and that some other compositions have interesting behavior.

These experiments demonstrate the power and the potential of the combinatorial approach to both polymer synthesis and coating development. These sets of data were generated in single experiments of 24 polymers or coatings. To make 24 polymers in a standard laboratory setting would require several weeks worth of effort. Even including the pre-combi preparation (monomer purification, solvent degassing, experimental design) and post-combi activities (sample work up, GPC and DSC analysis), a significant amount of useful data has been generated in a very short period of time. In the coatings experiment, 24 coating formulations were prepared and characterized in a single experiment that took about two days. Expanding the scope of the designs and conducting combinatorial experiments for only a few weeks would result in the generation of a large amount of valuable data describing the effect of composition and processing conditions on performance of a wide range of polymers and coating compositions.

CONCLUSIONS

The combinatorial approach for the synthesis of polymers and formulation of coatings is an extremely powerful method and requires the development and implementation of high throughput methods. We have built and implemented automated systems for polymer synthesis, coating formulation, coating application, and testing using surface energy measurements. This system is designed to be scaleable. Additional analytical measurement and physical property testing systems can be readily integrated into the information handling system. A great deal of data is generated in a single experiment and this data can be used to develop models of structure-property behavior and identify unique compositions that would not have been discovered if a large variable space had not been explored.

Figure 13—Change in contact angle of silicone-urethane coatings.



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