Development of Combinatorial Chemistry Methods for Coatings: High-Throughput Screening of Abrasion Resistance of Coatings Libraries

Radislav A. Potyrailo,*,† Bret J. Chisholm,‡ Daniel R. Olson,‡ Michael J. Brennan,† and Chris A. Molaison‡

Combinatorial Chemistry and Characterization Technologies, Polymer and Specialty Chemical Technologies, Global Research Center, General Electric Company, Schenectady, New York 12301

Design, validation, and implementation of an optical spectroscopic system for high-throughput analysis of combinatorially developed protective organic coatings are reported. Our approach replaces labor-intensive coating evaluation steps with an automated system that rapidly analyzes 8 × 6 arrays of coating elements that are discretely deposited on a single plastic substrate. Each coating element of the library is 10 mm in diameter and 2−5 μm thick. Performance of coatings is evaluated with respect to their resistance to wear abrasion because this parameter is one of the primary considerations in end-use applications. Upon testing, the coating materials undergo changes that are impossible to quantitatively predict using existing knowledge. Coatings are abraded using industry-accepted abrasion test methods at a single or multiple abrasion conditions followed by the high-throughput analysis of abrasion-induced light scatter. The developed automated system is optimized for the analysis of diffusively scattered light that corresponds to 0−30% haze. System precision of 0.1−2.5% relative standard deviation provides capability for the reliable ranking of coatings performance. Although the system was implemented for high-throughput screening of combinatorially developed organic protective coatings for automotive applications, it can be applied for a variety of other applications for which materials ranking can be achieved using optical spectroscopic tools.

At present, the successes of combinatorial chemistry and high-throughput chemical analysis in the pharmaceutical industry[1] are followed with the discovery of a wide variety of important materials in chemistry and materials science. These materials range from catalysts and polymers to luminescent and magnetoresistive compounds; high-temperature superconductors; dielectric, ferroelectric, and structural materials; and many others.[2,3] These new materials are discovered by measuring intrinsic properties of final products, starting materials, or both. Examples of measured properties of reaction components and final products in combinatorial libraries include catalytic properties of materials,[4−6] molecular weight[7] and vapor-sorption characteristics[8,9] of polymers, resistivity properties of superconductors[10] and magnetoresistive materials,[11] spectral emission properties,[12−14] thin-film dewetting,[15] materials mechanical properties,[16] and many others.

We advance combinatorial discoveries into more complex materials space, where simple intrinsic properties of starting or final materials no longer provide adequate information about long-term material performance. Our general approach employs fabrication of combinatorial libraries of materials, followed by their testing against single or multiple end-use parameters at several levels.[17,18] Single-level high-throughput performance testing has

---

* Corresponding author, E-mail: Potyrailo@crd.ge.com.
† Combinatorial Chemistry and Characterization Technologies.
‡ Polymer and Specialty Chemical Technologies.

(1) *A Practical Guide to Combinatorial Chemistry*; Czarnik, A. W., DeWitt, S. H., Eds.; American Chemical Society: Washington, DC, 1997.
(2) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2494−2532.
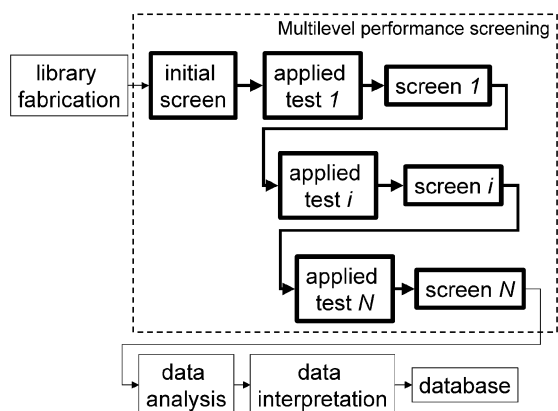(3) *High-Throughput Synthesis. Principles and Applications*; Sucholeiki, I., Ed.; Marcel Dekker: New York, 2001.

(4) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735−1737.
(5) Cong, P.; Doolen, R. D.; Fan, Q.; Giaquinta, D. M.; Guan, S.; McFarland, E. W.; Poojary, D. M.; Self, K. W.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 484−488.
(6) Su, H.; Hou, Y.; Houk, R. S.; Schrader, G. L.; Yeung, E. S. *Anal. Chem.* **2001**, *73*, 4434−4440.
(7) Brocchini, S.; James, K.; Tangpasuthadol, V.; Kohn, J. *J. Am. Chem. Soc.* **1997**, *119*, 4553−4554.
(8) Dickinson, T. A.; Walt, D. R.; White, J.; Kauer, J. S. *Anal. Chem.* **1997**, *69*, 3413−3418.
(9) Matzger, A. J.; Lawrence, C. E.; Grubbs, R. H.; Lewis, N. S. *J. Comb. Chem.* **2000**, *2*, 301−304.
(10) Xiang, X.-D.; Sun, X.; Briceño, G.; Lou, Y.; Wang, K.-A.; Chang, H.; Wallace-Freedman, W. G.; Chen, S.-W.; Schultz, P. G. *Science* **1995**, *268*, 1738−1740.
(11) Briceño, G.; Chang, H.; Sun, X.; Schultz, P. G.; Xiang, X.-D. *Science* **1995**, *270*, 273−275.
(12) Danielson, E.; Golden, J. H.; McFarland, E. W.; Reaves, C. M.; Weinberg, W. H.; Wu, X. D. *Nature* **1997**, *389*, 944−948.
(13) Danielson, E.; Devenney, M.; Giaquinta, D. M.; Golden, J. H.; Haushalter, R. C.; McFarland, E. W.; Poojary, D. M.; Reaves, C. M.; Weinberg, W. H.; Wu, X. D. *Science* **1998**, *279*, 837−839.
(14) Wang, J.; Yoo, Y.; Gao, C.; Takeuchi, I.; Sun, X.; Chang, H.; Xiang, X.-D.; Schultz, P. G. *Science* **1998**, *279*, 1712−1714.
(15) Meredith, J. C.; Smith, A. P.; Karim, A.; Amis, E. J. *Macromolecules* **2000**, *33*, 9747−9756.
(16) Zhao, J.-C. *Adv. Eng. Mater.* **2001**, *3*, 143−147.
(17) Potyrailo, R. A.; Olson, D. R.; Chisholm, B. J.; Brennan, M. J.; Lemmon, J. P.; Cawse, J. N.; Flanagan, W. P.; Shaffer, R. E.; Leib, T. K. Invited Symposium "Analytical Tools For High Throughput Chemical Analysis And Combinatorial Materials Science", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 4−9, 2001; paper 992.
(18) Potyrailo, R. A.; Chisholm, B. J.; Olson, D. R.; Brennan, M. J.; Molaison, C. A. *Proc. SPIE-Int. Soc. Opt. Eng.* **2002**, *4578*, 145−152.

Figure 1. Combinatorial approach for discovery of advanced materials.

been recently demonstrated, including impact testing of polymers[19] and flammability and ignition testing of flame-retardant materials.[20] Multiple levels of testing conditions provide more reliable ranking of performance of combinatorial materials libraries by comparing the ranking of materials at various levels of test conditions. Further, this method provides valuable information about the minimum required test level needed for the fastest reliable screening.

A schematic representation of the multilevel testing approach is illustrated in Figure 1. The testing process includes exposure of the library to an environment that imitates the end-use application and alters materials properties in a detectable manner. Upon testing, the materials undergo changes that are impossible to quantitatively predict using existing knowledge. Our scheme of evaluation of advanced combinatorial materials is very general and includes diverse testing methodologies. Examples include solar radiation, heat, mechanical stress, aggressive fluids, and many others. The effects of these testing conditions are determined in the in situ or post-testing screening.

We have implemented our strategy for high-throughput screening of combinatorially developed organic protective coatings for automotive applications. One of the primary considerations in the durable applications of such coatings is their resistance to wear abrasion that is caused by mechanical action that removes material from the surface of a coating. Abrasion measurement is of practical importance to both producer and consumer, because they are related to the appearance of protective coatings.[21]

Abrasion resistance of a protective coating is not a unique or isolated property of a material but is rather related to a variety of physical characteristics, including hardness, cohesive and tensile strength, elasticity, thickness, toughness, and some others. At present, the interdependence of these factors and the resulting influence on the properties of coatings is difficult to predict using known scientific principles.[21] For example, although the scratch test can be used to generate the same damage mechanisms as are observed in abrasive wear, the scratch test cannot be used for quantitative prediction of wear rate.[22]

Thus, the formulation of an effective coating commonly requires extensive labor-intensive end-use abrasion testing and analysis. Typical industry-accepted methods to induce abrasion include Taber,[23,24] falling abrasive,[25] oscillating sand,[26] and other tests. The degree of coating abrasion is often determined as abrasion-induced haze[27,28] which can be related to the amount of total and angularly resolved scattered light from the surface defects.[27, 29−31]

For the development of new abrasion resistant organic coatings, we coupled combinatorial chemistry methods for generation of coatings libraries with the industry-accepted abrasion test methods and with the high-throughput analysis of abrasion-induced loss of optical clarity of coatings. This paper reports the results of the design, validation, and implementation of an optical spectroscopic system for high-throughput analysis of these combinatorially developed libraries of protective organic coatings. The spectroscopic high-throughput analysis system was optimized for the adequate measurement precision of a broad variety of coatings and provides means for reliable ranking of coating performance.

PRINCIPLE OF OPERATION

Analysis of haze[27] is conventionally performed by illuminating a coating on a transparent substrate at an angle normal to its surface and measuring the transmitted and scattered components of light. If an analytical wavelength is far from the absorption peaks of UV absorbers in the coating and the instrument-related scatter is negligible, then the calculated percent haze H of a coating is given by[27,29]

$$H = 100 \, S_2/S_1 \tag{1}$$

where S_1 is the transmitted portion of collected light, and S_2 is the scattered portion of collected light. Assuming a constant small absorbance of different coatings at the analytical wavelength and a negligible instrument-related scatter, the total amount of collected light S from samples with different levels of haze is described by

$$S = S_1 + S_2 \tag{2}$$

Rearranging eq 1 and using eq 2, a transfer function between haze H and scattered light S_2 is given by

$$S_2 = SK/(1 + 100/H) \tag{3}$$

where K is an instrumental constant relating a conventional

(19) Meredith, C.; Sormana, J.-L.; Tona, A.; Elgendy, H.; Karim, A.; Amis, E. *Polymer Preprints* **2001**, *42*, 649−650.
(20) Gilman, J. W.; COMBI 2002 − The 4th Annual International Symposium on Combinatorial Approaches for New Materials Discovery, San Diego, CA, January 23−25, 2002.
(21) Morse, M. P. In *Paint and Coating Testing Manual*; Koleske, J. V., Ed.; American Society for Testing and Materials: Philadelphia, PA, 1995, pp 525−533.
(22) Bull, S. J. *Wear* **1999**, *233−235*, 412−423.
(23) *ASTM D 1044-94, Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion*; ASTM: West Conshohocken, PA; 1994.
(24) *ASTM D 4060-95, Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser*; ASTM: West Conshohocken, PA; 1995.
(25) *ASTM D 968-93, Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive*; ASTM: West Conshohocken, PA; 1993.
(26) *ASTM F 735-94, Abrasion Resistance of Transparent Plastics and Coatings Using the Oscillating Sand Method*; ASTM: West Conshohocken, PA; 1994.
(27) *ASTM D 1003-97, Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics*; ASTM: West Conshohocken, PA; 1997.
(28) Katsamberis, D.; Browall, K.; Iacovangelo, C.; Neumann, M.; Morgner, H. *Prog. Org. Coat.* **1998**, *34*, 130−134.
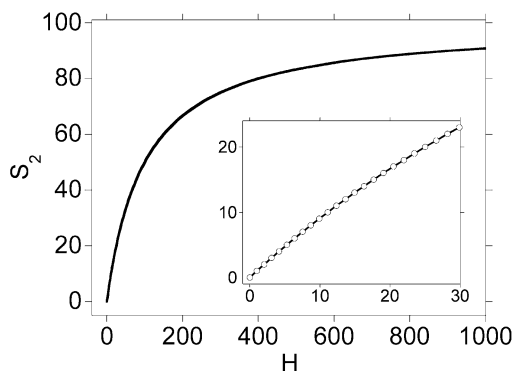(29) Billmeyer, F. W., Jr.; Chen, Y. *Color Res. Appl.* **1985**, *10*, 219−224.

Figure 2. Correlation between the scattered light signal S_2 and haze H computed using eq 3. Inset, S_2 vs H for the range of practical haze measurements from 0 to 30%.

instrument for manual measurements of haze and a high-throughput system for automatic measurements of scattered light.

A typical correlation plot between the scattered light and haze described by eq 3 is illustrated in Figure 2. Although this computer-simulated plot demonstrates a strong nonlinear dependence of scattered light signal S_2 as a function of haze H, it is important to note that the maximum haze value for practical applications should not be greater than 30%.[27] Coating materials having higher haze values are considered diffusing and should be measured using other methods.[27] An inset in Figure 2 demonstrates that scattered light signal S_2 almost linearly increases as a function of haze H over the range of haze from 0 to 30%.

It is important to emphasize that high-throughput screening of abrasion resistance of combinatorial libraries of coatings is performed after a screen for optical clarity of cured coatings before abrasion.[32] These measurements reject the coatings with a high initial scatter from being further tested for abrasion resistance. As a result, only the coatings with a consistent minimal initial scatter are used for abrasion testing. When the same wear abrasion method is implemented for testing of all coating compositions, its wear abrasion mechanism remains constant for different types of organic hard coatings.[33] This is due to the relatively mild abrasion conditions used for testing of combinatorial coating libraries. In this case, coatings do not experience a significant mechanical load that often leads to an additional surface-degradation mechanism, such as adhesion loss.[34] Because any additional adhesion-loss-related coating defects would lead to the additional light scatter, we controlled the abrasion test conditions in order not to initiate adhesion loss.[32,33] Thus, under our test conditions, the nature of abrasion-induced defects remains

the same for different types of coatings, with the size and the density of these defects inversely proportional to abrasion resistance of the tested coatings. As a result, the angular distribution of scattered light for different types of coatings remains essentially the same, because the source of the scatter is the action of the abrasive particles under the mild test conditions. Thus, for rapid ranking of coatings according to their abrasion resistance, it is convenient to measure scattered light at a single angle.

High-throughput quantitative measurements of scattered light can be performed with a system that is relatively straightforward to construct, as compared to haze measurements. Measurements of scattered light can be performed on individual coatings using, for example, a reflection fiber-optic probe. Alternatively, an entire library of coatings can be screened by imaging scattered light from all coatings in the array at once. In contrast, measurements of haze require the use of an integrating sphere[27] and its precise positioning over each individual sample for transmission-based measurements.

EXPERIMENTAL SECTION

Preparation of Coating Libraries. *Constant Composition: Variable Abrasion Level Library.* A coating derived from a mixture of methyltrimethoxysilane, colloidal silica, and *n*-butyl alcohol was flow-coated onto a 3-mm-thick polycarbonate sheet, dried in air for 10 min, and cured at 130 °C for 30 min. The cured coating was screened for optical clarity before abrasion testing. A mask with circular openings (3-mm diameter, 5-mm spacing between centers) was positioned on top of the coating for air blast abrasive test.

Variable Composition: Constant and Variable Abrasion Level Libraries. Small (10-uL) volumes of various coating oligomer formulations were discretely deposited onto a 0.5-mm-thick 12 × 9-cm polycarbonate sheet using a liquid dispensing robot (Packard Instrument Co., model Multiprobe II, Meriden, CT) to produce 48-element coatings libraries as 8 × 6 arrays. Each coating element is 10 mm in diameter and 2−5 μm thick. One coating library contained eight different coating formulations with six replicates each. Table 1 depicts the formulations used for the coating array. Coating formulations in columns 1−5 were from UCB Chemical Corp., North Augusta, SC. Coating formulations in columns 6−8 were from Sartomer Co., West Chester, PA. Another coating library contained 4 replicates of 12 different coating acrylate formulations. Coating formulations were cured upon exposure to UV radiation or temperature. Further details of the library preparation are reported elsewhere.[35] Libraries were screened for optical clarity before abrasion testing to prevent the coatings with a high initial scatter from being further tested for abrasion resistance. The libraries of coatings were abrasion-tested at a single or several abrasion conditions using the oscillating sand abrasion test.

Abrasion Testing Methods of Coating Arrays. *Air Blast Abrasive Test.* The flow-coated polycarbonate sheet with an attached mask was subjected to a stream of 50-μm Al$_2$O$_3$ particles at a constant pressure and flow rate. Abrasive particles were applied through a pencil-shaped nozzle with a 1-mm-diameter orifice. The sheet was automatically advanced under the nozzle at a speed of ∼15 cm/min using a single-axis translation stage.

(30) Stover, J. C. *Optical Scattering: Measurement and Analysis*; McGraw-Hill: New York, 1990.

(31) Bennett, J. M. *Surface Finish and Its Measurement*; Optical Society of America: Washington, DC, 1992.

(32) Chisholm, B. J.; Potyrailo, R. A.; Cawse, J. N.; Brennan, M. J.; Molaison, C. A.; Shaffer, R. E.; Whisenhunt, D. W.; Olson, D. R. In *Proc. 29th International Waterborne, High-Solids, and Powder Coatings Symposium*; New Orleans, LA, February 6−8, 2002, Storey, R. F., Thames, S. F., Eds.; University of Southern Mississippi: Hattiesburg, MS, 2002; pp 125−137.

(33) Chisholm, B. J.; Potyrailo, R. A.; Shaffer, R. E.; Cawse, J. N.; Brennan, M. J.; Molaison, C. A. In *Proc. International Coatings for Plastics Symposium*; Troy, MI, May 20−22, 2002; Paper Tue/2; MSU Management Education Center, Troy, MI, 2002.

(34) Muzeau, E.; Von Stebut, J.; Magny, B. *Met. Finish.* **2001**, *99*, 21−27.

(35) Saunders: D. L.; Akhave, J. R.; Potyrailo, R. A.; Olson, D. R.; Flanagan, W. P. *An improved combinatorial testing method and apparatus for coat material formulations and methods*; World Patent Application WO0132320, 2001.

Table 1. Coating Formulations

| column no.	coating formulation name	description
1	Ebecryl 1290 acrylated urethane	acrylated aliphatic urethane oligomer hexafunctional
2	Ebecryl 8804 aliphatic urethane	diacrylate; acrylated aliphatic urethane oligomer
3	Ebecryl 140 acrylate ester	tetraacrylate monomer
4	DPGDA acrylate ester	dipropylene glycol diacrylate monomer
5	Ebecryl 8301 acrylated urethane	acrylated aliphatic urethane oligomer
6	SR 238	1,6-hexanediol diacrylate
7	CD-401	cyclohexane dimethanol dimethacrylate; difunctional cycloaliphatic methacrylate monomer
8	SR 399	dipentaerythritol pentaacrylate
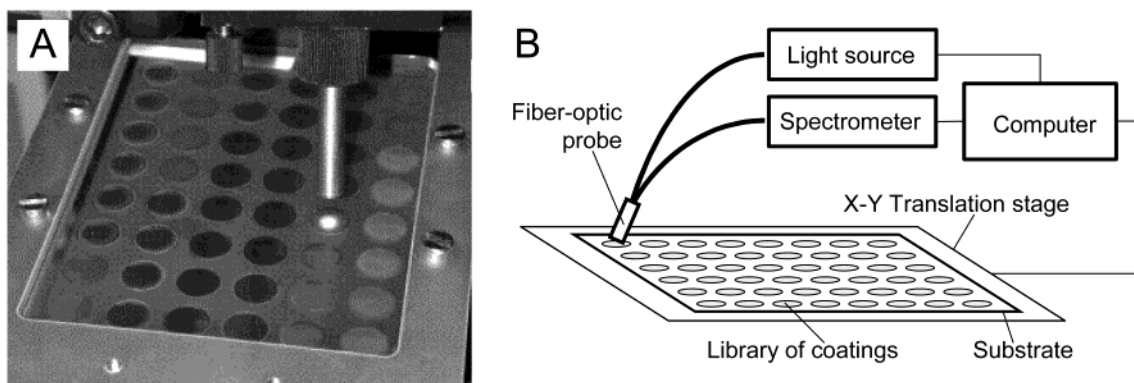
Figure 3. General view (A) and schematic representation (B) of the optimized high-throughput spectroscopic analysis system.

Seven levels of coating abrasion were induced by changing the distance of the nozzle to the coating surface from 2.5 to 10 cm in 1.25-cm increments. Each row of the coating was exposed through the mask to different levels of abrasion.

Oscillating Sand Test.[26] A layer of sand was placed onto the 48-element library of coatings which was secured in a container. The container was oscillated for a predetermined amount of time. Different levels of abrasion of the 48-element library of coatings were induced by performing the test for 10, 20, and 30 min.

Conventional Haze Analysis. Haze measurements of reference flow-coated samples of coatings (10×10 cm polycarbonate substrates) were performed after the Taber abrasion test using a conventional hazemeter (model Haze-Gard Plus, BYK-Gardner USA, Columbia, MD). A typical Taber-abraded region was formed as a circle with a 6-cm i.d. and a 1.5-cm width. About 1 cm² area of the coating was manually measured, and haze was calculated as the ratio of the diffuse transmitted light to the total transmitted light.[27] Haze measurements were made on each sample in four different locations (top, bottom, right, and left) in accordance to an approved Standard Operating Procedure. Similarly, each sample was further analyzed in four corresponding locations using the high-throughput spectroscopic setup.

High-Throughput Optical Analysis and Data Treatment. Spectroscopic measurements of scattered light were performed using a setup shown in Figure 3. The system included a white light source (450 W Xe arc lamp, SLM Instruments, Inc., Urbana, IL, model FP-024), a monochromator for selection of the illumination wavelength (SLM Instruments, Inc., model FP-092), and a portable spectrometer (Ocean Optics, Inc., Dunedin, FL, model ST2000). The spectrometer was equipped with a 600-grooves/mm grating blazed at 400 nm and a linear CCD array detector. The spectrometer covered the spectral range from 250 to 800 nm

with efficiency greater than 30%. Light from the monochromator was focused into one of the arms of a "six-around-one" bifurcated fiber-optic reflection probe (Ocean Optics, Inc., model R400-7-UV/vis. The common arm of the probe illuminated an element of the library at a small angle relative to the normal to the surface. The second arm of the probe was coupled to the spectrometer.

Illumination conditions were selected to have minimal contributions from light directly reflected from the coating back into the probe and to collect only the scattered portion of radiation interacting with the coating surface. The coatings were illuminated with the light beam that emerged from the fiber-optic tip and the transmitted portion of the beam diverged freely under the coating array. The distance from the fiber-optic tip to the nearest surface was sufficiently large not to generate any additional amount of light reflected back into the fiber-optic probe. In this design, the number of surfaces which interact with the light beam was minimal, which reduced the error in measurements.

For measurements of scattered light, the excitation wavelength was set to 500 nm or at the zero order of the monochromator. The common end of the fiber-optic probe was arranged on a $X-Y$ translation stage. The data acquisition was achieved with a computer using a program written in LabVIEW (National Instruments, Austin, TX). The program provided an adequate control of the data acquisition parameters and a real-time communication with the translation stage. Processing of collected spectra was performed using KaleidaGraph (Synergy Software, Reading, PA) and Matlab (The Mathworks Inc., Natick, MA).

RESULTS AND DISCUSSION

Validation of the High-Throughput Spectroscopic Setup. The spectroscopic setup was optimized to quantify haze levels from 0 to 30%. This range of haze was obtained in our traditional-
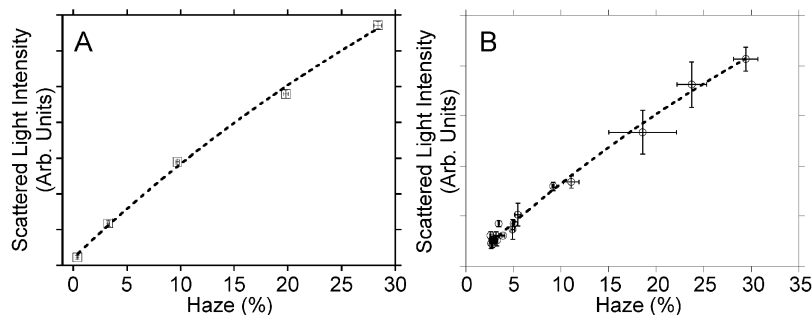
Figure 4. Validation of the high-throughput spectroscopic analysis system. (A) Correlation plot of scattered light intensity of the developed system vs haze of reference materials. Haze values were supplied with the reference materials. (B) Correlation plot of scattered light intensity of the developed system vs haze of different Taber-tested coating samples. Haze values were measured using a conventional hazemeter. Each data point is the mean of four measurements from different spatial locations on a measured sample. Error bars represent one standard deviation. Dotted lines in A and B are data fits using eq 3 with an R^2 of 0.997 and 0.995, respectively.

scale experiments. Optimization included a combination of three parameters that in concert provided the best sensitivity and precision of measurements of scattered light. The first optimization parameter was the probe angle. It was optimized with respect to the highest change in the detector response over the range of measured haze. The second optimization parameter was the distance from the probe to the coating. It was optimized with respect to the largest possible illumination spot size. This step was important to average the local heterogeneities of abraded coating surface and, thus, to improve the precision of measurements. Spatial or sample averaging is a common practice for measurements of heterogeneous solid materials to reduce the measurement errors.[36,37] Too small spot size (~1 mm over the longer direction of the illumination ellipse) resulted in a relatively insufficient averaging of the illuminated area and, thus, the relatively low measurement precision. Too large spot size (~8 mm) resulted in the large contributions from the coating edges. Thus, the compromise spot size was found to be ~4−6 mm. The third optimization parameter was the spectral acquisition conditions that provided the highest signal-to-noise in the repetitive measurements for the shortest integration time (20 ms).

Results of validation of the high-throughput spectroscopic analysis system are presented in Figure 4. Validation was performed using a set of haze standards (BYK-Gardner USA, Columbia, MD) and multiple samples of coatings flow-coated using conventional techniques on 10×10 cm polycarbonate substrates after the Taber abrasion test. These data show that the experimentally obtained relations between the scattered light intensity measured with the developed system and haze of reference materials and Taber-tested coatings are indeed described well by eq 3.

Measurement precision of the system using the reference haze samples is summarized in Table 2. With the measurement conditions used, the precision of 0.4−28.4% haze determinations was 0.1−3.1% RSD. If needed, a reduced precision at the minimum haze level can be easily improved by optimizing the measurement system for measurements of only low haze levels up to about 5% haze. Precision in measurements of Taber-tested samples was 12%

Table 2. Measurement Precision of the High-Throughput Analysis System

reference haze (%)	haze error (%)	%RSD in measured scattered light intensity
0.4	0.1	2.5
3.28	0.1	3.1
9.72	0.15	1.8
19.8	0.25	0.3
28.4	0.35	0.1

RSD. This variability agrees with previously reported within-laboratory variability of 10%. Other types of abrasion tests have comparable precision.[21]

Analysis of Constant Composition: Variable Abrasion Level Library. This library was used to determine the effects of abrasion testing conditions on the optical quality of coatings. Measurements of scattered light on the array of 3-mm abraded regions were performed with an illumination spot size of ~1.5 mm in diameter. Figure 5 demonstrates the variation of intensity of scattered light as a function of distance between the nozzle tip of the air blast abrasive sand apparatus and the coating. Multiple measurements with a 1-mm position offset of the fiber-optic probe over the abraded regions showed no significant differences in scattered light intensity, indicating an even abrasion of material at distances of 5−10 cm between the nozzle tip and the coating. As expected, decreasing the nozzle-coating distance increased the degree of abrasion as measured by the intensity of scattered light. However, under the selected abrasion conditions at short distances (<4 cm) the coating was almost completely removed, as shown by optical microscopy. This coating removal resulted in no incremental increase in the scattered light intensity when compared to coating regions abraded at larger nozzle-coating distances.

Analysis of Variable Composition: Single Abrasion Level Library. In our initial factory screening operation, we used a single abrasion level of each coating formulation with several replicates of each coating on a substrate. This approach was successfully implemented for a rough ranking of coating formulations. Results of analysis of abrasion resistance of coatings arrays using a single-level abrasion testing are presented in Figure 6. This typical data is provided from analysis of a coatings library that included eight formulations as different columns with six replicate coatings as shown in Table 1 and Figure 6A. Reproducibility of abrasion of

(36) ASTM1655-97 *ASTM E 1655-97, Standard Practices for Infrared, Multivariate, Quantitative Analysis*; ASTM: West Conshohocken, PA, 1997.
(37) Carr-Brion, K. G.; Clarke, J. R. P. *Sampling Systems for Process Analyzers*; Butterworth-Heinemann: Oxford, England, 1996.
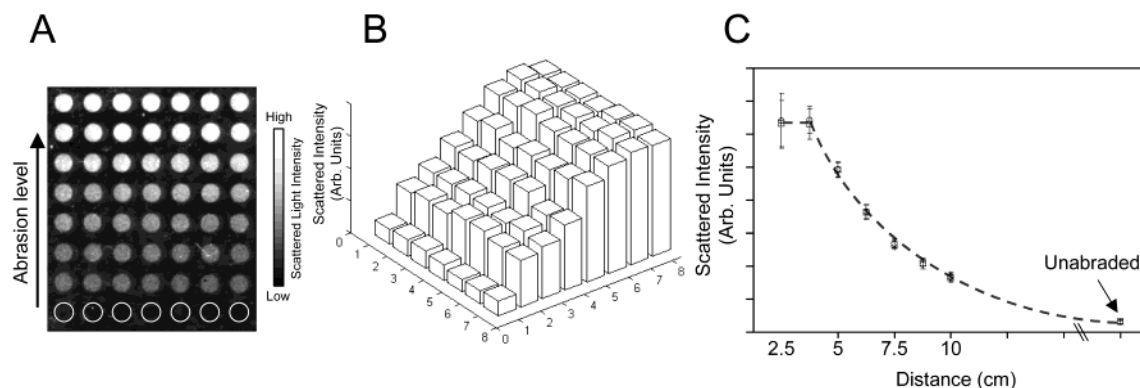
Figure 5. Analysis of abrasion resistance of a flow-coated coating using a multilevel air blast abrasion testing. (A) White light image of the array of abraded regions of coating. Each row in the image corresponds to a different degree of abrasion induced by the variation of the distance between the nozzle tip of the level air blast abrasive sand apparatus and the coating. (B) Reproducibility of abrasion of coating regions measured as the amount of scattered light. (C) Correlation between the scattered light intensity and the nozzle-coating distance. The error bars are one standard deviation from the mean of measurements of each row.
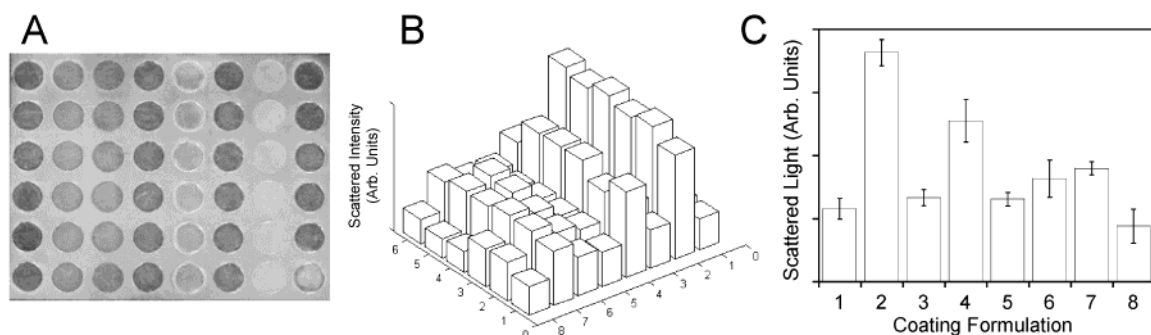

Figure 6. Analysis of abrasion resistance of coatings arrays using a single-level abrasion testing. (A) White light image of a coatings library (eight formulations as different columns with six replicate coatings) after an abrasion test. (B) Reproducibility of abrasion of coatings measured as the amount of scattered light. (C) Ranking of abrasion resistance of coatings based on a single-level abrasion testing. Coating 8 has the least abrasion-induced haze.

coatings measured as the amount of scattered light is summarized in Figure 6B. Finally, ranking of abrasion resistance of coatings based on a single-level abrasion testing is shown in Figure 6C, illustrating that coating 8 has the least abrasion-induced haze.

Analysis of Variable Composition: Variable Abrasion Level Library. For the more reliable ranking of coating performance, we implemented a new method of multilevel performance screening. Multiple levels of testing conditions when applied to combinatorial screening provide more reliable ranking of performance of combinatorial materials libraries by comparing the ranking of materials at various levels of test conditions. Further, this method provides valuable information about the minimum required test level needed for the fastest reliable screening. The advantages of the new multilevel performance screening were initially demonstrated using model coating compositions. To produce arrays for the multilevel testing, several daughter arrays were fabricated from a single mother set of coating formulations. Each daughter array was exposed to different abrasion conditions. Each array contained 4 replicates of 12 different coating formulations. The libraries of coatings were abrasion-tested at different abrasion conditions using the oscillating sand abrasion test. Different levels of abrasion were induced by performing the test for 10, 20, and 30 min. These test conditions were previously determined to be adequate for the abrasion testing.

Typical results of the multilevel performance screening experiments are presented in Figure 7 for several coatings with
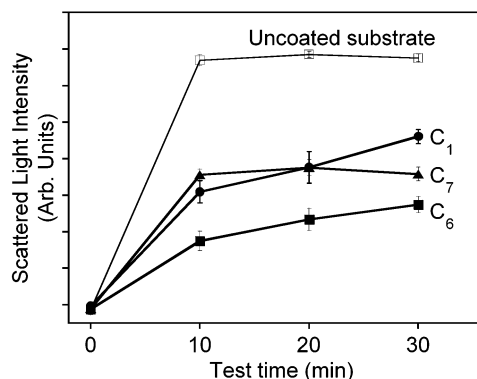

Figure 7. Analysis of abrasion resistance of coatings arrays using a multilevel abrasion testing for representative coatings C1, C6, C7, and an uncoated substrate. Error bars are 1 standard deviation ($n = 4$).

representative performance. An initial optical clarity is very similar for all coatings, as indicated by the consistent low-light scatter at zero abrasion time. Further, this Figure conclusively demonstrates several advantages of multilevel performance testing. First, it illustrates that a substrate unprotected with a coating reaches its maximum haze level upon abrasion at the lowest level (10 min), and this value stays the same under more aggressive abrasion conditions. Meanwhile, the abrasion-induced haze for coatings generally increases under more aggressive abrasion conditions. Second, the relative abrasion resistance of certain types of coatings
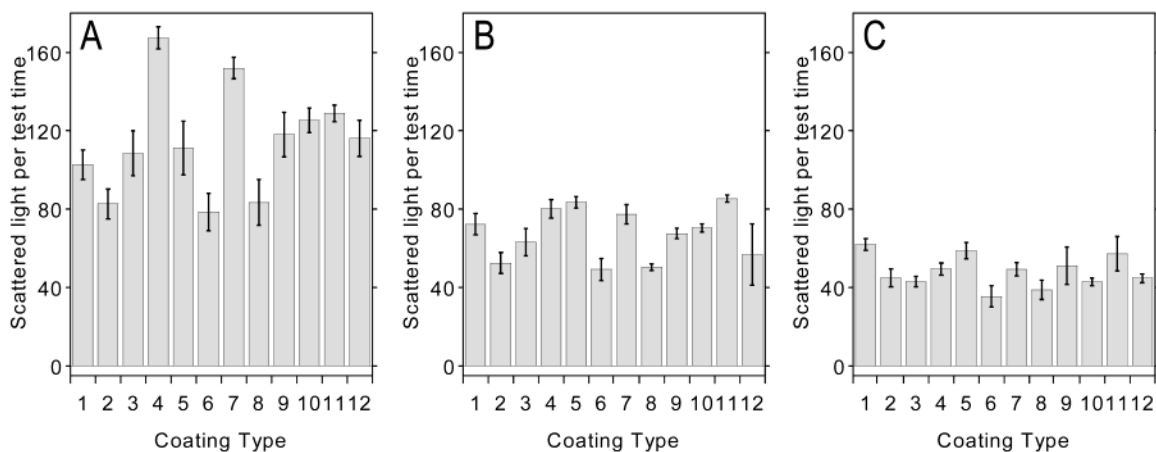
Figure 8. Ranking of 12 coating types under different abrasion conditions: (A) 10 min, (B) 20 min, (C) 30 min. Error bars are 1 SD ($n = 4$).

depends on the abrasion test conditions. This fact is illustrated by the relative change in slope of plotted responses for different coatings. Third, under the applied test conditions, the best coating (the lead) can be defined as the one which consistently has a minimal abrasion-induced scatter for all tested conditions.

Figure 8 summarizes the results of ranking of all 12 coating types under different abrasion conditions. These data were presented when the scattered light intensity was normalized by the time of the abrasion test. Such representation quantitatively captures any change in rank order of abrasion performance as a function of abrasion condition.

CONCLUSIONS

Coupling of the combinatorial chemistry methods with the industry-accepted abrasion test methods and high-throughput analysis provided a powerful set of tools for the accelerated discovery of new abrasion-resistant coating materials. Our "combinatorial factory" for coatings development is operated by two chemists and has a maximum daily throughput of 2−4 arrays of 48 coatings each.[32] Such an approach has led to an important productivity improvement of at least 10 times over a conventional coating development process, which at best has a throughput of 10 coatings/day with the same number of chemists. The key steps in the "combinatorial factory" process included experimental planning, coating preparation, application, and curing; testing against a performance parameter of interest; measurement of a resulting coating property; and data visualization.

An improvement in *measurement* throughput of the developed system over conventional strategy was more than 20 times. It was calculated by comparing the time required for manual and automated evaluation of the same number of coatings prepared using conventional and combinatorial methodologies, respectively. Evaluation of conventionally prepared coatings included manual haze measurements, recording data in a laboratory notebook, entering data into computer, and the use of available macros for data processing. Similarly, evaluation of combinatorially prepared coatings included automated scattered light measurements and the use of available macros for data processing.

A new method of multilevel performance screening implemented in this work provided more reliable ranking of performance of combinatorial materials libraries by comparing the ranking of materials at various levels of test conditions. In addition, this method provided valuable information about the minimum required test level needed for the fastest reliable screening. Several variations of this multilevel test method are possible, which can be more attractive for other applications. For example, the method can include several test levels with broad test conditions and can track a material that reaches a predetermined performance level last. Such a performance level can have any arbitrarily preset value, including a value from a reference material. Although the system described here was implemented for high-throughput screening of combinatorially developed organic protective coatings for automotive applications, it can be applied to a variety of other applications for which materials ranking can be achieved using optical spectroscopic tools.