

Application of Robotic Combinatorial Methods for the Synthesis and Screening of Hybrid Organic-Inorganic Marine Coatings

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ABSTRACT

A combinatorial robotic workflow has been developed and implemented at North Dakota State University for the synthesis and screening of marine coatings. Several traditional tools and methods for characterizing polymers and coatings have been customized for 24 to 96 well array formats. The goal of the workflow was to efficiently screen polymer and coating compositions for antifouling and/or fouling release performance in marine environments. These methods included screening for bulk mechanical properties such as glass transition temperature and modulus, surface properties such as surface energy, pseudobarnacle adhesion, bacterial biofilm growth and retention, and bacterial biofilm retraction. These combinatorial techniques were applied to the screening of several organic-inorganic coatings that possessed systematic variations in composition. The results demonstrate the utility of these methods for down-selecting promising candidates for further evaluation.

Keywords: combinatorial, high-throughput experimentation, marine coatings, fouling-release

1 INTRODUCTION

Combinatorial methods have been applied successfully to the rapid screening of new materials in several application areas including pharmaceutical discovery, catalysis, polymers, plastics, and coatings [1-10].

Coating formulation chemistry is one area that is ideally suited for combinatorial methods due to the inherent complexity of coating systems. When one considers the large number of variables, both compositional and process, involved in a typical formulation, the number of independent combinations can easily exceed 100+ experiments. With automated techniques it becomes reasonable to screen several hundred compositions in relatively short period of time.

Due to environmental pressures, one area of coating technology that has seen a resurgence of activity is the development of non-toxic fouling-release marine coatings. Prior to the development of fouling-release coatings, marine biofouling, the settlement and colonization of marine structures by bacteria, plants and animals, was

primarily controlled by the use of anti-fouling coatings containing tributyl tin or copper oxide. These coatings work on the principle of releasing toxic metals from an ablative matrix thereby deterring marine organisms from colonizing submerged portions of ship hulls [11].

The combinatorial tools at North Dakota State University have been customized around screening marine coatings for both anti-fouling and fouling-release performance. The authors have previously reported several process capability studies correlating high-throughput measurements to ocean site test data on model polysiloxane fouling-release coatings [12-13]. Additionally, Webster et al, have reported the synthesis, screening and down-selecting of several hybrid siloxane-urethane coatings for field testing using the combinatorial workflow [14-15].

The objective of this study was to further demonstrate the capabilities of using a suite of high-throughput combinatorial measurements to differentiate and down-select promising candidates for further evaluation and ocean site testing. The synthesis, formulation, and screening of a set of siloxane coatings functionalized with an organic biocide and crosslinked with isocyanates are discussed.

2 EXPERIMENTAL

2.1 Reagents

2,4,4'-trichloro-2'-hydroxydiphenyl ether (triclosan) was obtained from Alfa-Aesar. 4-methyl-2-pentanone (MIBK), 1,4-diazabicyclo[2.2.2]octane (DABCO), potassium hydroxide, acetic acid, toluene, anhydrous magnesium sulfate, and epichlorohydrin were obtained from Sigma-Aldrich. Carbinol terminated polydimethylsiloxane, 600-850 Mn (DMS-C16) and N-ethylaminoisobutyl terminated polydimethylsiloxane, 800-1000 Mn (DMS-A211) were obtained from Gelest Inc. Tolonate® HDT 90B, aliphatic polyisocyanate trimer solution 90% in butyl acetate (triisocyanate), was obtained from Rhodia. Desmodur W, bis(4-isocyanatocyclohexyl)methane (diisocyanate), was obtained from Bayer MaterialsScience. All reagents were used as received.

2.2 Experimental Design

Experimental design for the formulation of the siloxane-urethane coatings was prepared using Design-Expert, Stat Ease, Inc and Symyx Library Studio, Symyx Technologies, Inc. A representation of the design can be seen in Figure 1.

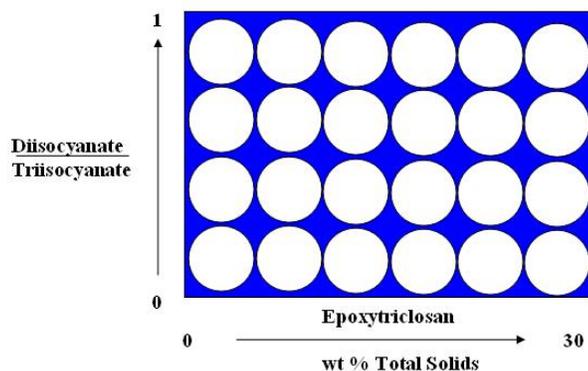


Figure 1: Array representation of the formulations

2.3 Synthesis of Epoxytriclosan

Triclosan (0.347 mols), epichlorohydrin (1.036 mols), and potassium hydroxide (0.345 mols) were added to a solution of toluene. Solution was refluxed overnight. The product was purified by hexane:water:acetic acid extractions and triply washed with distilled water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed by a rotary evaporator. Purity was determined to be 94 % by HPLC.

2.4 Synthesis of Epoxytriclosan Terminated Siloxanes

A mixture of epoxytriclosan and DMS-A211 were combined in a round bottom flask containing toluene. A slight molar excess of secondary amino-terminated siloxane was used to ring-open the epoxytriclosan. The solution was refluxed for 24 hours and reaction completion was verified by H^1 -NMR. Toluene was removed with a rotary evaporator under vacuum.

2.5 Coating Formulations

The coating formulations were prepared with a Symyx Formulation System [16]. All base resins were diluted 50 wt. % in MIBK prior to use. A working catalyst solution of DABCO in MIBK was prepared at 125 mg/mL. The epoxytriclosan concentration was varied from 0 to 30 wt. % based on total solids. The use of triclosan tethered to a hydrolytically stable siloxane matrix has been demonstrated

to significantly affect biofilm growth and retention and reduced biofouling in ocean field trials [17-18]. The coatings were crosslinked with isocyanates to help improve the durability of the coatings since conventional unfilled siloxanes suffer from poor mechanical durability. The diisocyanate to triisocyanate ratio was varied from 0 to 1 in order to have systematic variation of relative crosslink density. A hydroxyl terminated siloxane (DMS-C16) was added to dilute the epoxytriclosan terminated siloxanes in order to control overall epoxytriclosan concentration. The isocyanate to hydroxyl ratio was fixed at 1.1:1.0. The catalyst was also fixed at 0.5 wt. % of the total solids.

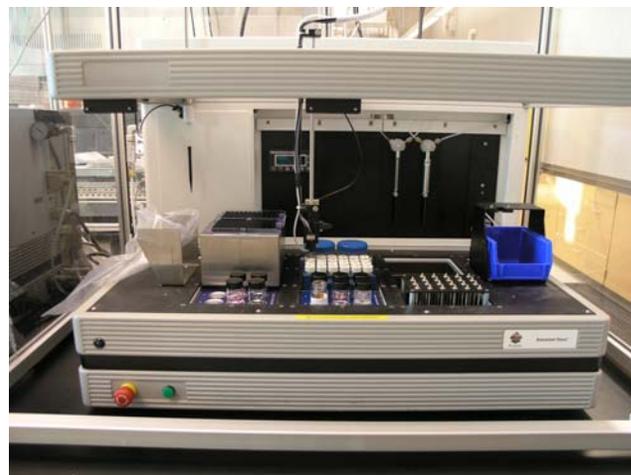


Figure 2: Symyx Formulation Station

2.6 Coating Application

In order to test the coatings for physical properties and against biological organisms, three coating array formats were utilized. Coatings were prepared for pseudobarnacle adhesion and surface energy tests using the Symyx Coating Application Station [16]. For parallel DMTA tests, the 24 coatings were deposited in replicates of four onto a 96-well Symyx parallel DMTA plate using the Symyx parallel DMTA deposition station [19]. Coatings for biological tests were deposited into a 24-well modified tissue culture plate using a Tecan EVO 200 multichannel liquid handling robot. All samples were allowed to air dry overnight followed by a 50°C oven cure for several hours and 80°C cure cycle for 1 hour.

2.7 Surface Energy and Dynamic Contact Angle Analysis

Coating array patches on two 4" x 8" aluminum panels were analyzed on the Symyx Surface Energy Station. For surface energy experiments, three water and diiodomethane droplets were imaged and contact angles were calculated.

The surface energy was calculated using the Owens-Wendt method [16].

For dynamic contact angle experiments, a fine capillary polyimide tip was used to continuously pump and expand a water droplet on the coating surface over a period of 60 seconds. This was followed immediately by aspirating the same dispensed volume over another 60 second period. Advancing contact angles were calculated from the first period and receding angles were calculated from the last period. The difference between the advancing and receding angle was calculated and reported as contact angle hysteresis.

2.8 Pseudobarnacle Adhesion

Three pseudobarnacle aluminum studs were adhered to each of the coating array patches using a 100 μm layer of Loctite[®] 1C-LV Hysol[®] epoxy adhesive. The maximum force (N) to remove each pseudobarnacle was captured automatically by the Symyx automated pull-off adhesion station [20].

2.9 Parallel Dynamic Mechanical Thermal Analysis (pDMTA)

The storage moduli and glass transition temperatures of all 24-coatings were measured using the Symyx Parallel DMTA System [19]. Modulus was measured from a temperature range of -100°C to 100°C at a rate of $1^{\circ}\text{C}/\text{min}$ and at a frequency of 10 Hz. Modulus (MPa) at 25°C was reported. The glass transition temperature (Tg) was reported in $^{\circ}\text{C}$.

2.10 *Cytophaga lytica* Biofilm Retraction

C. lytica, a marine bacterium, was cultured on each of the test coatings. Biofilm growth and retraction on the coating surfaces was determined and reported according to a previously published method [21].

2.11 *Halomonas pacifica* Biofilm Adhesion

H. pacifica, also a marine bacterium, was cultured on each of the coating surfaces. A 30 psi water jet was applied to each sample using an automated water jet apparatus for a duration of 5 seconds. Biofilm growth and percent removal was calculated and reported [22].

2.12 Algal Adhesion

Navicula incerta, a marine diatom, was inoculated and cultured on the coating surfaces. A 10 psi water jet was applied to the biofilms for a period of 10 seconds. Biofilm growth and percent removal were calculated and reported according to a previously published method [23].

2.13 Atomic Force Microscopy

Atomic force microscopy (AFM) analysis was conducted using a Dimension 3100[®] microscope with Nanoscope IIIa controller. Silicon probes with a spring constant of 0.1-0.4 N/m and resonant frequency 17-24 kHz were used in tapping mode in air at ambient conditions.

3 RESULTS AND DISCUSSION

The experiment was designed to evaluate biocide modified siloxane-urethane coatings with a suite of high-throughput combinatorial measurement tools. Out of the five physical property measurements conducted on these coatings, two measurements, modulus at 25°C and Tg, provided useful structure-property relationships, Figures 3 and 4.

Analysis of modulus at 25°C revealed that this property was dominated by the overall wt. percent of tethered epoxytriclosan in the coating. An increase in tethered epoxytriclosan resulted in a corresponding increase in room temperature modulus.

The glass transition temperature was also found to be function of primarily tethered epoxytriclosan concentration and diisocyanate to triisocyanate ratio. By increasing the tethered epoxytriclosan concentration the coatings had a corresponding increase in Tg. As the amount of diisocyanate increased the Tg decreased. Although there were differences detected between coatings with the other physical property tests, surface energy, contact angle hysteresis, and pseudobarnacle release force, they were unable to identify any significant compositional factors.

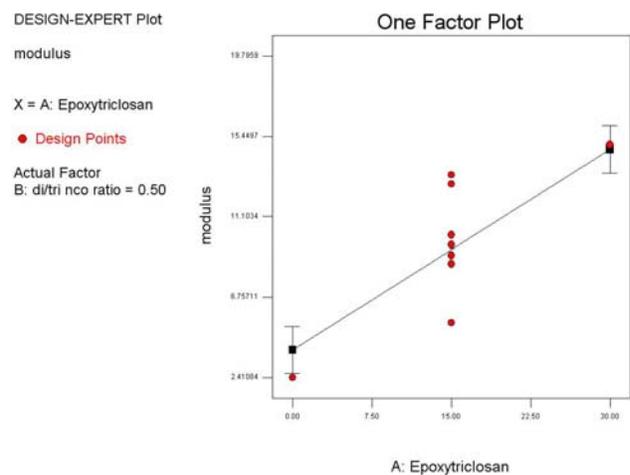


Figure 3: Modulus as a function of epoxytriclosan amount

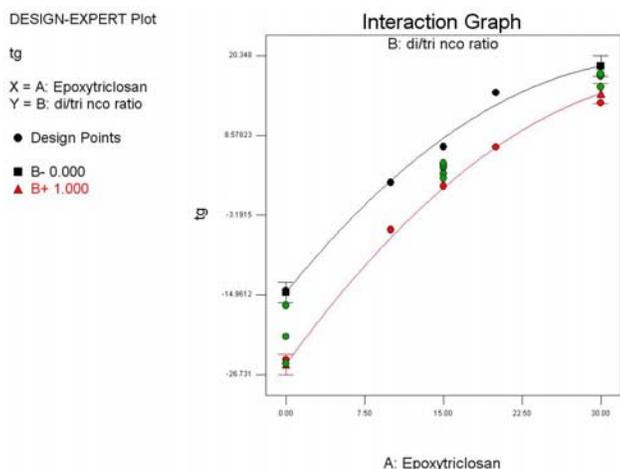


Figure 4: Tg as a function of epoxytriclosan amount and di to tri-isocyanate ratio

Epoxytriclosan was included in the design to ascertain any antifouling properties these coatings might possess. For the three organisms tested, the results indicated that the biofilm growth was comparable to a non-biocidal control coating. For fouling-release performance, epoxytriclosan level was found to significantly affect *H. pacifica* biofilm percent removal. Decreasing the epoxytriclosan level resulted in an increase *H. pacifica* removal. However, the correlation coefficient for this factor was relatively low.

To better understand other confounding compositional factors that may be contributing to these results, the overall amount of polydimethylsiloxane was calculated for each coating. It was determined that as the epoxytriclosan level increased, the overall level of siloxane in the coating decreased. When overall amount of siloxane is compared to Tg, and *H. pacifica* percent removal, there is a reasonable correlation. In the case of percent siloxane versus Tg the correlation value is high at -0.906 indicating that percent siloxane may be more significant to Tg than epoxytriclosan level. The same holds true for *H. pacifica* percent removal. Percent siloxane versus *H. pacifica* percent removal had a correlation value of 0.726 whereas epoxytriclosan was -0.695. Additionally, samples that had the highest percent removal for *H. pacifica* had no epoxytriclosan and had the highest levels of siloxane.

Conventional polydimethylsiloxanes crosslinked with alkoxy silanes and with oil additives have been shown to have reasonable fouling-release performance against a diversity of marine organisms [13]. However, *H. pacifica* typically releases better from polyurethane systems than polydimethylsiloxanes in previous water jetting experiments [22].

To better understand these effects, the surface physical properties were further investigated. Although there was a variation in the siloxane content of the coatings, surface energy results indicated that the surfaces were in the appropriate range of polydimethylsiloxane systems [11].

Furthermore, contact angle hysteresis experiments showed very similar performance of the coatings indicating that the surface compositions were relatively stable under exposure to water. Since surface composition of all the coatings appeared very similar, surface morphology was evaluated on a subset of the coatings using AFM in order to better understand the structure-property relationships. From this analysis, average surface roughness by AFM was found to be proportional to the diisocyanate to triisocyanate ratio. By increasing the concentration of diisocyanate, the average surface roughness increased.

4 CONCLUSIONS

A series of siloxane-urethane hybrid organic-inorganic coatings were synthesized, formulated, and tested with a suite of combinatorial high-throughput measurement tools. The evaluation of the data determined three assays were able to provide useful structure-property relationships on these classes of materials. An optimal region for *H. pacifica* biofilm percent removal was identified for future analysis and testing.

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