Combinatorial and High-Throughput Screening of the Effect of Siloxane Composition on the Surface Properties of Crosslinked Siloxane−Polyurethane Coatings

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Libraries of siloxane−polyurethane coatings were designed, formulated, and screened using high-throughput experimentation. Four independent variables that were analyzed were the molecular weight of poly(dimethylsiloxane) (PDMS), presence or absence of poly(ϵ-caprolactone) (PCL) blocks attached to the PDMS backbone, the length of the PCL blocks, and the siloxane polymer level in the coating formulations. In addition to the siloxane libraries (3-aminopropyl-terminated PDMS and poly(ϵ-caprolactone)-poly(dimethylsiloxane)-poly(ϵ-caprolactone) (PCL-PDMS-PCL) triblock copolymers), the coating formulation included a trifunctional isocyanate crosslinker, trifunctional poly(ϵ-caprolactone) polyol, 2,4-pentanedione (pot-life extender), dibutyltin diacetate (catalyst), and a blend of solvents. The resulting coatings were analyzed for their surface energy and pseudobarnacle adhesion both before and after aging the coatings for 30 days in water. The water and methylene iodide contact angle averages increase with increasing molecular weight of PDMS. Coatings prepared from PCL−PDMS−PCL triblock copolymers have lower surface energies than coatings prepared from 3-aminopropyl-terminated PDMS; however, lower pseudobarnacle adhesion results were obtained for the coatings prepared from 3-aminopropyl-terminated PDMS than coatings prepared from PCL−PDMS-PCL triblock copolymers. The siloxane polymer level in the coating formulations does not have a significant effect on the surface energy of the coatings, but it resulted in higher pseudobarnacle adhesion.

1. Introduction

Fouling of ships by marine organisms (e.g., barnacles, tubeworms, bacteria, algae) is an ancient problem which continues to trouble us today and has serious consequences on ship performance and mission capability. Because of biological fouling, extensive maintenance of ships becomes necessary and increases the cost of operation. Fouling reduces ship speed, maneuverability, and range, which impedes mission performance. Several solutions have been sought including the use of toxic paints, and these have been successfully used to minimize fouling. However, the use of toxic paints (e.g., containing organo-tin compounds) can harm nontargeted sea-life. The International Maritime Organization has proposed a ban on the new application of toxic paints starting in 2003 and complete removal from all ships by 2008. Excellent reviews of this issue can be found in the literature.[1−4]

Fouling-release coatings appear to be a promising nontoxic alternative to coatings containing biocides or toxic compounds. These coatings do not necessarily prevent the settlement of marine organisms but permit their easy removal via the application of shear to the surface. The ideal case is thought to be where the velocity of the ship creates sufficient shear to remove the foulants. It has been shown that coatings with a low modulus and low surface energy can provide easy removal of marine organisms from the surface. Poly(dimethylsiloxane) (PDMS) has a low modulus and low surface energy, and crosslinked PDMS elastomers are a leading candidate for nontoxic fouling-release coatings. A key disadvantage of silicones is their poor adhesion and poor durability.[5−9] Siloxane−polyurethane systems may be a good alternative approach to nontoxic fouling-release coatings. Previous studies on non-crosslinked siloxane−polyurethane systems demonstrated good initial properties; however, their performance deteriorated rapidly because of the rearrangement of the initially hydrophobic polymer into a hydrophilic polymer after water immersion.[10−12]

To overcome the previous consequences of siloxane−polyurethane systems, a self-stratified, *crosslinked* siloxane−polyurethane system as illustrated in Figure 1 is being explored.[13] Self-stratified coatings are coatings that are applied in a single step and then via various driving forces (degree of incompatibility, glass transition temperature, molecular weight, type of solvent, surface energy, etc.) separate into more than one phase having different functions within the coating.[14−18] A key driving force in a siloxane−polyurethane self-stratifying coating system will be the low surface energy of the siloxane. Thus, a siloxane−polyurethane self-stratified coating system will provide a low surface energy, low-modulus PDMS top layer, and a tough,

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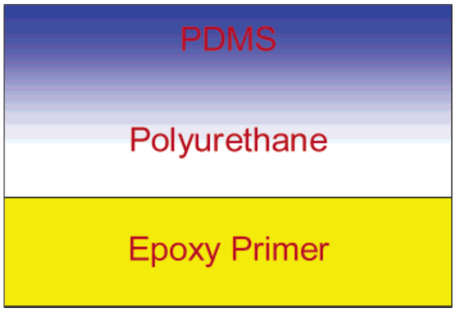

Figure 1. Cross-section representation of self-stratified siloxane−polyurethane coating.

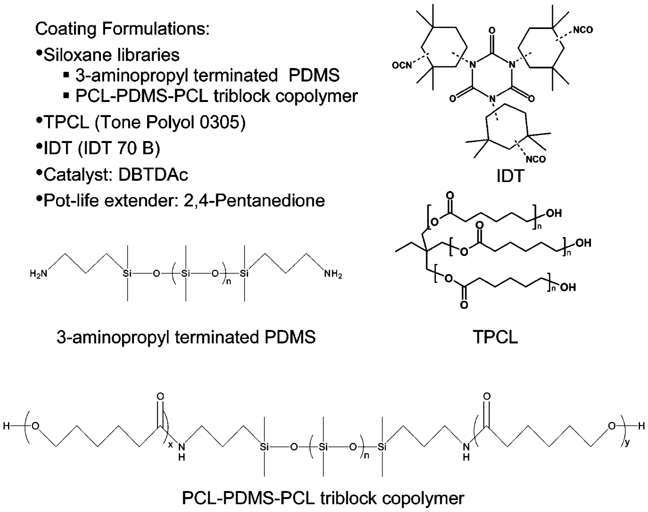

Figure 2. Siloxane−polyurethane coating formulation components.

durable lower layer. Another advantage of the polyurethane underlayer is that the isocyanate groups may react with the hydroxyl groups from the epoxy primer resulting in good adhesion to the primer. In addition, crosslinking is intended to provide stability to the coating, locking the stratified morphology in place, resulting in the prevention of rearrangement of the hydrophobic polymer into a hydrophilic polymer after water immersion.

The use of combinatorial and high-throughput experimentation (CHTE) in polymer and coatings science is rapidly growing.[19−31] Coating formulations typically have a large number of different ingredients such as polymer, solvent, crosslinker, catalyst, etc. Optimization of all the ingredients in terms of final coating properties requires a significant amount of time and effort. Therefore, the application of CHTE to the development of new coating systems is essential. The use of CHTE is being applied to polymers and coatings science. Several studies have been reported regarding experiment design, polymer synthesis, and coating formulation using combinatorial methods and high-throughput instruments.[32−34]

The prototype siloxane−polyurethane coating system is composed of an organofunctional siloxane polymer, an organic polyol, a multifunctional isocyanate, curing catalyst, pot life extender, and solvents as seen in Figure 2. It is not known what polymer composition or combination of formulation ingredients will result in a coating having the optimum morphology or what morphology will yield the best properties. It is expected that both the compositional variables (siloxane, polyol, isocyanate) and formulation variables (solvent, catalyst, etc.) will all play a role. In this study, the effect of four parameters related to the siloxane component of the binder system on the properties of siloxane−polyurethane coatings is explored using combinatorial and high-throughput experimentation. The variables explored are (1) the PDMS molecular weight, (2) the addition of poly(ϵ-caprolactone) (PCL) blocks to the PDMS backbone, (3) the length of PCL blocks, and (4) the amount of siloxane polymer in the coating formulation. The coatings are screened for their surface energy via contact angle measurements, pseudobarnacle adhesion, and stability upon water immersion.

2. Experimental

2.1. Reagents. 2,4-Pentanedione, ethyl 3-ethoxypropionate (EEP), dibutyltin diacetate (DBTDAc), HPLC grade water, and methylene iodide (MI) were purchased from Aldrich. TPCL (Tone Polyol 0305) was received from Dow Chemical. IDT (Tolonate IDT 70B, 70% in butyl acetate) isocyanate was received from Rhodia. IDT is a triisocyanurate resin of isophorone diisocyanate. Polyurethane grade methyl *n*-amyl ketone (MAK) was received from Eastman. Toluene was received from VWR International. All materials were used as received without further purification.

2.1.1 Combinatorial Synthesis of 3-Aminopropyl-Terminated PDMS and Poly(ϵ-caprolactone)-poly(dimethylsiloxane)-poly(ϵ-caprolactone) (PCL−PDMS−PCL) Triblock Copolymers. Libraries of 3-aminopropyl-terminated PDMS and PCL−PDMS−PCL triblock copolymers were prepared according to the procedure described by us previously.[19] Two combinatorial libraries were prepared as shown in Figure 3. Briefly, the synthesis was carried out in two steps using an automated batch synthesis system. In the first step, 3-aminopropyl-terminated PDMS of varying molecular weight was synthesized through the base-catalyzed ring-opening equilibration polymerization of bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) with octamethylcyclotetrasiloxane (D_4). Benzyltrimethylammonium hydroxide was used as the catalyst, and the reaction was carried out at 80 °C. The ratio of D_4 to the disiloxane determines the final molecular weight of the PDMS. To synthesize the triblock copolymers, ϵ-caprolactone monomer was reacted with the 3-aminopropyl-terminated PDMS polymers (rows B, C, and D) (catalyst was tin(II)-2-ethyl hexanoate), thus forming the PCL−PDMS−PCL triblock copolymers. The polymers were used in the coating formulations without further purification.

2.2. Experiment Design. Symyx Library Studio software was used to design polymer and coating formulation libraries. The software allows for both full factorial and statistical experimental designs, and these designs are stored in a common database. A 3D visualization of the experiment design is seen in Figure 4.

2.3. Coating Formulation. The preparation of the coating formulations was done using a Symyx Coating Formulation System according to Library Studio designs. The dispensing of the coating ingredients such as the polymer library, crosslinker, solvent, catalyst, pot-life extender, and other

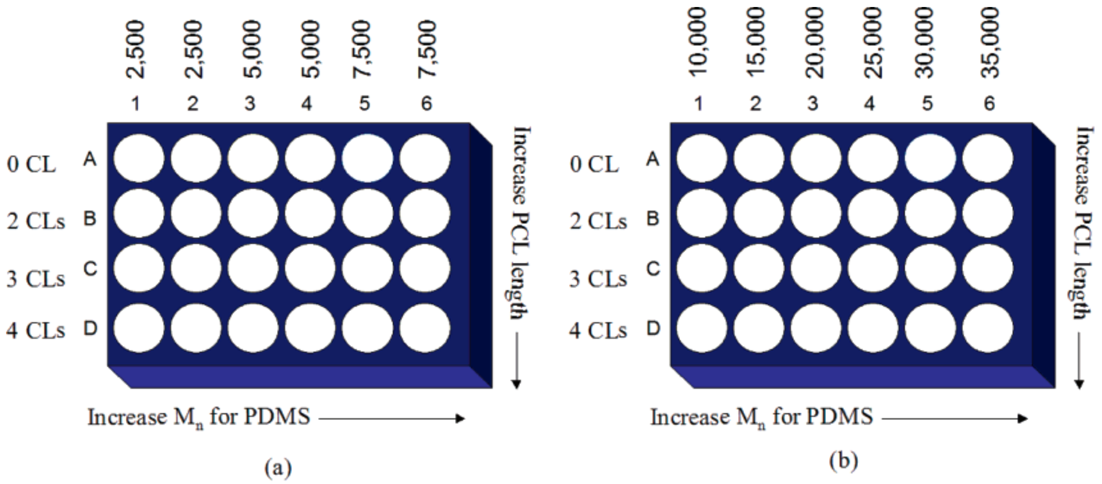

Figure 3. Library designs for siloxane synthesis experiments: (a) low molecular-weight siloxane library (LMS) and (b) high molecular-weight siloxane library (HMS).

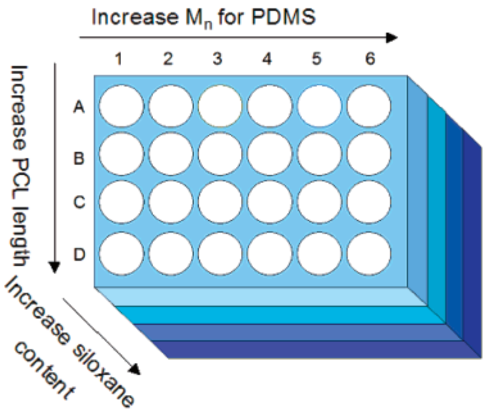

Figure 4. Library design of coating formulations in 3D visualization.

additives is done using disposable pipettes to avoid cross-contamination, and mixing is accomplished with magnetic stirring. Coating formulations in this study are composed of the siloxane libraries (3-aminopropyl-terminated PDMS and PCL−PDMS−PCL triblock copolymers), IDT, TPCL, 2,4-pentanedione, and DBTDAc, as shown in Figure 2. Stock solutions of 30% siloxane library in EEP, 90% TPCL in MAK, and 1% DBTDAc in MAK were prepared to form easily dispensed mixtures. The ratio of isocyanate to other functional groups (amine or hydroxyl) was kept at 1.1:1.0. The amount of catalyst DBTDAc was 0.075% on solids, and the amount of 2,4-pentanedione was 10% on solids for all coating formulations. First, stock solutions of the siloxane library, TPCL, and 2,4-pentanedione (nonreactive components) were placed into the reagent holders of the formulation system and dispensed with the liquid handling robot into a 6 × 4 array of 8 mL vials. Coating formulations were prepared by adding 10, 20, 30, and 40% by weight siloxane polymers into the formulations as seen in Figure 5 (the ultimate design library for coating formulations is seen in 3D in Figure 4). After completion of the dispensing of the nonreactive components, the vials were capped, and the mixtures were mixed with magnetic stirring overnight. The next day, the DBTDAc solution and IDT were dispensed into the vials using the robotic pipet. After completion of the dispensing of the reactive components, the vials were capped again, and the solutions were mixed with magnetic stirring until sufficient viscosity was achieved for coating application.

2.4. Coating Deposition. Coating deposition was done using a Symyx Coating Application System. The coating deposition system is used to deposit coating samples on standard 4 × 8 in. substrates in an array format. The 24 elements in the 6 × 4 formulation are applied in array format to a pair of 4 × 8 in. panels, as shown in Figure 6 using a liquid dispensing pipet and drawn down using an adjustable doctor blade. Coating formulations were placed into the holders of coating application system and aluminum test panels (4 × 8 in. Q-panel, 0.6 mm thickness, type A = alloy 3003 H14) were placed onto the holders of application station. Vacuum was applied to prevent movement of the panels during the coating application with the robotic doctor blade. The 6 × 4 formulation library was deposited onto 2 aluminum panels in an array format (Figure 6); 80 μL aliquots of the coating formulations were deposited on the substrate using a new disposable pipet for each sample to prevent cross-contamination. Doctor blade gap thickness was set to 200 μm. After each application, the automated doctor blade was washed with toluene using sonication 3 times and dried with blowing air. After completion of the application of all the coatings, the panels were removed from the coating-application station, placed in a dust-free environment, and left for overnight curing at ambient temperature. The next day, the panels were placed into an oven for complete curing for 45 min at 80 °C.

2.5. Coating Characterization. 2.5.1. Surface Energy. Surface-energy measurements were done using a Symyx Coating Surface Energy System. The surface-energy system measures and averages contact angles of various liquids and calculates the surface energy. The system receives two 4 × 8 in. coating array panels. The images of three droplets of each test liquid are taken by a CCD camera, and the contact angles are determined using automated image analysis. Water and methylene iodide (MI) are used as test liquids, and the surface energies are calculated using the Owens−Wendt method.[35]

2.5.2. Pseudobarnacle Adhesion. Pseudobarnacle adhesion measurements were done using a Symyx Automated

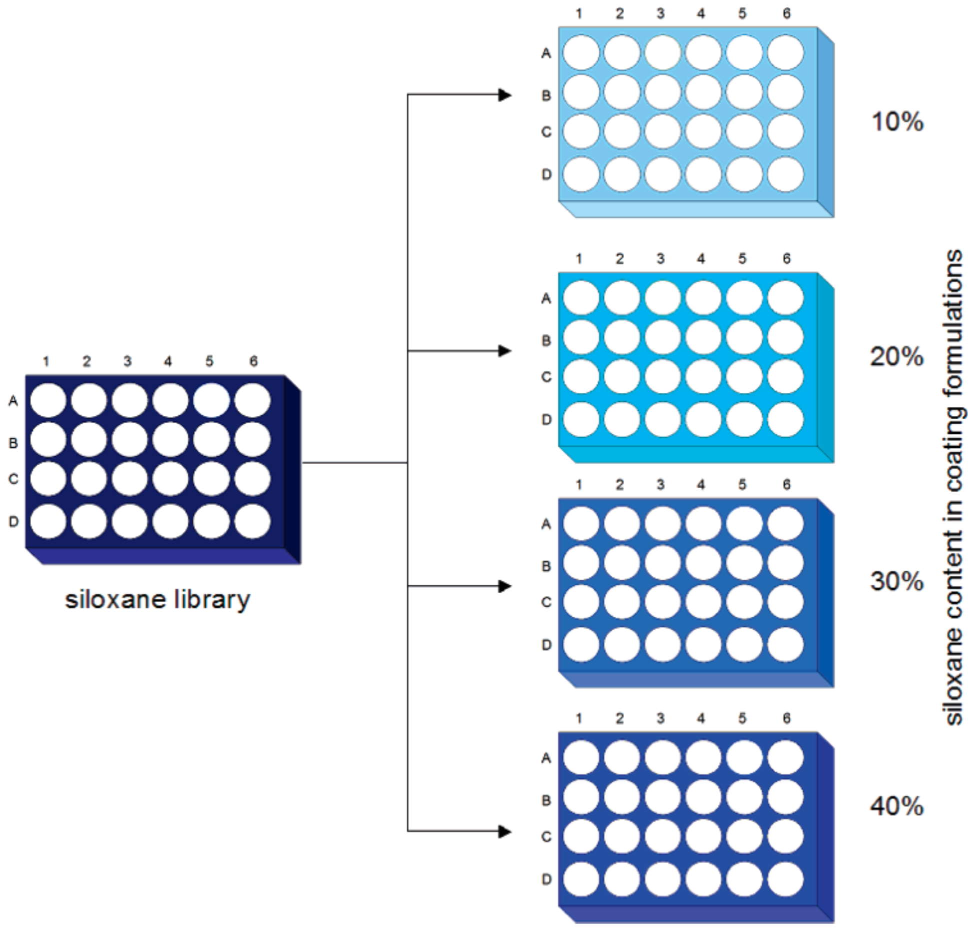

Figure 5. Formulation of siloxane−polyurethane coatings from the siloxane libraries synthesized.

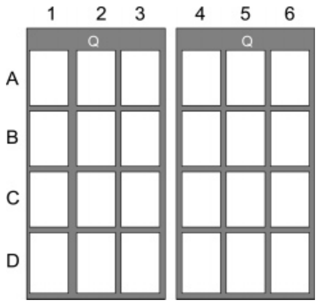

Figure 6. Coating deposition of 6 × 4 library on two 4 × 8 in. Q-panels in an array format.

Pull-Off Adhesion System. The adhesion system can be used to either determine the adhesive strength of a coating on the substrate or the adhesive strength of an epoxy to the coating surface (pseudobarnacle). The instrument can receive two 4 × 8 in. coating array panels. First, the two array panels were placed onto the holders of coating adhesive application system by applying a vacuum underneath the coatings. Then, a plastic template was placed on top of the coatings using pins on the substrate holder for alignment. The plastic sheets have three 7 mm diameter holes over each coating on the array panel. Then Loctite Hysol Epoxy 1C-LV glue was spread on the coatings through the custom-made plastic sheets, resulting in the placement of three 7-mm spots of adhesive on each coating. The plastic sheet was removed and the panels were removed from the adhesion preparation station and placed into clamping jigs. After the panels were clamped, three aluminum studs per coating sample were placed into the clamping jig on top of the applied glue. Weighted foam blocks were placed on top of the studs and the epoxy glue was cured overnight. The next day, the clamped panels with the holders still attached to them were placed into the holders of the automated adhesion system. A pull-off head removes each test stud and the maximum force at failure is recorded. The three values are then averaged.

2.5.3. Water Aging. The coatings were aged in a recirculating dionized water bath. Clean water is maintained by using a UV sterilizer, submicrometer filter, and an activated charcoal filter.

2.6. Data Analysis. Data analysis was done using Spotfire 8.0 analysis software.

3. Results and Discussion

The objectives of this study were to explore variables related to the siloxane component of the siloxane−polyurethane coating system, to determine which variables are significant, and to identify those coating compositions that have interesting performance properties. Since the effect of these molecular parameters on the performance properties of the siloxane−polyurethane coating system is not known, this broad combinatorial screening will be used initially to identify coatings which have promising properties, and then subsequent experimentation will be carried out to understand the causes of the performance properties at a more detailed level.

A previous study of a self-stratified siloxane−polyurethane coating system helped identify the catalyst and solvent

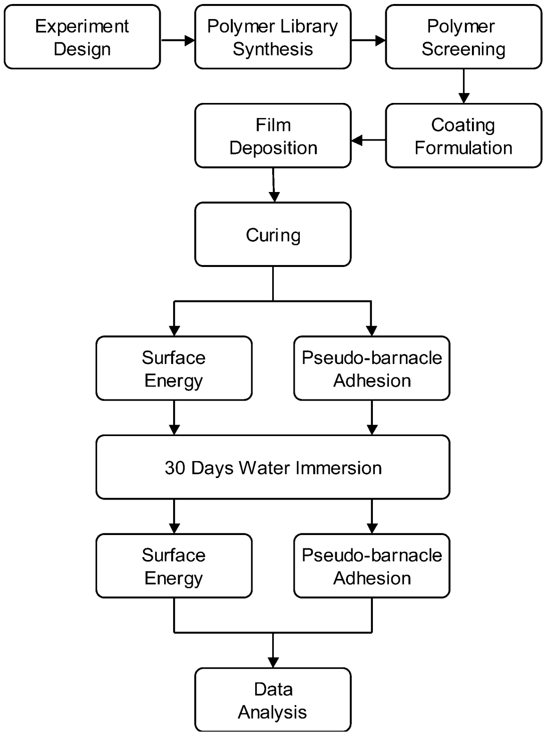

Figure 7. Combinatorial workflow for screening of self-stratified coatings.

composition used in this study.[13] Since PDMS is known to be immiscible with other polymers because of its low surface energy and low solubility parameter, it is important that the PDMS be chemically bound to the polyurethane network. Thus, 3-aminopropyl-terminated PDMS was selected because the amine group will react rapidly with the isocyanate crosslinker. Block copolymers with PCL were also explored to improve the compatibility of the PDMS polymer with the polyurethane coating formulation prior to crosslinking. Since a trifunctional PCL polyol is used in the polyurethane coating formulation, the addition of PCL blocks to the PDMS polymer should improve its compatibility with the coating formulation, ensuring that the PDMS is well anchored into the polyurethane coating network.

The workflow used in this study is shown in Figure 7. The workflow starts from experimental design, and the designs were done using Library Studio software. Coating formulation libraries were prepared following the polymer synthesis and characterization steps. After coating formulation preparation, the coatings were deposited on the test substrates and cured. The final coatings were analyzed both initially and after 30 days of water immersion to check the stability of the coatings, as well as to determine any property changes that occur after water immersion. After all of the data were gathered, the data were analyzed to identify key trends and identify leads for further experimentation.

The PDMS polymer libraries were designed to explore PDMS molecular weight, addition of PCL blocks to PDMS backbone resulting in PCL−PDMS−PCL triblock copolymers, and the PCL block length in PCL−PDMS−PCL triblock copolymers as shown in Figure 3. The molecular weight of PDMS (or PDMS block length) increases column-wise and ranges from 2500 to 35 000 g/mol. Row A consists of 3-aminopropyl-terminated PDMS, and rows B, C, and D consist of PCL−PDMS−PCL triblock copolymers. The length of the PCL blocks increases row-wise. The lengths of PCL blocks are 2, 3, and 4 ϵ-CLs for rows B, C, and D, respectively. The synthesis experiments resulted in 48 functional siloxane oligomers. Details of the synthesis and characterization of these oligomers was reported by us previously.[19]

In this initial screening study, the PCL block length was limited to a maximum of four ϵ-CL units so that the resulting block copolymers would be amorphous at room temperature. Even though the PCL block length is relatively short, for some of the compositions at lower PDMS molecular weight, it is significant. For example, for a PDMS target M_n of 2500 and PCL block lengths of 2, 3, and 4 units, PCL content is 15, 22, and 27% of the total composition. Even though the contribution of the PCL blocks, as a fraction of the overall block copolymer composition, decreases as the molecular weight of the PDMS increases, we explored this range of PCL block lengths throughout the experiment since the main purpose of the PCL blocks is to anchor the PDMS endgroups in the polyurethane matrix. Our previous study also indicated that all PDMS end-groups had initiated ϵ-CL polymerization even at these low PCL levels.[19]

The composition of the coating formulations is summarized in Figure 2. Coating formulations were composed of the siloxane libraries, TPCL, IDT, 2,4-pentanedione, and DBTDAc. (While we used an organo-tin compound as a catalyst for urethane formation, the level of tin catalyst used here (0.075%) is much less than that used in tin-based marine antifouling coatings.)[36] The polymers from the siloxane libraries were incorporated into the siloxane−polyurethane coatings at four different levels, 10, 20, 30, and 40% by weight, as shown in Figure 5. For example, polymer A5 in Figure 3a is composed of 3-aminopropyl-terminated PDMS with a target molecular weight of 7500 g/mol and no ϵ-CL linked to PDMS. Polymer A5 was used to prepare four coating formulations at 10, 20, 30, and 40 wt %, and the balance of the coating formulation is composed of TPCL and IDT. Similarly, polymer D2 in Figure 3b is composed of a PCL−PDMS−PCL triblock copolymer with a PDMS target molecular weight of 15 000 g/mol and a PCL block length of 4 ϵ-CLs per amine. Polymer D2 was also incorporated into the coating formulations at 10, 20, 30, and 40% by weight. Since all 6 × 4 coating formulation libraries followed the same array format as the synthesis library array format (6 × 4 arrays), 192 coatings were formulated from the 48 siloxane oligomers that were synthesized. Thus, the effects of four variables, PDMS molecular weight, addition of PCL blocks to PDMS backbone, PCL block length, and siloxane polymer level, on the properties of the siloxane−polyurethane coatings were explored in this combinatorial experiment.

Since the coatings that were formulated are intended to be used for underwater marine applications, the coatings were analyzed both initially and after 30 days of water immersion to check their stability after water immersion. For surface-energy analysis, water and MI were used as test liquids, and the average of 3 droplets were done per each test liquid. Therefore, for 192 coatings, 1152 individual contact angle

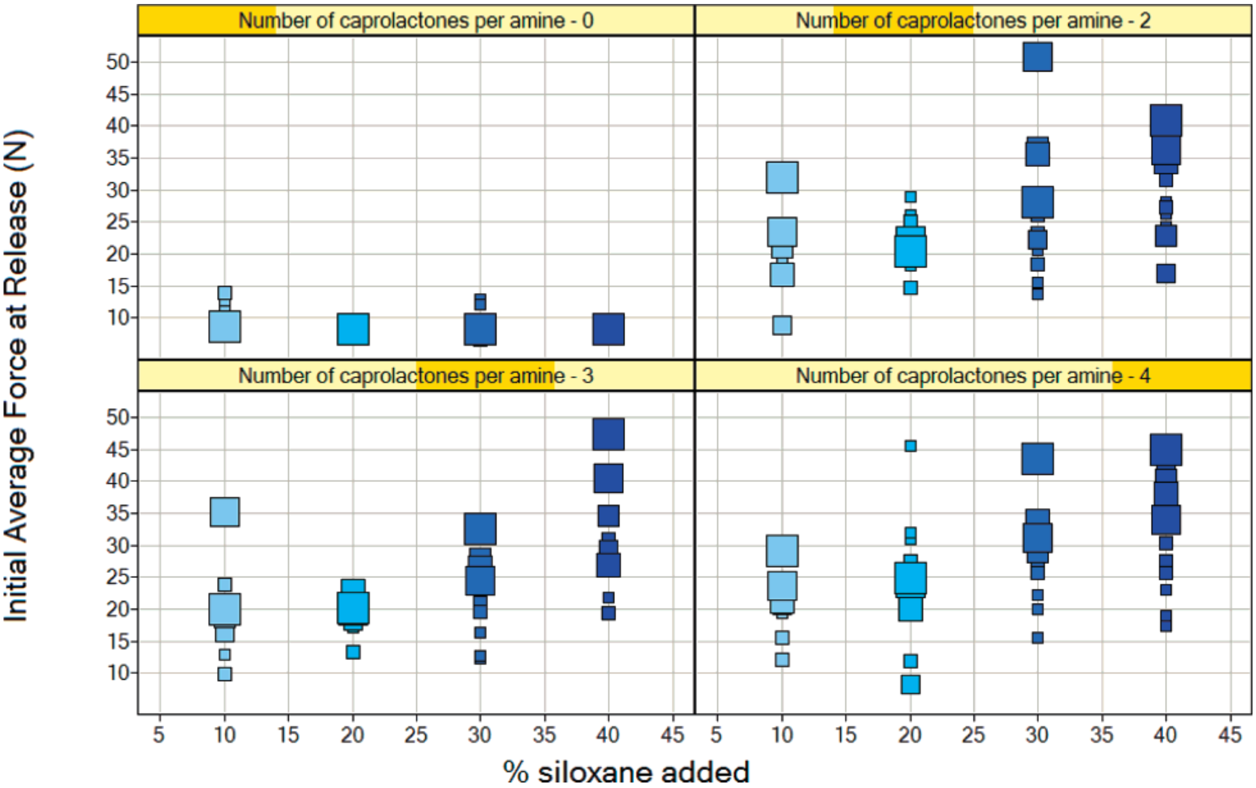

Figure 8. Initial pseudobarnacle adhesion results vs amount of siloxane in coating formulations trellised by number of ϵ-CLs per amine. The size of the data points increases as target molecular weight of PDMS increases. The color of the data points gets darker as siloxane polymer level increases.

data points were taken initially, and 1152 contact angle data points were taken after 30 days of water immersion resulting in a total of 2304 individual contact angle data points. For the pseudobarnacle adhesion test, 3 individual measurements were made per coating sample. Therefore, 576 pseudobarnacle adhesion data points were taken initially, and 576 pseudo-barnacle adhesion data points after 30 days of water immersion resulting in a total of 1152 pseudobarnacle adhesion data points. Thus, for full screening of all 192 coatings, 3456 individual data points were taken and analyzed.

From these 3456 individual data points, the average values of the three individual measurements were obtained for initial water contact angle, water contact angle after water immersion, initial methylene iodide contact angle, initial pseudobarnacle adhesion, and pseudobarnacle adhesion after water immersion of the 192 coatings were obtained. The change or difference in each of these values as a result of water immersion was then calculated. Surface energy was calculated from water and methylene iodide contact angles. Therefore, initial surface energy, surface energy after water immersion, and change in surface energy of the 192 coatings were obtained. Therefore, from the 3456 individual data points, 2304 property values (192 coatings × 12 properties) were obtained and used for analysis. All of the data that was obtained can be plotted in a number of different ways to identify the key property trends of the coatings that were prepared. However, here we are going to present only the most clear-cut, striking, and important observations.

In Figure 8, the initial pseudobarnacle adhesion (initial average force at release) versus the percent of siloxane polymer added is plotted. The data was plotted by trellising according to the number of ϵ-CLs per amine. It is seen that with 0 ϵ-CLs per amine, the average force at release values for all of the coatings are below 15 N. The siloxane polymer level does not have any significant effect on the initial pseudobarnacle adhesion results of the coatings prepared with the 3-aminopropyl-terminated PDMS. However, for coatings made from PCL−PDMS−PCL copolymers containing 2, 3, and 4 ϵ-CLs per amine, the initial average force at release values vary widely from below 10 N to above 50 N. A general trend seen is that as the siloxane polymer level increases the initial average force at release values tend to increase.

In Figure 9, the average force at release values after water immersion versus the percent of siloxane polymer added is plotted. Figures 8 and 9 are essentially identical except that Figure 8 presents the initial pseudobarnacle adhesion results, whereas Figure 9 presents pseudobarnacle adhesion results after 30 days of water immersion. The same observations seen in Figure 8 can be made from the data in Figure 9. A difference between Figures 8 and 9 is that in Figure 9 the trends can be seen somewhat more clearly than in Figure 8. It is believed that water can plasticize the polyurethane coating and allow the coating to reach an equilibrium state.

Since before and after 30 days of water immersion, some differences in measured property values were observed in each of the properties measured, this data can be used to assess the stability of the coatings. Table 1 summarizes the average property values of all of the coatings before and after water immersion. The average change of all 192 coatings after 30 days of water immersion for the water

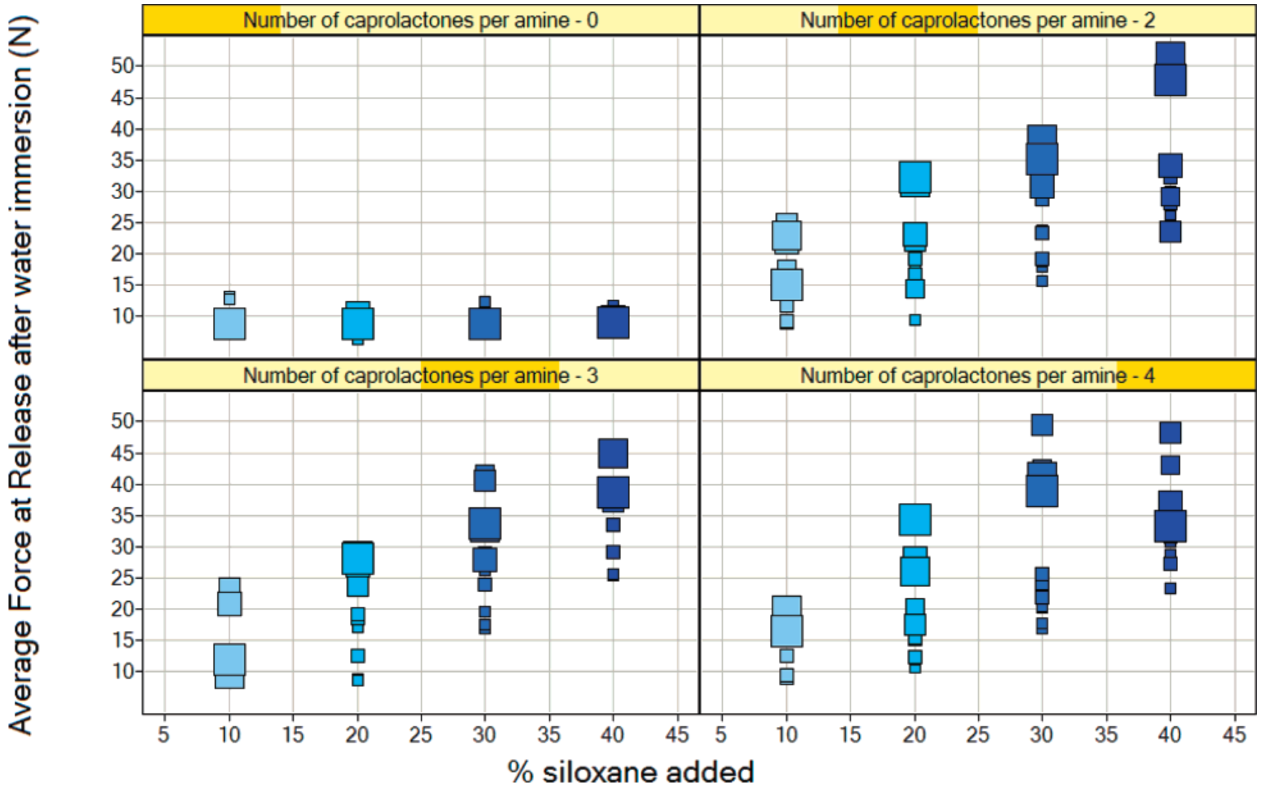

Figure 9. Pseudobarnacle adhesion after 30 days of water immersion vs amount of siloxane in coating formulations trellised by number of ϵ-CLs per amine. The size of the data points increases as target molecular weight of PDMS increases. The color of the data points gets darker as siloxane polymer level increases.

Table 1. Average Values of Properties of All 192 Coatings (with Standard Error)

	water contact angle (deg)	methylene iodide contact angle (deg)	surface energy (mN/m)	pseudo-barnacle adhesion (N)
initial	97.3 ± 0.57	80.3 ± 0.98	22.8 ± 0.58	20.6 ± 0.69
after water immersion	99.5 ± 0.46	80.3 ± 0.71	22.2 ± 0.42	20.4 ± 0.80
change	+2.2 ± 0.39	0 ± 0.68	−1.6 ± 0.55	−0.2 ± 0.41

contact angle is +2.2°, for methylene iodide contact angle is 0°, for pseudobarnacle adhesion is −0.2 N, and for surface energy is −1.6 mN/m. The standard error values indicate that the change in surface energy and water contact angle are statistically significant, while the change in pseudobarnacle and methylene iodide contact angle are insignificant. Practically, however, the change in all of these values is small; thus, the coatings are generally stable. Significant rearrangement of the coatings would result in changes in water contact angle values in excess of 10°. The change in coating properties is small, and no change of surface properties from hydrophobic to hydrophilic was observed, as seen in previous studies. Therefore, the goal of developing crosslinked self-stratified coatings with stable hydrophobic surfaces has been achieved.

Since better trends and observations are seen after 30 days of water immersion compared to the initial results, only the properties after water immersion are presented in the remainder of this paper. Since these coatings are intended for underwater marine applications, it is better to evaluate the properties after water immersion because these values will be more relevant to the final application of the coating.

In Figure 10, the average force at release after 30 days of water immersion is plotted versus the percent of siloxane added. In this figure, each data point was obtained by averaging the data for each value of percent of siloxane. This technique of data averaging is a commonly used technique in data mining and is one method of exploratory data analysis.[37−38] Since there are 192 coatings and only four data points in Figure 10, each data point is the average of the values of 48 coatings prepared. It can be clearly seen that the average force at release after water immersion increases almost linearly as the siloxane polymer level in the coating formulation is increased. This observation supports one of the conclusions drawn from both Figures 8 and 9, but the trend is clearer when the data is averaged over all of the remaining independent variables. To summarize, the lowest pseudobarnacle adhesion was obtained with 10% siloxane polymer (10% siloxane added). In addition, the lowest pseudobarnacle adhesion is obtained when the 3-aminopropyl-terminated PDMS oligomers are used and is generally higher when the triblock copolymers are used (Figures 8 and 9).

Water contact angle averages after 30 days of water immersion are plotted versus the number of ϵ-CLs per amine in Figure 11. It can be seen that the water contact angle of the coatings increases as the molecular weight of the PDMS blocks increases. Coatings prepared from 3-aminopropyl-terminated PDMS generally have a broader range of water contact angles than coatings prepared from the PCL−PDMS−PCL triblock copolymers. The addition of PCL

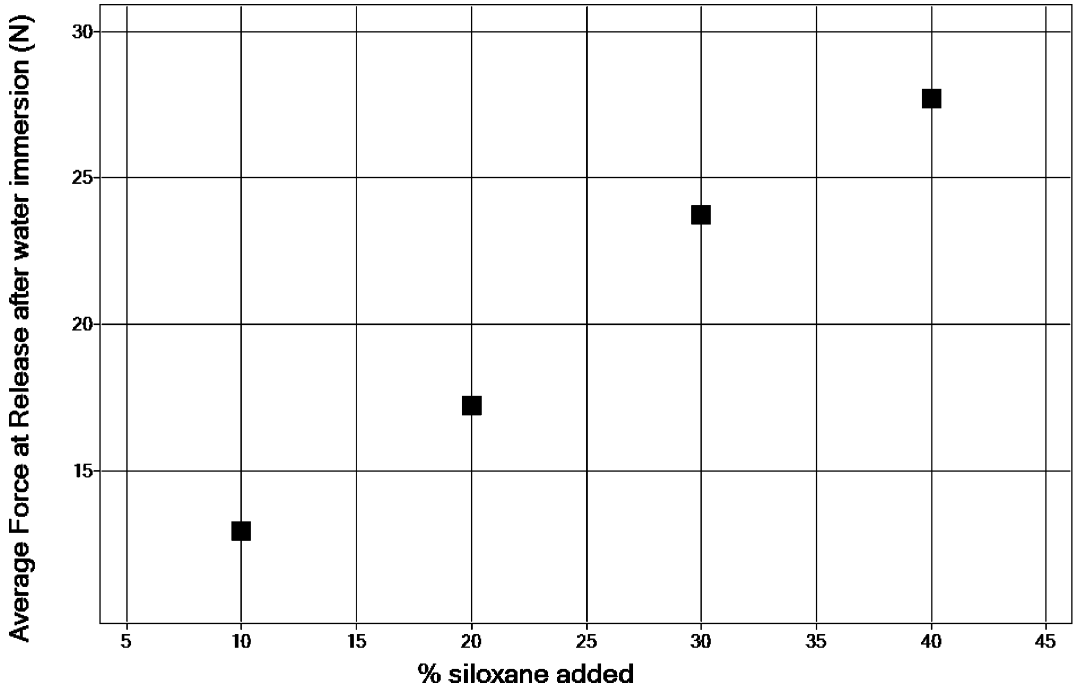

Figure 10. Pseudobarnacle adhesion after 30 days of water immersion vs amount of siloxane in coating formulations.

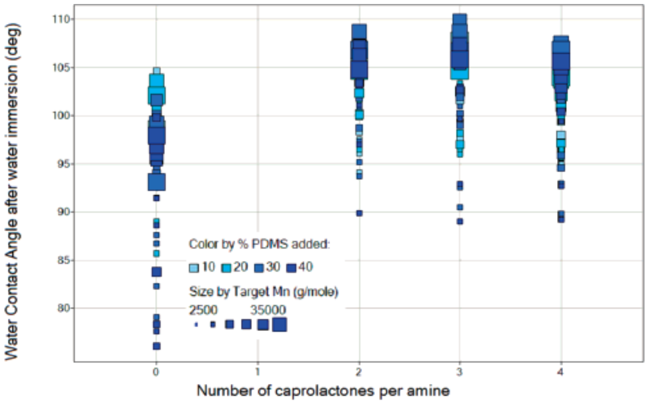

Figure 11. Water contact angle averages of 192 coatings after 30 days of water immersion vs number of ϵ-CLs per amine. Size of the data points increases as target molecular weight of PDMS block increases, and the color of the data points gets darker with increasing PDMS content in coating formulations.

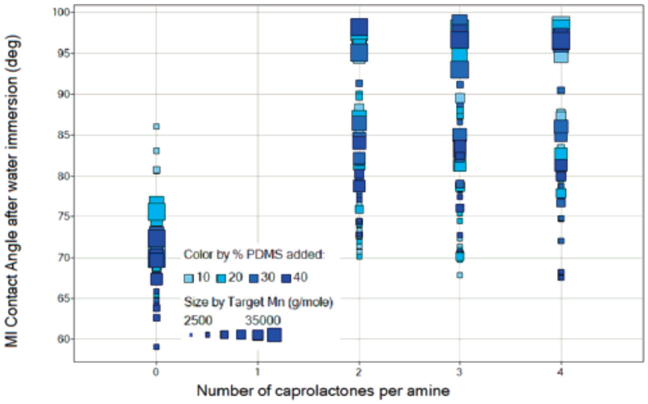

Figure 12. Methylene iodide contact angle averages of 192 coatings after 30 days of water immersion vs number of ϵ-CLs per amine. The size of the data points increases as target molecular weight of PDMS block increases, and the color of the data points gets darker with increasing PDMS content in coating formulations.

blocks to PDMS backbone increases the water contact angle by almost 8–10°, and only a few coatings based on the triblock copolymers have contact angles below 90°. The siloxane polymer level in the coating formulations does not have a significant effect on the water contact angle of the coatings. Slightly higher water contact angle averages are observed for PCL block length of 3 ϵ-CLs per amine than for 2 ϵ-CLs per amine, and the water contact angle averages are also lower for 4 ϵ-CLs per amine. Thus, there is a limited effect of the ϵ-CL chain length on the water contact angle data, and no need to increase the ϵ-CL chain length further.

The methylene iodide (MI) contact angle values of the 192 coatings after 30 days of water immersion versus number of ϵ-CLs per amine are plotted in Figure 12. The MI contact angle increases as the molecular weight of the PDMS blocks in the coating formulations increase. Coatings prepared from 3-aminopropyl-terminated PDMS have lower MI contact angle averages than coatings prepared from PCL–PDMS–PCL triblock copolymers. The addition of PCL blocks to PDMS increases the MI contact angle averages of the coatings by almost 25°. The siloxane polymer level in the coating formulation does not have a significant effect on the MI contact angle averages of the coatings.

In Figure 13, the surface energy of the coatings after 30 days of water immersion is plotted versus target molecular weight of the PDMS blocks. The surface energy of the coatings was calculated from the water and MI contact angle data. The graph is plotted by averaging the data over all of the other independent variables. It is clearly seen that surface energy of the coatings decreases as the molecular weight of the PDMS blocks in the coating formulations increases. The surface energy of the coatings decreases rapidly until a PDMS molecular weight of 20 000 g/mol and finds its lowest value at around a molecular weight of 30 000 g/mol. This is expected because higher-PDMS molecular weight results in a longer chain length between the endgroups which are reacted with the polyurethane network. A longer PDMS chain

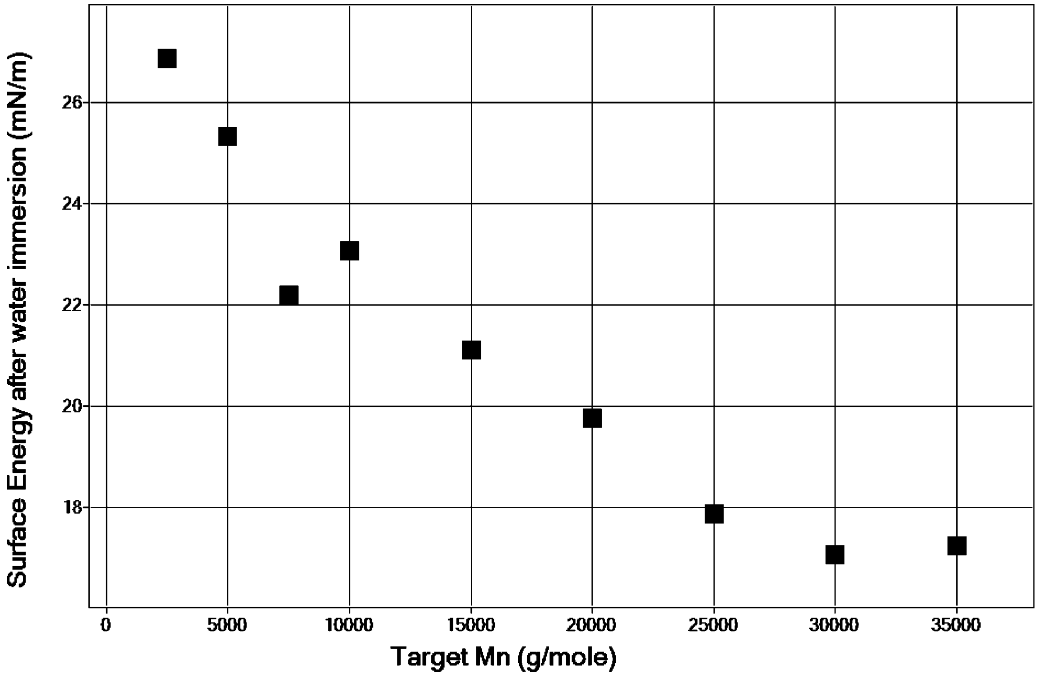

Figure 13. Surface energy after water immersion vs molecular weight of PDMS in coating formulations.

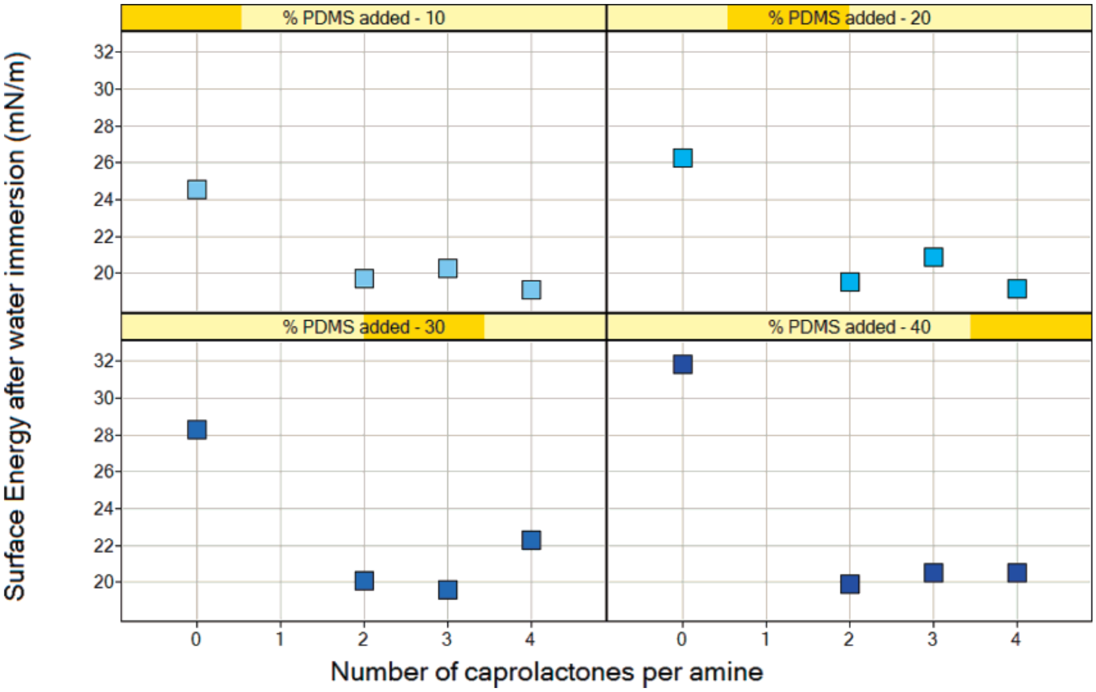

Figure 14. Surface energy after water immersion vs number of ϵ-CLs per amine trellised by amount of siloxane in coating formulations and averaged by number of ϵ-CLs per amine over all of the other independent variables. The color of the data points get darker as siloxane polymer level increases.

length may result in greater surface coverage by the PDMS, resulting in a lower surface energy.

Surface-energy data after 30 days of water immersion are plotted in terms of siloxane polymer level and the number of ϵ-CLs per amine in Figure 14. The data were plotted by both trellising and averaging data points dependent on the number of ϵ-CLs per amine over the other independent variables. Trellising was done on the basis of siloxane polymer level in coating formulations. It is clearly seen that coatings prepared from 3-aminopropyl-terminated PDMS have higher surface-energy values than coatings prepared from PCL−PDMS−PCL triblock copolymers. An increase of the siloxane content results in a slight increase in the surface-energy values of the coatings prepared from 3-aminopropyl-terminated PDMS. The coatings prepared from PCL−PDMS−PCL triblock copolymers have surface-energy values in the range of 19−22 mN/m. No significant trend was observed as a function of siloxane content in the coating formulation or PCL block length in coatings prepared from the PCL−PDMS−PCL triblock copolymers.

To summarize, the following key observations were made after the completion of the screening process.

The addition of PCL blocks to PDMS increases the water contact angle, increases the methylene iodide contact angle, decreases the surface energy, and increases pseudobarnacle adhesion. The presence or absence of PCL blocks is a significant variable.

Increasing the siloxane polymer level in coating formulations slightly decreases the water contact angle, slightly decreases the methylene iodide contact angle, slightly increases the surface energy, and increases pseudobarnacle adhesion. These effects are significant when the PCL−PDMS−PCL block copolymers are used, but minimal for coatings containing the 3-aminopropyl PDMS polymers.

Increasing the PCL block length within PCL−PDMS−PCL block copolymers results in a slight decrease in the water contact angle, a slight increase in the surface energy, and no effect on the methylene iodide contact angle and pseudobarnacle adhesion. Thus, over the range studied, the block length of PCL in the triblock copolymers does not have a significant effect on the performance of the coatings.

Increasing PDMS molecular weight increases the water contact angle, increases the methylene iodide contact angle, decreases the surface energy, and increases pseudobarnacle adhesion. Thus, the molecular weight of the PDMS is a significant variable.

The combinatorial study resulted in a number of very interesting observations. The key variables found to have significant effects on performance properties of the coatings are the PDMS molecular weight and the presence/absence of PCL blocks in the PDMS polymer. In addition, the amount of siloxane polymer had a significant effect for coatings containing the PCL−PDMS−PCL block copolymers. The result that the coatings with lower surface energy had higher pseudobarnacle adhesion is especially intriguing. It is believed that lower surface energy should result in lower pseudobarnacle adhesion. However, in our case polyurethane coatings prepared from PCL−PDMS−PCL triblock copolymers have lower surface energy but higher pseudobarnacle adhesion when compared with the coatings prepared from 3-aminopropyl-terminated PDMS.

The results of this study are being used in a subsequent study involving a smaller number of coating samples to explore these effects in more detail and to determine the coating morphologies that are giving rise to these properties. These coatings are also being subjected to various biological screens to identify correlations between the high-throughput laboratory assays of surface energy and pseudobarnacle adhesion and marine organism attachment and removal. The results will be reported in future publications.

4. Conclusions

The effects of PDMS molecular weight, addition of PCL blocks to PDMS backbone, length of PCL blocks, and siloxane polymer level on the properties of siloxane−polyurethane coatings were explored. Siloxane−polyurethane coatings were formulated, deposited, and screened using combinatorial high-throughput experimentation. Key properties screened were surface energy, determined by contact angle measurements using water and methylene iodide, and pseudobarnacle adhesion. Measurements were made both before and after 30 days of immersion in water. The average change of coating properties was minimal, indicating that the coatings were stable in water. Of the variables screened, the presence or absence of PCL blocks on the PDMS polymer and the molecular weight of the PDMS were the most significant.

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