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Influence of solvent composition and degree of reaction on the formation of surface microtopography in a thermoset siloxane–urethane system

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Abstract

The effects of solvent composition and degree of reaction prior to film formation leading to the formation of a biphasic microtopographical surface in a crosslinked siloxane–urethane coating system were explored. For the solvent composition study, a D-optimal mixture design study was carried out using methyl *n*-amyl ketone (MAK), toluene, ethyl 3-ethoxypropionate (EEP), butyl acetate (BA) and isopropyl alcohol (IPA) as solvents. The study revealed that the presence of slow evaporating solvents MAK, EEP and the absence of fast evaporating solvent IPA in the solvent composition with a minimal amount of BA favored formation of a structured surface. Control over the domain size could be obtained by varying the MAK:EEP ratio in solvent compositions having a fixed amount of BA. The effect of mixing time on the formation of surface domains was studied. At short mixing times (<2 h) and long mixing times (>7 h), no surface phase separation is observed, while at intermediate times a 'window' was found where surface microdomains of similar size are generated. Doubling the level of catalyst halves the mixing time required to generate surfaces with microdomains. Scanning electron microscopy (SEM) studies with energy dispersive X-ray mapping and dynamic mechanical analysis (DMA) were done in order to understand the development of the phases in the PDMS-polyurethane system.

Keywords: Polyurethane; Polydimethyl siloxane; Solvent composition

1. Introduction

The solvent composition of a multi-component thermosetting coating formulation is one of the most important variables. It plays a role in the initial compatibility of the components during mixing and also guides the phase separation during evaporation and curing; hence can control the final surface structure. Polymer–solvent interaction has been utilized to control surface morphology of block copolymers. Reversibly switchable morphology was obtained with a PS–PMMA diblock copolymer upon exposure to acetone and CS_2 [1]. Rate of evaporation of the solvent during casting has an effect on morphology of polymer blend [2]. The shape of a polymer chain in ternary solution has been studied by Monte Carlo simulation and blob model was used to study a polymer blend of two-crosslinked polymers in presence of a common solvent [3,4]. The demixing of incompatible macromolecular liquids and then subsequent removal of one or more phases by selective solvents might induce topography at the polymer surface [5]. Other effects such as chemical patterning over the surface and applied electric field might influence surface topography of copolymers [6,7]. In block copolymers, chemically distinct blocks separate into domains and the domains can adopt variety of morphologies and sizes depending upon chemical nature of the polymers and their molecular weights [8]. The surface of a solvent-cast block or graft copolymer system is composed predominately of the lowest surface energy component. This is especially the case in copolymer systems composed of poly (dimethyl siloxane) (PDMS) segments. Previous studies on the surface composition of PDMS block and graft copolymer systems have shown that PDMS predominates on the surface even at low bulk concentrations [9–16]. This is due to a number of factors including its low surface energy relative to other organic polymers, incompatibility with other polymers due to large difference in solubility parameter, and high chain flexibility. It has been found that copolymers of PDMS with polyurethane when exposed to water tend to rearrange over time due to migration of the hydrophilic polyurethane components to the surface [17–20]. Other than chemical nature of the polymers and solvent compositions, the kinetics of the reaction during mixing and film formation plays an important role in controlling the surface structure of a coating. A morphological

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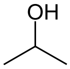
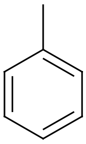
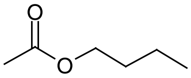
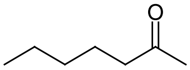
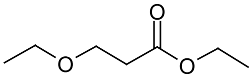
Table 1
Structure and properties of the solvents used in the solvent study

Name	Structure	Boiling point (°C)	Solubility parameter (cal/cm^3)$^{0.5}$		
			Polar	Nonpolar	Hydrogen bonding
Isopropyl alcohol		82.4	3.0	7.7	8.0
Toluene		111.0	0.7	8.8	1.0
Butyl acetate		126.0	1.8	7.7	3.1
Methyl *n*-amyl ketone		151.0	2.8	7.9	2.0
Ethyl 3-ethoxypropionate		170.0	1.6	7.9	4.3

change results from a dynamic ordering process at the late stage of a reaction has been observed due to change in kinetics [21]. Pattern formation in a polymer mixture can also be caused by competition between phase separation and chemical reaction [22]. Since, materials interact with the environment mainly through their surfaces, properties such as biocompatibility, appearance, etc. are all affected by the topography and chemical composition of the surface [23,24]. The interaction between the biological system such as micro-organisms and the surface for their settlement can be well understood with micro-engineered silicone surface [25,26]. We have recently reported the discovery of a spontaneously formed stable biphasic microtopographical surface based on a crosslinked siloxane–urethane system [27]. In this paper, this system is explored in more detail as we systematically investigate the role of solvent composition based on a statistical design and the effect of time and catalyst level in controlling the formation of a micro-topographical siloxane–urethane surface.

2. Experimental

2.1. Materials

Aliphatic polyisocyanate Tolonate XIDT70B (XIDT, 70% in butyl acetate) was obtained from Rhodia. XIDT is the triisocyanurate of isophoronediisocyanate and it has an isocyanate equivalent weight of 342 g/equiv. Tone Polyol 0305 (PCL) was obtained from Dow Chemical. This is a trifunctional polycaprolactone with a hydroxyl equivalent weight of 180 g/equiv. α,ω-Bis [3-(2′-hydroxyethoxy) propyl] polydimethylsiloxane (PDMS) with hydroxyl equivalent weight 500 g/equiv, was obtained from Chisso Corporation. Polyurethane grade methyl *n*-amyl ketone (MAK) and polyurethane grade butyl acetate (BA) were supplied by Eastman Chemical. Dibutyltin diacetate (DBTDA), 2,4-pentanedione, toluene and ethyl 3-ethoxypropionate (EEP) were obtained from Aldrich. Isopropyl alcohol (IPA) was obtained from VWR International. Structures and properties of the solvents are given in Table 1. Stock solutions of 30 wt% of PDMS, 90 wt% of PCL, 1 wt% of DBTDA were prepared separately in the five solvents studied (MAK, Toluene, EEP, BA and IPA). Other reagents were used as received.

2.2. Instrumentation

An automated coating formulation system manufactured by Symyx Discovery Tools, Inc. was used to prepare the formulations for the solvent study [28]. Materials were dispensed into 24 vials using a robotic pipette and mixed with a magnetic stir bar in each vial. Stock solutions of the PDMS, PCL, DBTDA in the five solvents were used so that the same resin composition could be maintained in the different solvent blends required by the statistical design. The resin portion of the coating formulation consists of 10 wt% PDMS on resin solid, 10% 2,4-pentanedione as pot life extender, NCO:OH equivalent ratio of 1.1:1.0. All of the nonreactive components (PDMS, PCL and 2,4-pentanedione) were dispensed first, followed by addition of the reactive components (DBTDA, XIDT). Drawdowns were made over Sherwin-Williams Macropoxy® 646 primer coated aluminum substrate and also on bare aluminum panels using an automated coating application unit with an adjustable doctor blade manufactured by Symyx Discovery Tools, Inc. [28]. Following application, the coatings were kept at ambient conditions for 24 h followed by oven curing at 80 °C for 45 min.

Atomic force microscopy (AFM) studies were performed on a Dimension 3100® microscope with Nanoscope IIIa controller (Digital Instruments, Inc., California). Experiments were operated under tapping mode in air at ambient condition using silicon probes with spring constant 0.1–0.4 N/m and resonant frequency 17–24 kHz. The setpoint ratio was 0.9.

For TEM (transmission electron microscopy) samples were embedded in Epon-Araldite-DDSA and cross-sectioned using a microtome at 60 nm thickness. Images of the cross-sections were obtained using a JEOL JEM-100CX II electron microscope.

For SEM (scanning electron microscopy) experiments, samples were mounted on aluminum mounts and coated with gold using a Technics Hummer II sputter coater. Images were obtained using a JEOL JSM-6300 scanning electron microscope. X-ray information was obtained via a ThermoNoran EDS detector using a VANTAGE Digital Acquisition Engine.

Dynamic mechanical tests were carried out with a TA Instruments Q-800 DMA analyzer. Samples were run under tension from −140 to 200 °C at a heating rate of 2 °C/min with 0.3% strain.

2.3. Software

Design-Expert Version 6.0.7 was used for statistically based design of experiments and response analysis. Nanoscope 5.12r5 software was used for image analysis of the AFM images.

2.4. Laboratory scale coating preparation

During the solvent composition study, one set of formulations with eight selected solvent compositions was prepared using conventional laboratory methods. All reagents other than the isocyanate were weighed and mixed in a 20 ml vial with magnetic stirring. After thorough mixing, isocyanate was added and mixed well for 4 h. Coatings were drawn down over aluminum panels and kept under ambient conditions for 24 h followed by oven curing at 80 °C for 45 min. Coating film thickness was 50–75 μm. Dry film thickness was measured using a Defelsko Corporation PosiTector 6000.

To study the effect of mixing time on the resulting coating surface morphology, two formulations with 0.075 and 0.15% DBTDA catalyst were prepared based on 10 wt% PDMS on resin solid, 10% 2,4-pentanedione as pot life extender, NCO:OH equivalent ratio of 1.1:1.0 and EEP:MAK:BA in 43:12:45 as the solvent composition. Ingredients were mixed thoroughly and then coatings were drawn down onto aluminum panels at 30 min intervals. The coatings were kept under ambient conditions for 24 h followed by oven curing at 80 °C for 45 min.

To measure the isocyanate conversion during mixing, the change in the amount of free isocyanate content with time was determined by the titration method ASTM D 2572-97. According to this method, the coating mixture was reacted with an excess of di-*n*-butylamine in toluene for 15 min to ensure completion of the reaction. The excess di-*n*-butylamine was determined by back titration with standard hydrochloric acid.

Calculation for NCO content is as follows

$$\text{NCO, \%} = \frac{[(B-V)\times N\times 0.042]}{W}\times 100$$

where B, volume of HCL for titration of the blank (ml); V, volume of HCL for titration of the specimen (ml); N, normality of HCL; 0.042, milliequivalent of the NCO group, and W, grams of specimen weight (g).

%NCO conversion as a function of time, t, was calculated from the following equation:

$$\text{\%NCO conversion} = \left(1-\frac{\text{\%NCO}, t=t}{\text{\%NCO}, t=0}\right)\times 100$$

3. Results and discussion

We recently reported the discovery of a specific crosslinked siloxane–urethane composition that resulted in the spontaneous formation of a microstructured surface structure [27]. The polymer composition consisted of a low molecular weight hydroxyl alkyl terminated PDMS (MW = 1000), a polycaprolactone triol, and a polyisocyanate crosslinker based on isophorone diisocyanate. In the system composed of 10% PDMS, a microstructured surface with domains having an average diameter of 1.5 μm and height of 60 nm was found. In contrast, for compositions containing 20 and 30% PDMS, the surfaces were featureless and consisted primarily of PDMS. It was also found that the microtopographical surface was stable after water immersion, thus, the crosslinking locks the surface morphology in place preventing rearrangement.

A large number of factors can be expected to play a role in the formation and size of the surface microtopography observed in this system. The solvent composition is important since it can provide initial compatibility to the precursor oligomers. In addition, both the polarity and evaporation rate of the solvent can dictate the rate of curing and point of phase separation as the coating cures on the substrate. Another factor that has been identified is the time between mixing of the coating ingredients and application of the coating to the substrate. During this time period, the degree of conversion is increasing leading to the formation of higher molecular weight polyurethane oligomers. The degree of conversion achieved prior to coating application and film formation can play a role in the formation of the microstructured surface domains.

3.1. Solvent composition study

In order to efficiently explore the role of different solvents and their mixtures on the generation of the microtopographical surface, a solvent study was carried out using a statistical experimental design approach, based on a D-optimal special cubic mixture design. MAK, Toluene, EEP, BA and IPA were taken as solvents for the formulation. MAK, EEP, and BA were chosen since they are common polar solvents for polyurethane systems, but have different evaporation rates. IPA has been recently shown to be an effective solvent for polyurethanes and has a large hydrogen bonding component of the solubility parameter [29]. Toluene was chosen since it is a good solvent for PDMS. Since the XIDT crosslinker is supplied containing BA, all compositions contained a minimum amount of BA. Hence during the design of the experiments, the amount of BA

Table 2
Summary of the experimental design

Study type: mixture; initial design: D-optimal		Number of experiments: 35; design model: special cubic	
Component	Name	Low value	High value
A	MAK	0	55
B	Toluene	0	55
C	EEP	0	55
D	BA	45	100
E	IPA	0	55
Condition: A+B+C+D+E=100			

was varied from 45 to 100% and the balance of the solvents was varied from 0 to 55%. Properties of the solvents are given in Table 1 and a summary of the experimental design is shown in Table 2. The 35 solvent compositions used are shown in Table 3. The experiments were run in random order. Following coating application and curing, AFM images of all 35 coatings were taken by tapping mode in air. Formation of microdomains and their density at the surface were guided by their solvent compositions. All 35 AFM images are shown in Fig. 1. A range of behavior is observed depending on the solvent compositions used. Domains are absent for some coatings and, when present, a range in domain size is apparent. In order to develop quantitative models of the behavior, numerical responses must be generated. Domain formation was considered as one of the responses. ‘No domains’ at the surface was assigned ‘0’ and ‘1’ was assigned for the presence of domains, regardless of their size. For the surfaces with domains, the number of domains per μm^2 was calculated by the image analysis software and the numerical value was considered in the response. The responses were fit to statistical models. Eqs. (1) and (2) are the equations of the best fit models for domain formation and domain density, respectively (variable definitions are in Table 2):

$$\text{Domain} = 0.97\text{A} + 0.99\text{B} + 1.17\text{C} + 1.01\text{D} + 0.34\text{E} - 3.17\text{B}^{*}\text{D} \quad (1)$$

$$\text{Sqrt}\,(\text{domain density} + 0.01) = 0.47\text{A} + 0.66\text{B} + 0.35\text{C} + 0.76\text{D} + 0.18\text{E} - 1.85\text{B}^{*}\text{D} - 1.26\text{D}^{*}\text{E} \quad (2)$$

Table 3
Solvent compositions for solvent study

Run order	A: MAK	B: Toluene	C: EEP	D: BA	E: IPA
1	27.50	0.00	27.50	45.00	0.00
2	5.50	5.50	5.50	78.00	5.50
3	55.00	0.00	0.00	45.00	0.00
4	0.00	0.00	0.00	100.00	0.00
5	0.00	0.00	0.00	45.00	55.00
6	5.50	5.50	5.50	50.50	33.00
7	18.33	18.33	0.00	63.33	0.00
8	18.33	0.00	18.33	63.33	0.00
9	0.00	0.00	55.00	45.00	0.00
10	18.33	0.00	18.33	45.00	18.33
11	0.00	18.33	18.33	45.00	18.33
12	18.33	18.33	0.00	45.00	18.33
13	0.00	0.00	27.50	72.50	0.00
14	27.50	0.00	0.00	45.00	27.50
15	0.00	27.50	0.00	45.00	27.50
16	27.50	27.50	0.00	45.00	0.00
17	0.00	0.00	0.00	72.50	27.50
18	0.00	18.33	0.00	63.33	18.33
19	18.33	0.00	0.00	63.33	18.33
20	0.00	27.50	0.00	45.00	27.50
21	0.00	0.00	0.00	72.50	27.50
22	5.50	5.50	33.00	50.50	5.50
23	33.00	5.50	5.50	50.50	5.50
24	0.00	27.50	27.50	45.00	0.00
25	5.50	33.00	5.50	50.50	5.50
26	0.00	0.00	27.50	45.00	27.50
27	0.00	0.00	18.33	63.33	18.33
28	27.50	0.00	27.50	45.00	0.00
29	27.50	0.00	0.00	72.50	0.00
30	27.50	0.00	0.00	72.50	0.00
31	0.00	27.50	0.00	72.50	0.00
32	0.00	18.33	18.33	63.33	0.00
33	18.33	18.33	18.33	45.00	0.00
34	0.00	55.00	0.00	45.00	0.00
35	0.00	27.50	27.50	45.00	0.00

Both of these models revealed that interaction terms between the solvents were important. For domain formation, the interaction term B*D and for domain density interaction terms B*D and D*E were significant factors. As all these interaction terms had a negative coefficient, these solvent combinations do not favor domain formation. Thus, this implies that combinations of the faster evaporating solvents (BA, toluene and IPA) in any solvent composition would not favor formation of a structured surface. Since all solvent compositions had a minimum amount of BA, the presence of toluene or IPA in the solvent composition would not favor the formation of a structured surface due to their interactions with BA.

Further insights on the effect of solvent composition on domain formation can be obtained by specifying a target condition and generating a set of solutions. We obtained two sets of solutions, the first set by specifying domain formation equal to zero (i.e. no domain) as shown in Table 4 and second set by specifying domain formation equal to one (domain formation) as shown in Table 5. The suggested solvent compositions in Table 4 revealed that the absence or a minimal amount of MAK and EEP with a high amount of IPA alone or with a high amount of both toluene and BA does not favor formation of a surface with microstructured domains. On the other hand, from Table 5, the suggested solvent compositions revealed that the absence or a minimum amount of IPA and the presence of MAK and EEP would favor formation of microstructured surface domains. These two sets of solvent compositions can be separated with respect to vapor pressure and solubility parameter. For ‘no domain’ formation, the vapor pressure of the solvent compositions was in the range of 13.95 mm Hg to 24.89 mm and the solubility parameter varied from 8.61 to 9.84 (cal/cm^3)$^{0.5}$. For domain formation, vapor pressure of the solvent compositions was in the range of

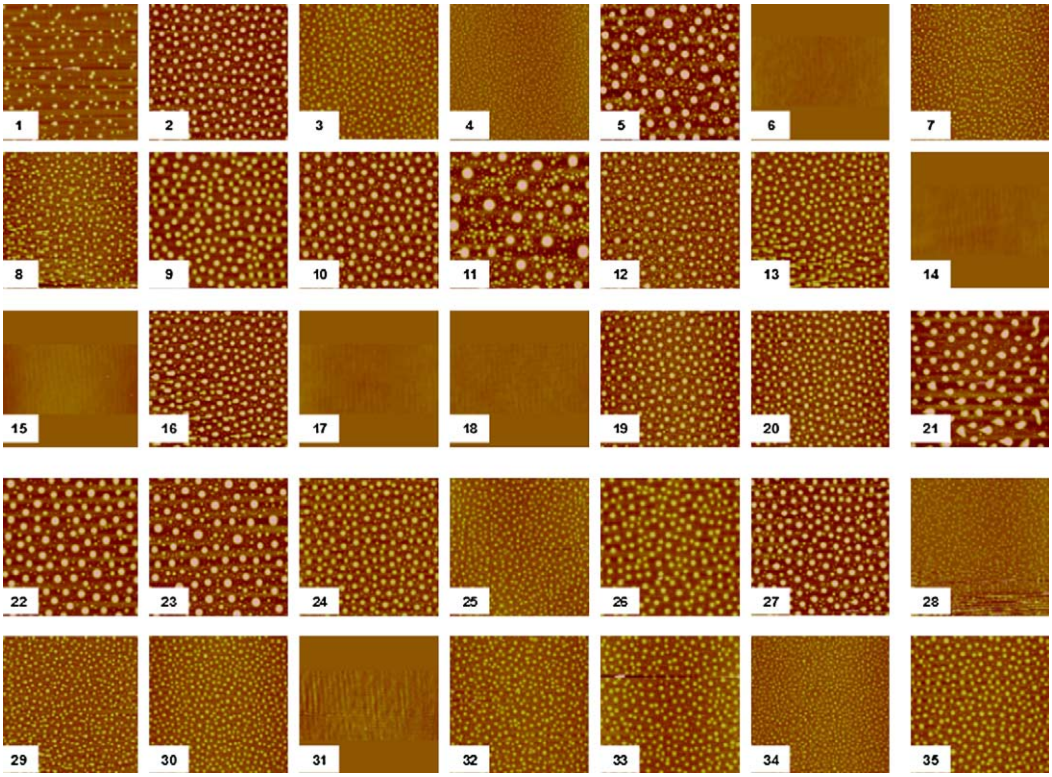


Fig. 1. AFM height images (40 μm×40 μm) of the surfaces from 35 solvent compositions in Table 3.

5.27–10.54 mm and the solubility parameter varied from 8.56 to 8.62 $(\mathrm{cal/cm^3})^{0.5}$.

After considering the negative interaction terms in the models (between toluene-butyl acetate and butyl acetate-IPA) and the suggested solvent compositions from Table 5, eight different solvent compositions—without toluene and IPA—were selected for further evaluation on the effect of solvent composition on domain size. The selected solvent compositions are shown in Table 6. The amount of BA was kept at its minimum level of 45% and the ratio of MAK:EEP was varied systematically from 45:10 to 10:45. Coatings were prepared using the automated formulation and application unit and each of the eight coatings was prepared three times to generate a single library of 24 samples. Drawdowns were made over both primer coated aluminum panels and also over bare aluminum panels. Another set of coatings were prepared in the laboratory over bare aluminum panels. AFM images revealed that these eight solvent compositions always generated microstructured surfaces, as predicted. Hence, the formation of microstructured surface was favored by the elimination of toluene and IPA from the solvent composition as indicated by the model response along with the use of a minimal amount of BA.

In order to understand the effect of solvent composition on the size of the domains, the mean diameter of the domains was plotted against the MAK:EEP ratio, shown in Fig. 2. For coatings prepared using the automated units, the mean domain diameter varied from 0.41 to 1.35 μm when applied over the primer coated aluminum panel and was from 0.53 to 0.97 μm when applied over the bare aluminum panel. For coatings prepared in laboratory, the mean diameter increased from 1.2 to 1.9 μm as the MAK: EEP ratio was changed from 45:10 to

Table 4
Calculated solvent compositions for surface without domains

Solutions	A: MAK	B: Toluene	C: EEP	D: BA	E: IPA
1	0.00	2.02	0.08	47.73	50.16
2	0.00	4.31	0.00	45.15	50.54
3	0.00	1.03	0.00	48.70	50.27
4	0.00	5.25	0.00	45.00	49.75
5	0.00	24.53	0.00	70.01	4.56

Table 5
Calculated solvent compositions for surface with domains

Solutions	A: MAK	B: Toluene	C: EEP	D: BA	E: IPA
1	32.24	2.01	14.45	49.80	1.50
2	14.96	12.47	22.94	49.40	0.23
3	34.76	3.48	12.56	48.56	0.64
4	40.20	0.18	11.69	46.64	1.29
5	43.03	2.57	8.43	45.83	0.14

Table 6
Selected solvent compositions for structured surface

Formulation	MAK	EEP	BA
Si-PU 1	45	10	45
Si-PU 2	40	15	45
Si-PU 3	35	20	45
Si-PU 4	30	25	45
Si-PU 5	25	30	45
Si-PU 6	20	35	45
Si-PU 7	15	40	45
Si-PU 8	10	45	45

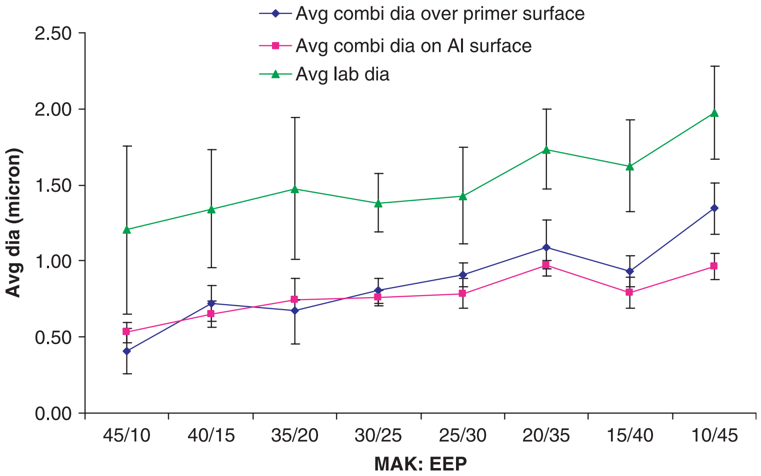


Fig. 2. Average diameter of the microstructued domains vs. MAK:EEP ratio in solvent composition.

10:45. Note that the variability of the mean diameter is much reduced for the coatings prepared using the automated systems. Since these are relatively thick films, it is not expected that the substrate will affect the formation of surface domains and this is reflected in the coatings prepared on the two different substrates using the automated equipment. While it is not totally clear why there is a size difference between the coatings prepared in the laboratory and by the automated unit, this might be due to differences in applied shear during the drawdown process.

Two things occur as MAK is replaced with EEP in this series of formulations. The overall solubility parameter of the solvent compositions increases due to the contribution from the hydrogen bonding interaction parameter. In addition, the overall evaporation rate slows. This means that favorable hydrogen bonding interactions between the solvent and polyurethane occur over a longer time. The higher amounts of EEP may delay the process of phase separation after application, which allows the domains to grow in size.

A TEM image of the cross section of the formulation Si-PU 8 is shown in Fig. 3 in order to understand the arrangement of the domains in the film. TEM analysis revealed that the domains are mainly concentrated at the air interface and are darker than the surrounding matrix, which is expected as these domains were mainly composed of PDMS. Domains of a similar size are also observed distributed in the bulk of the sample as well.

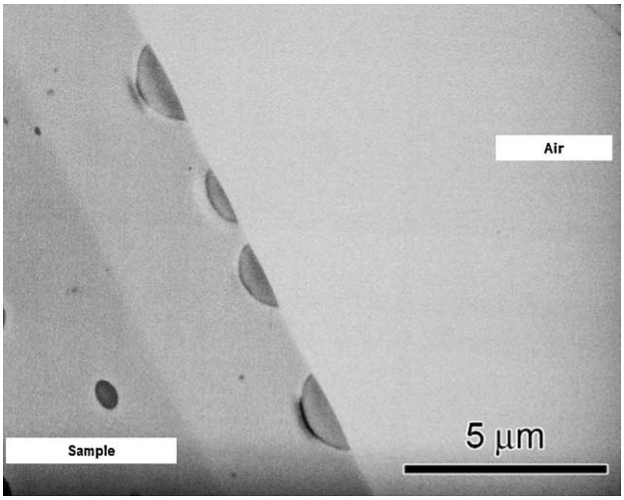


Fig. 3. TEM image of the cross section of the coating Si-PU 8.

3.2. *Effect of mixing time*

In all of our previous experiments, the time between mixing of the components and application on the substrate and curing was held constant at 4 h. In order to understand the effect of mixing time on domain formation, two formulations with the same resin composition, the same solvent composition (MAK:EEP:BA = 12:43:45) and pot life extender (2,4-pentanedione, 10% with respect to resin solids) but with two different levels of DBTDA catalyst (0.075%, series A and 0.15%, series B) were used. During the preparation of the coatings, all of the reagents other than isocyanate were mixed thoroughly. After isocyanate addition and thorough mixing, draw downs were made at 30 min intervals over a period of 30 min to 8 h or to 4 h for series A and series B, respectively. Drawdowns of the coatings were then made and the coatings were cured.

3.2.1. *AFM study*

AFM images of the cured films were made in air using tapping mode of the series of coatings. The images of series A (0.075% DBTDA) and series B (0.15% DBTDA) are shown in Fig. 4. Series A can be subdivided into three stages: (1) no domain formation was observed for coatings applied and cured within the first 2 h of mixing (a1 to a4). (2) Domains were first observed after 2.5 h of mixing (a5) and became uniform in size after 3 h of mixing (a6). The domains were uniform in size up to 4.5 h of mixing (a7–a9). (3) The domains started to decrease in size after 5 h of mixing (a10) and disappeared completely to generate a smooth uniform surface for coatings prepared after 7 h of mixing (a14). This study indicates that the formation of

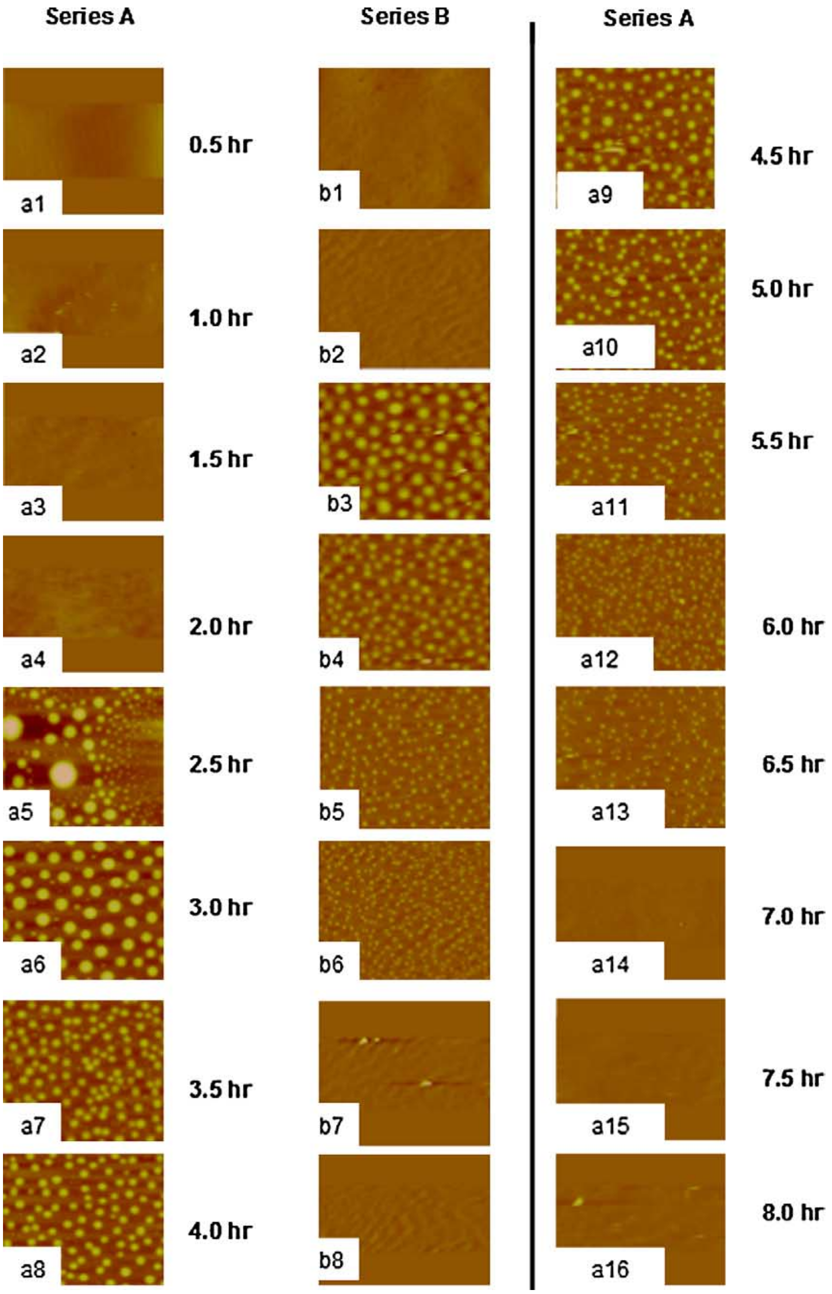


Fig. 4. AFM height images (40 μm × 40 μm) of siloxane–urethane surfaces as a function of mixing time, (a1)–(a16) with 0.075% catalyst and (b1)–(b8) with 0.15% catalyst.

microstructured surface domains is a function of the mixing time prior to application and curing.

Since the rate of the reaction between isocyanate and hydroxyl groups increases with an increase in catalyst level [30–34], domain formation was expected to appear earlier using a formulation having double the amount of catalyst. In series B, coatings with double catalyst, domains of uniform size occurs after 1.5 h of mixing (b3), which was exactly equal to half of the time that required in series A. Similarly, domains started to decrease in size after 2.5 h of mixing (b5) compared to 5 h of mixing in series A (a10) and disappeared completely after 3.5 h of mixing (b7) as compared to 7 h (a14) in series A. The plots of domain size vs. time with 0.075 and 0.15% DBTDA catalyst are shown in Fig. 5. Since there was a wide size distribution in the series A sample at 2.5 h, three data points are plotted, one for each major domain size observed.

Several conclusions can be drawn from these results. First, a minimum mixing time is required in order for domains to form on the surface of the coating. This further indicates that some reaction must occur between the oligomeric species during mixing prior to application and curing in order for surface domains to form. For the series A coatings, there is also an interesting ‘window’ between 3.5 and 5.5 h where the domain size is relatively constant. Eventually, the domain size decreases and finally surface domains disappear indicating that further reaction results in a more homogeneous system

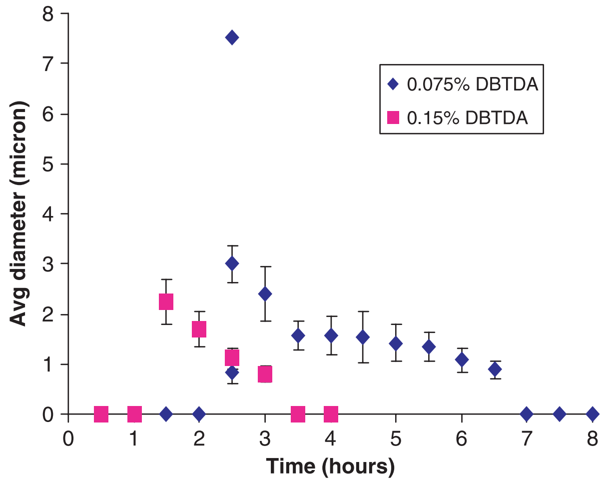


Fig. 5. Average diameter of the domains as a function of mixing time at 0.075% DBTDA and 0.15% DBTDA catalyst. Data points at 0 indicate that no domains were observed.

where surface phase separation does not occur. The occurrence of similar stages of domain formation within a shorter period of time when double the amount of catalyst was used shows that both the formation and size of the domains can be controlled kinetically.

3.2.2. Degree of conversion during mixing

To obtain a preliminary assessment of the extent of reaction taking place during the mixing stage, the isocyanate conversion was analyzed by titration as a function of time for the coating formulation containing 0.075% catalyst (Fig. 6). The results indicate that isocyanate reacts fairly rapidly over the first few hours, and reaches ∼56% conversion at 3 h of mixing. From then there is a very gradual increase in conversion up to 7 h (∼59%), where the measurements stopped. It should be noted that the system does not gel macroscopically until after approximately 14 h of mixing.

This, it appears that at mixing times of less than two and a half hours, sufficient reaction between the isocyanate and the PCL polyol and hydroxy functional PDMS has not occurred to lead to phase separation on the surface of the system. It is also interesting to note that very little additional reaction takes place between 3 and 7 h of mixing; this is the mixing time during which the surface microdomain size decreases. Thus, the surface domain size appears to be highly sensitive to the extent of reaction prior to film formation.

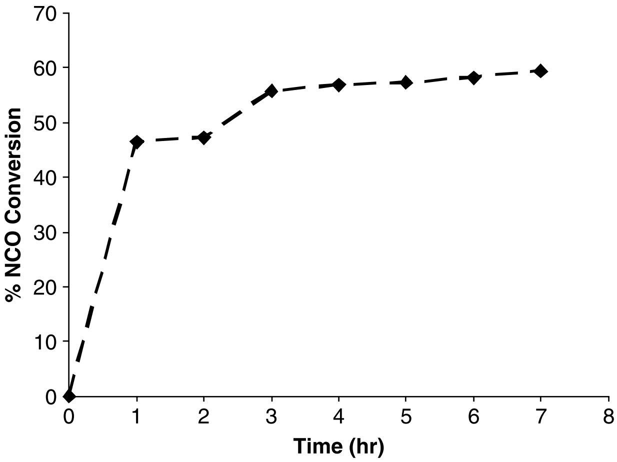


Fig. 6. Conversion of isocyanate groups as a function of time during mixing of coating formulation prior to application.

Detailed analysis of the composition of the oligomeric species being formed during mixing as well as that of the phase separated domains is required for a complete understanding of the system and how the structure is formed. These experiments are in progress.

3.2.3. SEM study with X-ray mapping

SEM imaging of the surfaces was used to further verify the generation of the microstructured polymer surface. SEM images of the surfaces after 0.5, 3.5, and 7.5 h of mixing (a1, a7, a15 of series A from Fig. 4) showed the absence of microstructured domains at 0.5 and 7.5 h, but presence of domains at 3.5 h (Fig. 7(a)–(c)). The corresponding energy dispersive X-ray mapping of silicon indicated that the domains were rich in silicon as shown in Fig. 7(e), however, energy dispersive X-ray mapping of silicon revealed the existence of diffuse silicon-rich regions (Fig. 7(d)) when the time of mixing was 0.5 h. Silicon was uniformly distributed over the surface (Fig. 7(f)) when mixing time was 7.5 h. This SEM study with X-ray mapping revealed that in the initial stage of cross linking reaction PDMS was separated into some discrete regions and as the reaction progressed, silicon rich microdomains were generated at the surface and finally formed a featureless surface where silicon was uniformly distributed.

3.2.4. DMA analysis

In order to further understand the effect of the reaction kinetics on the morphology of the coatings, dynamic mechanical analysis (DMA) was performed on selected siloxane–urethane samples with a control polyurethane containing no PDMS. Typically, siloxane–urethane systems are expected to show a transition around −128 to −90 °C due to the well phase-separated PDMS segments. But it has been shown that in systems with low molecular weight PDMS (900 g/mole) there may be substantial microphase mixing [35–39]. Although we used a low molecular weight PDMS (1000 g/mole), in the early stages of mixing (0.5 h), a transition associated with PDMS was observed at approximately −90 °C as shown in the loss modulus vs. temperature curve in Fig. 8. As the reaction progresses (4.0 h), an intermediate phase appears centered around 5 °C, while there is still a suggestion of a transition remaining at −90 °C. Apparently, it is this intermediate phase, composed of both PDMS and polyurethane that results in the phase separated surface structures observed.

At a longer mixing time prior to curing (7.5 h), however, the discrete low temperature and intermediate transitions disappear and the upper transition broadens, indicating that the system has become more homogeneous. This time of reaction corresponds with the situation where no surface microdomains are observed in the cured coating. Thus, it appears that the longer reaction time prior to curing results in a more uniform

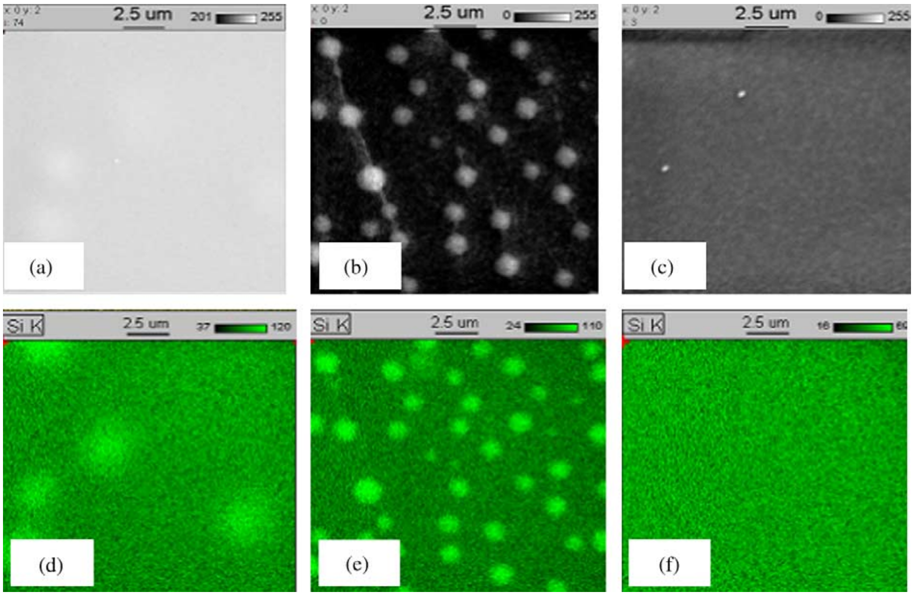


Fig. 7. SEM images of siloxane–urethane coating at selected mixing times: (a) 0.5 h, (b) 3.5 h, (c) 7.5 h and their corresponding ‘Si’ mapping (d)–(f).

network and phase separation is not occurring to a large extent. The uniform bulk morphology results in a coating surface that has a uniform composition, where the PDMS is evenly distributed over the surface.

4. Conclusions

A study on the effect of solvent composition and reaction time on the formation of coatings having biphasic micro-topographical siloxane–urethane surfaces revealed that the surface structure could be controlled to generate domains with various sizes varying from 0.41 to 1.9 μm with uniform size distributions. The effect of solvent composition was explored using a statistical experimental design with five different solvents. Statistical models were obtained for domain formation and domain density. Interaction terms between the solvents with negative coefficients were significant and the presence of slow evaporating solvents MAK, EEP and absence of the fast evaporating solvent IPA in the favors formation of microstructured surfaces. Control over the domain size could be obtained by varying the MAK:EEP ratio in solvent compositions having a fixed amount of BA. The average domain size increases as MAK is replaced with EEP. Domain formation and domain size is also a function of time between mixing and coating application. The occurrence of similar stages of domain formation were observed with two levels of catalyst and with 0.15% catalyst the time required to reach each stage was equal to exactly half of the time that required with 0.075% catalyst. Titration experiments showed that isocyanate conversion reached ∼55% in the first 3 h of mixing and then

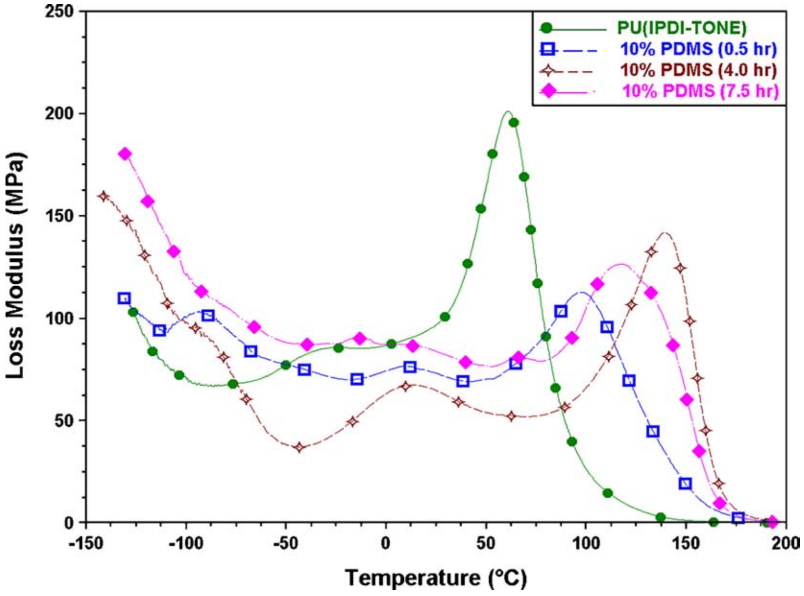


Fig. 8. Loss modulus data of polyurethane and siloxane–urethane coatings as a function of mixing time before coating application.

slowly increased up to 7 h. An SEM study with energy dispersive X-ray mapping and DMA analysis revealed that initially PDMS was contained in diffuse phases in the urethane matrix and as the reaction prior to curing progressed more well-defined microdomains composed of PDMS and polyurethane were formed and finally at longer times of mixing a uniform composition was formed where no substantial surface phase separation occurred.

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