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Surface microtopography in siloxane–polyurethane thermosets: The influence of siloxane and extent of reaction

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Abstract

The effect of polydimethylsiloxane (PDMS) content, PDMS molecular weight, and the extent of prepolymerization reactions between hydroxyl functional PDMS and polyisocyanate were explored in order to understand the influence of these variables on the formation of surface microtopography in a siloxane–polyurethane thermoset. The system is based on a difunctional hydroxyalkyl terminated PDMS, trifunctional poly(caprolactone) polyol, and a polyisocyanate. The effect of PDMS content was studied with PDMS of MW 1000 and 2000. PDMS of MW 1000 was varied from 5% to 15% and with PDMS of MW 2000 the level was varied from 5% to 12%. Tapping mode AFM images of the surface topography were used to characterize the system. The extent of reaction prior to film formation was studied by FTIR and correlated with microdomain formation in the final polymer film. Two different mixing strategies were explored: one where all of the ingredients were mixed together and a second approach where PDMS and polyisocyanate were mixed first, followed by the addition of the trifunctional polyol. Monte Carlo simulation of the polymerization with 10% PDMS of MW 1000 in the formulation revealed that there was a window of conversion for both PDMS and isocyanate at which the system spontaneously phase separates to form a microtopographical surface.

Keywords: Polyurethane; Phase separation; Siloxane

1. Introduction

Surface topography plays an important role in controlling the interaction between materials and the environment [1,2]. Thus, there has been increasing interest in generating polymer surfaces having defined surface topography [3,4]. Tanaka et al. showed that pattern formation in a polymeric mixture can be caused by competition between phase separation and chemical reaction [5]. Other methods such as selective removal of one of the component phases by solvation [6] or degradation [7] have been used to form microtopographical surfaces. Electric field and polymer-on-polymer stamping have also been used to control domain size on chemically patterned substrates [3,8].

Surface composition analysis of block and graft copolymers containing polydimethylsiloxane (PDMS) segments has shown that PDMS predominates on the surface due to its immiscibility with other polymers and its low surface energy [9–14]. Most previous studies appear to indicate that PDMS forms a smooth and continuous overlayer on the surface of PDMS-containing polymer systems. We have previously reported the discovery of a highly unique crosslinked PDMS–polyurethane system that spontaneously forms microtopographical surface domains, composed primarily of PDMS, surrounded by a polyurethane matrix [15]. The surface microtopography does not rearrange substantially upon exposure to water, which is attributed to the fact that this is a crosslinked system. Thus, this represents a novel and practical approach to the generation of polymer surfaces having microtopographical features.

Heterogeneous surfaces based on amphiphilic crosslinked networks or with amphiphilic side chains have been shown to be effective in reducing the interactions associated with

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biofouling [16,17]. Baum et al. have shown that the self-cleaning property of whales is due to the nano-rough gel-coated epidermal surface of the skin [18]. PDMS elastomers with well-defined microtopographical features prepared by contact molding have been shown to inhibit settlement of fouling organisms [19–22]. Hence, this system which generates a PDMS-rich microtopographical surface by mixing all the ingredients in one pot, followed by application and curing, has a great deal of potential in this field. We have studied the adhesion properties of pseudobarnacles and liver barnacles to these microtopographical siloxane–polyurethane surfaces and have shown that the presence of the surface microtopography can reduce the adhesion strength. Thus, these unique materials may have application as anti-biofouling coatings [23].

The PDMS–polyurethane system consists of a large number of ingredients that may participate together to influence the formation of the microstructured surface. Illustrated in Fig. 1, the polymer system consists of a hydroxyalkyl terminated PDMS, an organic polyol based on poly(ε-caprolactone), and a polyfunctional isocyanate derived from isophorone diisocyanate. The system also contains a catalyst for the isocyanate-hydroxyl reaction, a volatile pot life extender, and a blend of solvents. A typical procedure for preparing the materials involves mixing all of the ingredients with the exception of the polyisocyanate crosslinker, then adding the crosslinker and mixing for a specified time, followed by casting a film of the material (Fig. 2). When the crosslinker is added, the hydroxyl groups on PDMS and polyol can begin to react with the isocyanate crosslinker in solution. We have reported that there is a “window of mixing time” in order to generate materials having a phase separated surface structure, which is attributed to the reactions taking place in solution [24].

After the solution is cast on the substrate, the solvents and volatile pot life extender can begin to evaporate, the isocyanate-hydroxyl reactions can continue to proceed, and eventually the system gels. The solvents used in the system can influence the compatibility of the ingredients in solution and the relative evaporation rates, coupled with the rate of crosslinking reactions, can affect the phase separation of the system. Indeed, we have demonstrated that the solvent composition can play an important role in the development of both a phase separated surface and the resulting size of the isolated PDMS surface domains [24].

Thus, it is apparent that this is a highly complex system consisting of a number of variables that may interact in ways that are difficult to predict to affect the development of surface microtopography. Our approach has been to systematically explore the key variables that may influence surface phase separation with the eventual goal of developing a more thorough understanding of the parameters that lead to the observed microtopography.

In a polyurethane system the role of catalysts, polyols and isocyanates in controlling the reaction kinetics and the degree of reaction can readily be followed experimentally using FTIR [25–31]. Monte Carlo simulation can also be used to study network formation during polymerization [32–37]. Since we have determined that mixing time prior to network formation is an important controlling variable, it is necessary to understand in detail the reactions that are occurring during the time of mixing in solution. This can be achieved through an experimental method such as FTIR combined with a Monte Carlo computational simulation. Here, we study the role of PDMS content and its molecular weight and the extent of prepolymerization during the mixing step in controlling the formation of a microtopographical surface. The degree of reaction with respect to the isocyanate groups of the polyisocyanate and the hydroxyl groups of PDMS was followed by FTIR and compared with Monte Carlo simulations in order to further understand the window of conversion at which the system spontaneously phase separates to form a microtopographical surface.

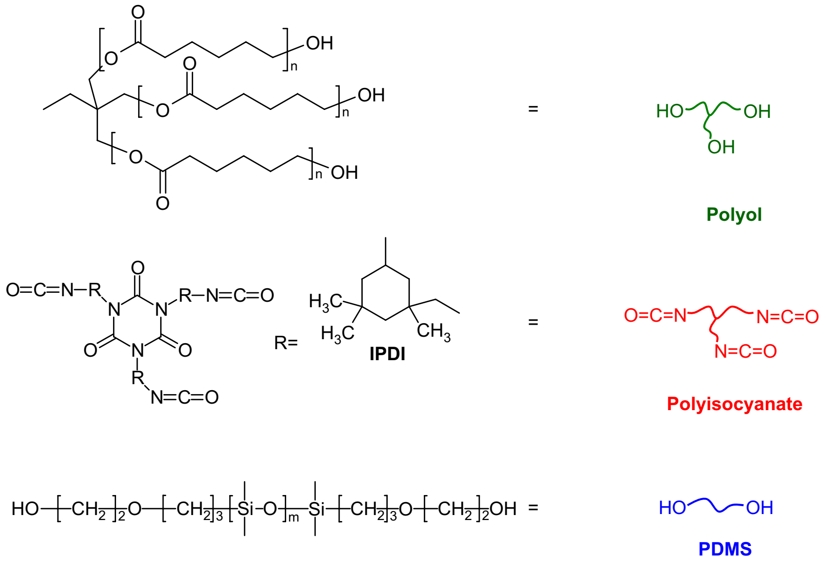


Fig. 1. Components of the thermosetting siloxane–polyurethane system.

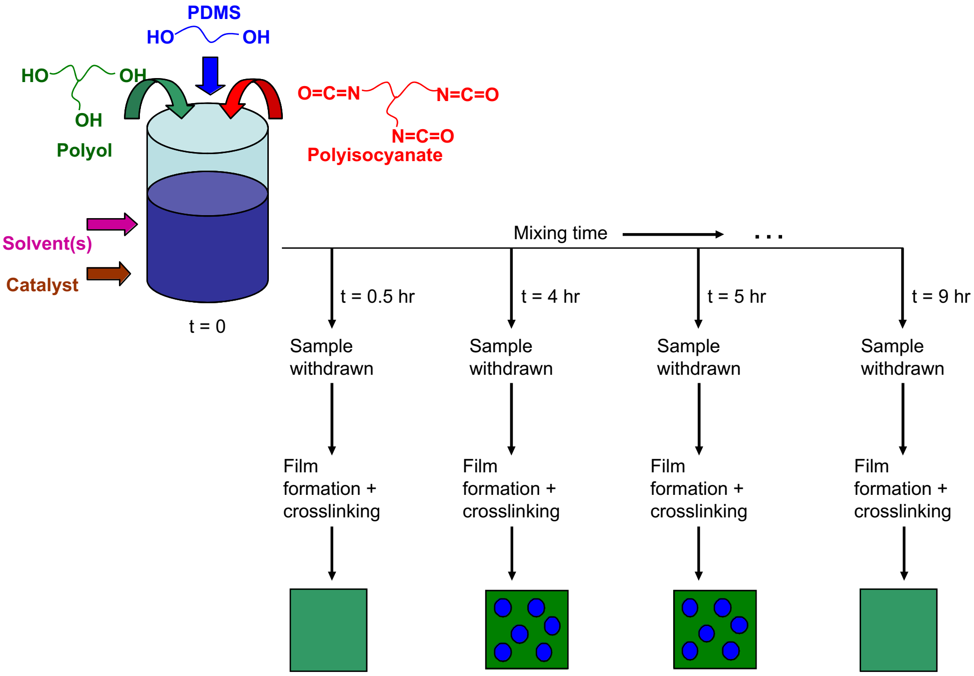


Fig. 2. Illustration of the mixing protocol used. The mixing time is defined as the elapsed time after polyisocyanate is added to the mixture and the polymer is formed on the substrate.

2. Experimental

2.1. Materials

Aliphatic polyisocyanate Tolonate IDT70B (IPDI trimer, 70% in butyl acetate) was obtained from Rhodia. Trifunctional polyol Tone 0305 (Polycaprolactone, PCL) was obtained from Dow Chemical. α,ω-Bis[3-(2′-hydroxyethoxy)propyl] polydimethylsiloxane (PDMS) with hydroxyl equivalent weight 500 g/mol and 1000 g/mol was obtained from Chisso Corporation. Unreacted cyclics are not present in these PDMS oligomers as determined by GPC analysis. Dibutyltin diacetate (DBTDA), 2,4-pentanedione, and ethyl 3-ethoxypropionate (EEP) were obtained from Aldrich. Polyurethane grade methyl *n*-amyl ketone (MAK) and butyl acetate (BA) were supplied by Eastman Chemical. Stock solutions of 30 wt% of PDMS in EEP, 90 wt% of PCL in EEP, and 1 wt% of DBTDA in MAK were used to prepare formulations. Other reagents were used as-received.

2.2. Coating preparation

For all formulations, 0.075% of DBTDA catalyst and 10% of 2,4-pentanedione as pot life extender were added on the basis of resin solids. NCO:OH equivalent ratio was kept constant at 1.1:1.0. In order to prepare coating formulation based on 10 wt% of PDMS, 1.67 g of 30% solution of PDMS, 1.48 g of 90% solution of PCL, 0.50 g of 2,4-pentanedione, and 0.37 g of 1% solution of DBTDA were weighed and mixed in a 20 ml vial with magnetic stirring. After thorough mixing, 4.52 g of polyisocyanate solution was added and mixed well for specified times before application. The wait time between mixing and coating application was varied from 15 min to 9 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.

2.3. Instrumentation

Atomic force microscopic (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 conditions with a set point ratio of 0.9 using silicon probes with a spring constant 0.1–0.4 N/m and resonant frequency 17–24 kHz. Topographical images of 40 μm × 40 μm are presented. Samples for IR studies were prepared by spin coating 2–3 drops of polymer solution at 1300 rpm for 15 s on KBr plates. IR studies were conducted on a Nicolet Magna-IR® 850 spectrometer. Scanning resolution was 4 cm^{-1} and 32 scans were taken to obtain each spectrum.

2.4. Software

Nanoscope 5.12r5 was used for image analysis. Grams/AI was used for FTIR data analysis. Monte Carlo simulation was conducted using DryAdd-Pro+ v 4.33 (Intelligensys Ltd).

3. Results and discussion

The formation of topographical features in a phase separated network structure is a complex phenomenon. In most cases, increasing the molecular weight of crosslinked network increases the thermodynamic driving force for phase separation [38,39].

In some cases, kinetic trapping by intermolecular covalent crosslinking reactions has been used to control the surface features of crosslinked network films [40]. In a PDMS–polyurethane (PU) system, the phenomenon of phase separation in the solid state was attributed to the difference in the solubility parameter of PDMS and the other component of the PU, such as polyether [41,42]. However, Wilkes and Yilgor have reported a substantial amount of microphase mixing with low molecular weight PDMS in PDMS–PU copolymers [43].

To understand the key variables that influence the formation of surface microdomains in the crosslinked PDMS–polyurethane system, we have previously systematically investigated the role of solvent composition, catalyst level and time of mixing prior to crosslinking in controlling the formation and size distribution of the surface microtopography [24]. Other factors such as wt% of PDMS in the formulation, molecular weight of PDMS, and the sequence of mixing the components are expected to play a role in the formation and controlling the structure of the surface microdomains.

3.1. Effect of PDMS content and MW

Preparation of the coatings to study the effects of PDMS content and its MW involves mixing of all the hydroxyl functional components with the isocyanate component. All reagents other than the polyisocyanate crosslinker were weighed and mixed in a 20 ml vial. After thorough mixing, the polyisocyanate crosslinker was added and mixed well. Coatings were drawn down onto aluminum panels after allowing the system to mix for 3 h, 4 h and 5 h when PDMS of MW 1000 was used in the formulations. These experimental times before drawdown were chosen because our previous study indicated that a minimum mixing time was required for domain formation [24]. The mixing time is defined as the time elapsed between the crosslinker addition and the drawdown; the mixing protocol is illustrated in Fig. 2. PDMS (MW 1000) content in the formulations was varied from 5% to 15% on the basis of resin solids. Following application, coatings were kept at ambient conditions for 1 day, after which they were cured at 80 °C for 45 min. AFM images of the surface topography for the formulation with 12% PDMS are shown in Fig. 3. It is evident that with 12% PDMS in the formulation a minimum mixing time of 4 h is required in order for surface domains to form.

The average size of the domains varies as a function of both PDMS amount and mixing time and this relationship is plotted in Fig. 4a. With 15% PDMS in the formulation, surface domains were not formed even after allowing a longer mixing time. Hence 12% of PDMS of MW 1000 in the formulation was considered to be the upper limit of PDMS incorporation in the formulation for the formation of a microtopographical surface. This study also revealed that after allowing 5 h of mixing the size of the domains was generally independent of the PDMS content in the formulation.

The surface area (SA) coverage of the domains may be calculated using the following equation:

$$\mathrm{SA}\ (\%) = \left[\text{Avg area of a domain}\left(\mu\mathrm{m}^2\right) \times \text{count}/1600\ \mu\mathrm{m}^2\right] \times 100$$

where 1600 μm^2 is the total area of scanning by AFM. The surface area coverage of the domains as a function of PDMS content and mixing time is shown in Fig. 4b. The surface area coverage of the domains increases with the increase in PDMS content. After 5 h of mixing, the average diameter of the domains was ~1.2 μm but the surface area covered by these domains increases from 5% to 23% as the amount of PDMS increased from 5% to 12%. Since PDMS has the lowest surface energy, PDMS-rich domains tend to have higher surface coverage as PDMS content in the formulation increases. This increase in surface coverage while the average domain size remains constant also indicates that the spacing between the domains decreases as the wt% of PDMS in the formulation increases. Coupled with the effects of solvent composition and mixing time [24], this means that the domain size and spacing can be precisely tuned.

To explore the effect of PDMS molecular weight on the formation of polymers with microtopographical surfaces, a series

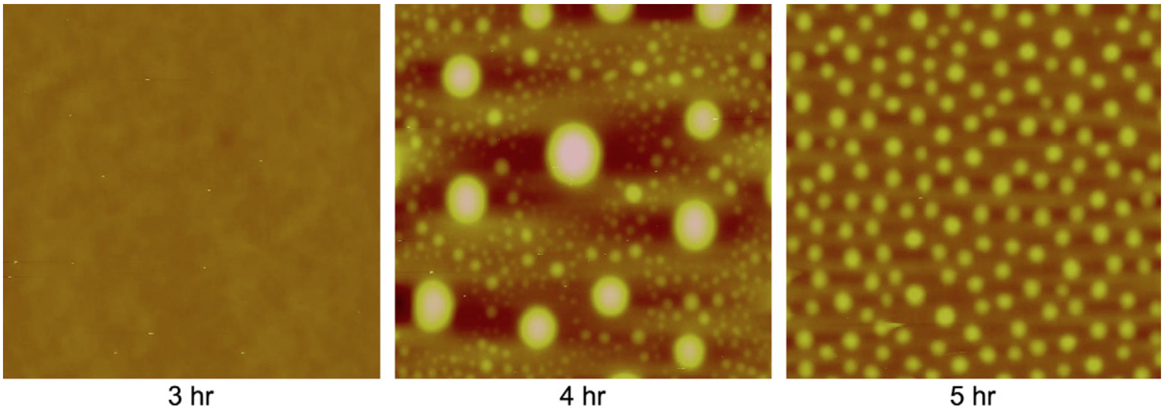


Fig. 3. AFM images of formation of the microtopographical surface with 12% PDMS in the formulation after allowing different mixing times before drawdown. AFM images were taken over 40 μm × 40 μm area.

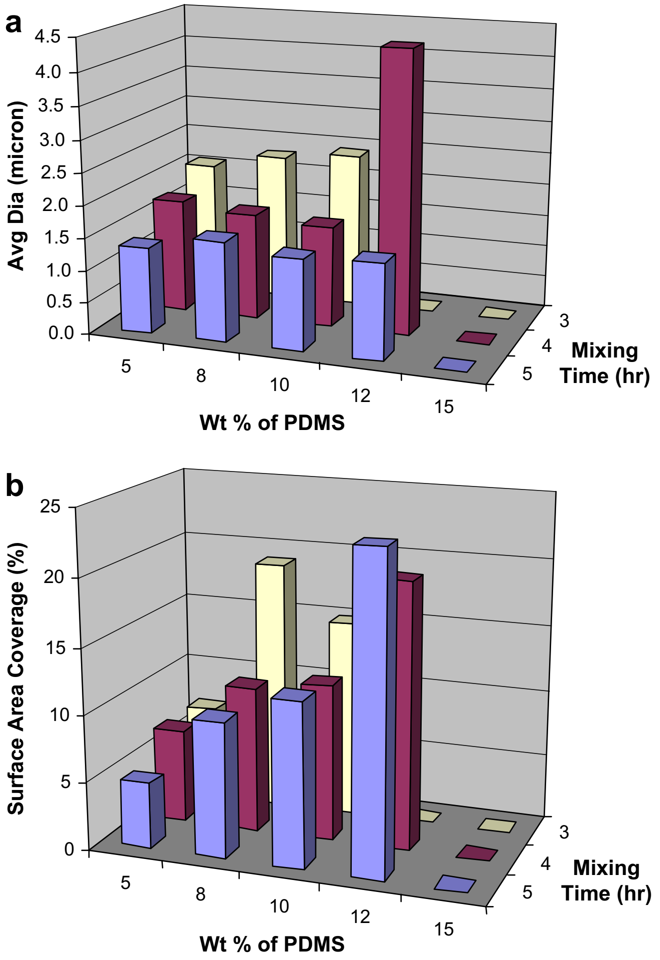


Fig. 4. (a) Average diameter of the surface domains as a function of PDMS (MW = 1000) content and mixing time in the formulations. (b) Surface area coverage by domains with different wt% of PDMS (MW = 1000) in the formulations.

of coatings were prepared using a hydroxyalkyl PDMS of MW 2000 g/mol. The wt% of PDMS (MW 2000) was varied from 5% to 12% in the formulations on the basis of resin solids. As before, a trifunctional polyol (PCL) and a polyisocyanate crosslinker (IPDI trimer) were the other components of the coating system. The time of mixing before the drawdown was varied from 2 h to overnight. The results are shown in Table 1. Surface microdomains with uniform spherical shapes were observed only with 5% PDMS (MW 2000) in the formulation and after allowing 2 h of mixing time. Microdomains with irregular spherical shapes were formed with the formulations containing PDMS up to 12 wt%. Formation of depressions was also observed along with irregular spherical microdomains. With 5% PDMS (MW 2000) in the formulation, formation of depressions was observed after 4 h of mixing and with 8–12% PDMS (MW 2000) in the formulation, depressions were observed for coatings prepared after 2 h of mixing. No microdomains were formed with 10% and 12% PDMS in the formulation after allowing overnight mixing before the drawdown.

3.2. Effect of mixing order on microtopographical surface formation

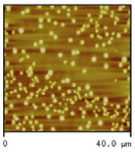
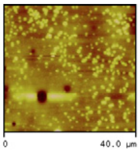
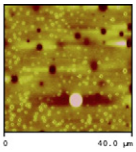
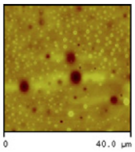
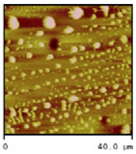
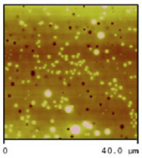
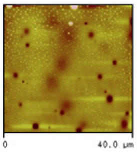
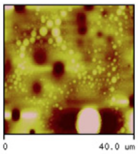
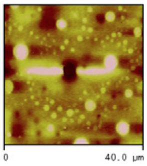
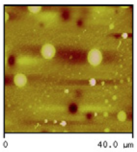
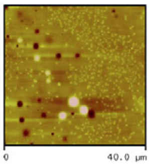
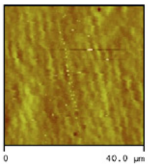
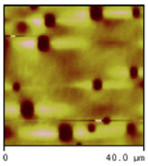
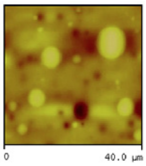
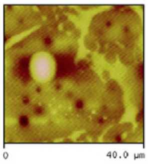
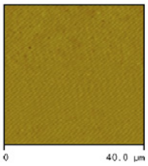
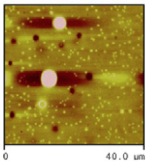
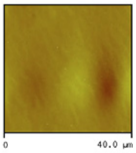
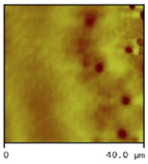
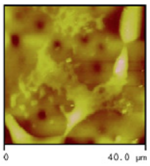
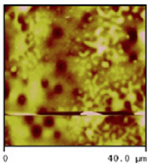
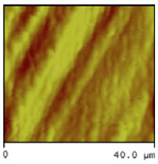
All of the previous coatings were prepared by mixing all of the reactive components in one single step as illustrated in Fig. 2. An alternate mixing method involves first mixing the hydroxyl functional PDMS with polyisocyanate and allowing this to react for a period of time to form a prepolymer, followed by the addition of the polycaprolactone polyol and mixing for another period of time before making the drawdown and curing the coating. This procedure is called the "two-step" approach and is illustrated in Fig. 5. This approach for the formation of microtopographical surfaces was conducted with 10% PDMS of MW 1000 in the formulation. The extent of the prepolymerization reaction was controlled by varying the time of mixing between PDMS and polyisocyanate. A series of prepolymers were formed with mixing times of 1 h, 2 h, 3 h, 4 h, and overnight. Trifunctional polyol was added after these mixing times and drawdowns were made over aluminum panels after allowing 15 min to 4 h of mixing.

Topographical images of the cured films were obtained by AFM. The results are shown in Table 2. Surface microdomains were formed within 15 min after the addition of polycaprolactone when the prepolymerization reactions were carried out for 2 h and 3 h. This study revealed that the extent of reaction between PDMS and polyisocyanate plays an important role in controlling the surface topography. There is a threshold value for the degree of prepolymerization after which, when polycaprolactone was added, the system spontaneously phase separates to generate a microtopographical surface. This might be due to the difference in the solubility parameter between PDMS ($14.2\ \mathrm{MPa}^{1/2}$) and polycaprolactone ($17.9\ \mathrm{MPa}^{1/2}$) [44]. Although the difference in the solubility parameter between PDMS and polyisocyanate ($21.9\ \mathrm{MPa}^{1/2}$) is also very high, PDMS is incorporated into the system as urethane linkages are formed during the prepolymerization reaction [45]. Hence at higher prepolymerization times, PDMS–IPDI becomes more compatible with PCL–IPDI and some of the IPDI trimer might act as a common linking group between PDMS and PCL. So there is less chance of formation of a phase separated structure when polycaprolactone was added after allowing higher degrees of prepolymerization (prepolymerization for 4 h and overnight).

3.3. Isocyanate conversion by FTIR

To gain further insight into the system and the reactions that are occurring during the mixing step, isocyanate conversion was measured for the formulation with 10% PDMS of MW 1000 by following the disappearance of the characteristic peak of the isocyanate group at $2257\ \mathrm{cm}^{-1}$. The integrated absorbance under the isocyanate peak was normalized against the integrated absorbance of the CH_2 groups (between $2600\ \mathrm{cm}^{-1}$ and $3030\ \mathrm{cm}^{-1}$) [31]. Three readings were taken to obtain average isocyanate conversion at a particular time. In the "one-step" approach the isocyanate conversion was measured using two different solvent compositions in the

Table 1
Domain formation with PDMS MW 2000

PDMS–OH (M_n=2000)	Time					
	2 h	4 h	6 h	8 h	10 h	Overnight
5%						Gel formation
8%						Gel formation
10%						
12%						

AFM images were taken over 40 μm × 40 μm area.

formulation. One solvent consisted of a mixture of methyl *n*-amyl ketone (MAK), ethyl 3-ethoxypropionate (EEP), and butyl acetate (BA) in a ratio of 12:43:45 as a ‘‘solvent blend’’ and the other consisted of BA only. The AFM images of the surfaces obtained at different extents of isocyanate conversion are shown in Table 3. The isocyanate conversion for the formation of microtopographical surfaces was very similar for both solvent compositions. With the ‘‘solvent blend’’ the isocyanate conversion was 22.51% and with BA as a solvent the isocyanate conversion was 18.98%. Similarly, when the isocyanate conversion exceeded 35.1% with the ‘‘solvent blend’’ and 33.29% with BA as a solvent, the system no longer phase separated to form a microtopographical surface.

The extent of isocyanate conversion in the ‘‘one-step’’ and in the ‘‘two-step’’ approaches was compared with the ‘‘solvent blend’’ as a solvent composition in the formulation having 10% PDMS. The results are shown in Fig. 6. In the ‘‘one-step’’ approach the isocyanate conversion was ∼23% after 3 h of mixing and the coating applied at this point formed a microtopographical surface. Similarly the threshold isocyanate conversion was ∼6.5% during prepolymerization before the addition of polycaprolactone for the formation of microtopographical surface. No microstructure domains were formed when isocyanate conversion was ∼15% for the prepolymerization and >35% for the polymerization in one step. Hence, there is a window of isocyanate conversion for the formation of microtopographical surfaces in the ‘‘one-step’’ and in the ‘‘two-step’’ approaches.

3.4. Monte Carlo simulation

Monte Carlo simulations were carried out in order to understand the nature of the polymer growth at the various stages of the reaction. A commercial software package, DryAdd-Pro+ v 4.33, was used for the simulation, which creates a distribution of specified reaction sites and lets these sites combine according to the user specified kinetic information, thereby simulating the individual random reaction events of a real polymerization. Since IPDI has primary and secondary NCO groups, IPDI isocyanurate contains both secondary and primary isocyanates in the ratio of 67:33, respectively. The relative rate of the reaction between the secondary isocyanate with primary hydroxyl groups is 6.3 times faster than the reaction between the primary isocyanate and the primary hydroxyl groups [46]. Hence the following relative reaction conditions were specified to study the polymerization during the

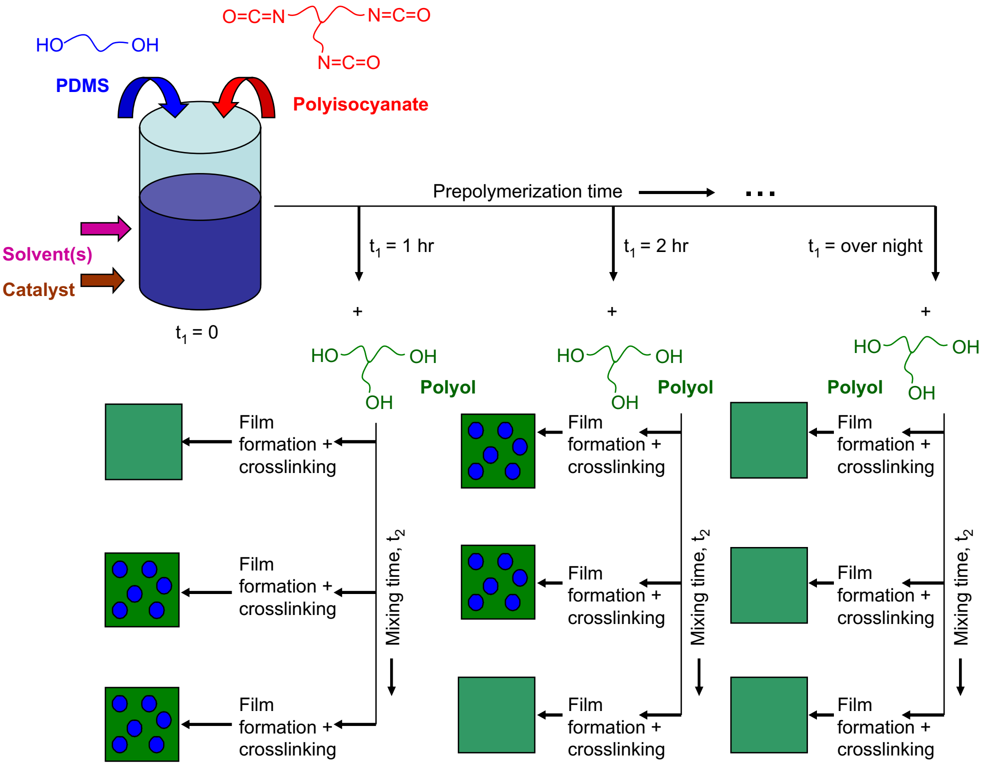


Fig. 5. The "two-step" mixing approach. PDMS and polyisocyanate are mixed first to form a prepolymer and then polyol is added and mixed before coating formation.

"one-step" approach. Here IPDI isocyanurate is designated as IDT. It was assumed that the relative rate of reactions of the hydroxyl groups, either from PDMS or from PCL, with isocyanate was the same.

$$\mathrm{PDMS{-}OH + IDT(secondaryNCO) \rightarrow urethane(relrate = 6.3)}$$

$$\mathrm{PDMS{-}OH + IDT(primaryNCO) \rightarrow urethane(relrate = 1.0)}$$

$$\mathrm{PCL{-}OH + IDT(secondaryNCO) \rightarrow urethane(relrate = 6.3)}$$

$$\mathrm{PCL{-}OH + IDT(primaryNCO) \rightarrow urethane(relrate = 1.0)}$$

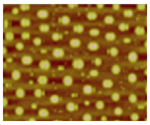
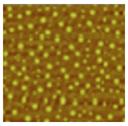
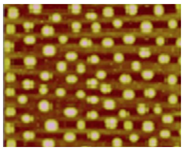
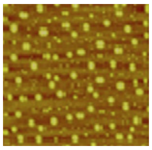
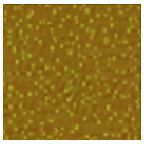
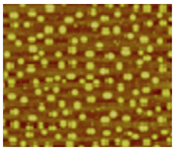
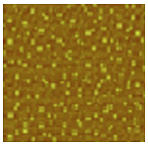
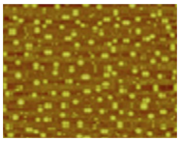
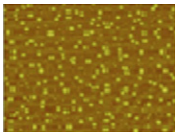
Similarly, for the "two-step" approach the first two reaction conditions were specified. The results from the simulations for the "one-step" and the "two-step" approaches are shown in Fig. 7a and b. In these figures, the percent of unreacted monomer and number average molecular weight of the polymer formed are plotted as a function of isocyanate conversion. In the "one-step" approach, the polymer is formed mainly due to reactions between the more reactive secondary isocyanate and the hydroxyl groups from PDMS and PCL. In the "two-step" approach, the prepolymer formation was dominated by the reaction between the secondary isocyanate and the hydroxyl groups from PDMS. The simulation was used to obtain an idea about the PDMS conversion during the progress of the polymerization.

PDMS conversion vs. isocyanate conversion from the Monte Carlo simulation using the two different mixing approaches is plotted in Fig. 8. The shaded boxes are drawn indicating the experimental threshold values of NCO conversion to yield surface microdomains. It is interesting that in both cases the corresponding PDMS conversion is similar, ca. 50%. Hence, the degree of reaction of PDMS with the isocyanate plays an important role in the formation of surface microdomains. A threshold conversion for both PDMS and isocyanate is required for the system to start the formation of microtopographical surfaces when crosslinked. For PDMS, the threshold value of conversion was close to 50%, and for isocyanate, the threshold value was close to 23%. At longer mixing times when PDMS conversion in solution was ~80%, the system no longer phase separates to form a microtopographical surface.

A separate simulation was performed to determine the gel point of the reaction mixture in the "one-step" approach. The gel point is reached when the isocyanate conversion is >45%. Experimentally, surface domains are not obtained when the isocyanate conversion in solution is greater than 33–35%. Thus, microtopographical surfaces were formed when isocyanate conversion in solution is in a range that is below the gel point during the solution reactions.

With the results of these experiments, coupled with some of our previous results [24], we can now begin to develop an understanding of the key factors resulting in the formation of surface PDMS domains in this crosslinked siloxane–

Table 2
Extent of prepolymerization and domain formation

PCL	Prepolymer				
	1 h	2 h	3 h	4 h	Overnight
0.25 h	No domain			No domain	No domain
1 h				No domain	No domain
2 h			No domain	No domain	No domain
3 h		No domain	No domain	No domain	No domain
4 h		No domain	No domain	No domain	No domain

AFM images were taken over 40 μm × 40 μm area.

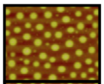
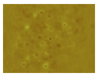
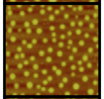
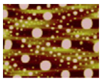
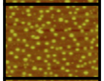
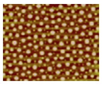
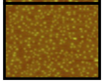
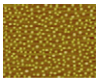
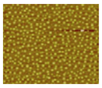
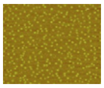
polyurethane system. First, the process used to form these materials must be reviewed. The functional PDMS, organic polyol, and polyisocyanate crosslinker are mixed in solution along with a catalyst and volatile pot life extender. While in solution, the reactive groups on PDMS and polyol can begin to react with the isocyanate crosslinker forming urethane groups. At various times during this mixing process, samples are withdrawn, deposited on a substrate where the solvents evaporate, the volatile pot life extender evaporates, additional isocyanate-hydroxyl reactions proceed and a crosslinked film is formed. There is a specific window of time during mixing in solution where the resulting crosslinked coating film develops PDMS-rich surface microdomains. We have now related this time to the degree of conversion of isocyanate. Using an alternative two-step mixing method, we have also shown that the conversion of PDMS is a critical factor in achieving a phase separated surface microstructure.

The molecular weight of PDMS is also an important factor in achieving a phase separated surface structure. In other siloxane–urethane systems, it has been found that low molecular weight PDMS (MW = 1000) is partially miscible with polyurethane [43]. Indeed, with higher molecular weight PDMS (MW = 2000), we found that the surface structure is not as well defined as with the PDMS 1000 MW and there is a more limited range of composition and mixing time which yields a phase separated surface structure.

At short mixing times, the PDMS conversion in solution is low, thus after casting and crosslinking, PDMS can readily migrate to the surface to form a continuous layer. In the appropriate "window" of conversion, at least half of the PDMS functional groups has reacted with isocyanates forming PDMS–urethane species. When the film is cast, the PDMS–urethane phase partially phase separates, however, cannot form a continuous overlayer due to constraints of molecular weight, partial reaction with the polyurethane network, and partial miscibility. At longer reaction times, PDMS is more completely reacted with the isocyanate groups and is miscible with the polyurethane network and does not form a separate phase [24]. Thus, in this situation, surface domains are not formed since PDMS is homogeneously distributed throughout the polyurethane network.

Another contributing factor is the relatively slow kinetics of this system, resulting in the ability to "catch" the system

Table 3
Extent of isocyanate conversion and surface topography

Mixing time	PDMS–OH (10%) solvent=MAK:EEP:BA		PDMS–OH (10%) solvent=BA	
	%NCO conversion by IR	AFM image (tapping mode)	%NCO conversion by IR	AFM image (tapping mode)
0.25 h	5.8 ± 0.6	↑	4.38 ± 0.6	↑
0.50 h	9.8 ± 3.3	No surface structure	4.65 ± 0.9	No surface structure
1 h	14.41 ± 3.7	↓	6.80 ± 0.5	↓
2 h	17.75 ± 3.8		11.37 ± 1.2	
3 h	22.51 ± 3.9		15.67 ± 1.2	
4 h	26.64 ± 4.8		18.98 ± 0.4	
5 h	28.95 ± 3.6		21.60 ± 1.6	
6 h	31.10 ± 4.1		26.44 ± 1.9	
7 h	35.10 ± 3.7		29.02 ± 0.2	
8 h			31.22 ± 0.7	
9 h			33.29±1.9	

AFM images were taken over 40 μm × 40 μm area.

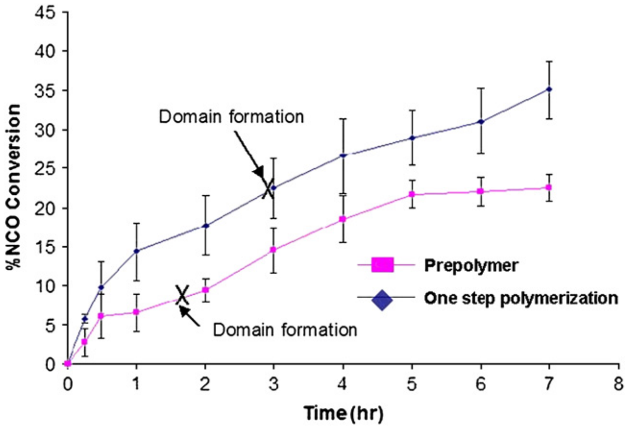


Fig. 6. Isocyanate conversion vs. time for "polymerization in two-step via prepolymerization" and "polymerization in one-step" approach.

in a stage of partial miscibility. Experiments using a more reactive PDMS (with faster reacting aminopropyl endgroups), or a faster reacting polyisocyanate (hexamethylene diisocyanate trimer), do not yield films having surface microstructure. In these cases it is believed that the reactions between PDMS and isocyanate can occur rapidly, moving the system quickly into the region where the low molecular weight PDMS is compatible with the polyurethane network.

4. Conclusions

The effects of the amount of PDMS, molecular weight of PDMS, and the extent of prepolymerization reactions on the formation of microtopographical surface domains were explored. Variation in the wt% of PDMS (MW 1000) in the

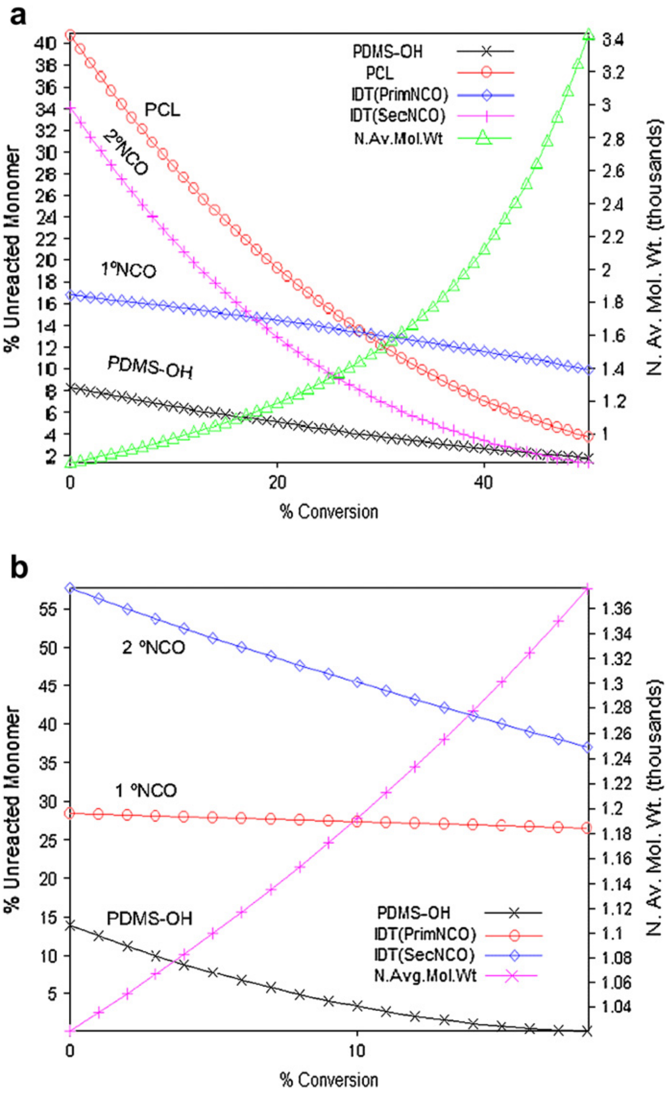


Fig. 7. Monte Carlo simulation of the polymerization in the (a) "one-step" approach and (b) the prepolymerization in the "two-step" approach.

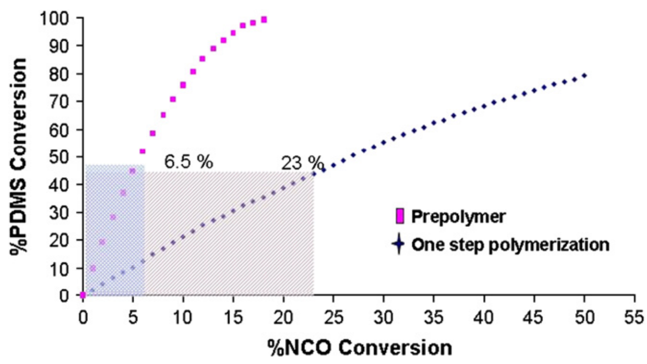


Fig. 8. PDMS vs. isocyanate conversion from Monte Carlo simulation.

formulation revealed that the microtopographical surface domains were formed with PDMS amounts of up to 12%. Although the sizes of the domains were independent of PDMS content, the surface area covered by these domains increased from 5% to 23% as PDMS content was varied from 5% to 12%. With PDMS of MW 2000 microtopographical surfaces were formed when PDMS content was varied from 5% to 12% in the formulations. However, the sizes of the domains were nonuniform. Prepolymerization between PDMS (MW 1000) and IPDI trimer could also control the formation of microtopographical surface. A minimum degree of prepolymerization was required after which, when polycaprolactone was added, the system phase separated to form microtopographical surface. Phase separated domains were not formed with longer prepolymerization reaction times. Isocyanate conversion by FTIR and Monte Carlo simulation study with the formulation having 10% PDMS on the basis of resin solid revealed that there was a window of conversion for both PDMS and isocyanate to form a microtopographical surface.

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