

# Plastic–PDMS bonding for high pressure hydrolytically stable active microfluidics

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We explore the application of organofunctional silanes for bonding plastic substrates to PDMS membranes. Such devices would enable actuated membrane microfluidics in plastic devices. Bond strength degradation in aqueous environments can be reduced by using bis-silanes with larger alkoxy end groups to promote organofunctional bond formation with the plastic substrate. Hydrolytic failure can also result from low silane crosslink density or interface hydrophilicity. A test device consisting of three-valve peristaltic pumps is fabricated out of polycarbonate (PC) and bonded to PDMS through isopropoxy modified bis-trimethoxy-silyl-propyl-amine. Valves operated up to 60 psi in aqueous environments without failure. Solutions of DI water and 1 M HCl were also pumped through the device *via* peristaltic actuation at 18 psi for 2 weeks without bond failure. 1 M NaOH was also tested but resulted in bond failure after 115 hours.

## Introduction

PDMS has greatly reduced the entrance barrier for research in microfluidics based chemistry and biology. The introduction of the elastic microvalve has led to the creation of highly integrated systems capable of automated experimentation, with examples such as whole blood PCR analysis,<sup>1</sup> microbial cell culture,<sup>2,3</sup> protein crystallization,<sup>4</sup> and multicellular manipulation and analysis,<sup>5</sup> and particle production.<sup>6</sup> However, for actuated microfluidics to transition from customized prototype devices to industrial scale device production, a transition must be made from elastomers to plastics. Plastics can be manufactured using mass fabrication technologies such as injection molding and hot embossing with well established bonding processes.<sup>7</sup> Plastics are also more dimensionally stable, rigid, and chemically resistant.<sup>8</sup>

Plastics will provide many benefits for microfluidic devices not offered by PDMS. Rigidity enables a variety of reliable external interface options, such as manifold integration, direct barbed tubing connections, and gasket connectors. Additionally, integrating flexible membranes into rigid plastics will enable a variety of new devices currently not possible in PDMS due to chip elasticity such as large area or high pressure membrane deformation, on-chip pressure regulators, full volume pumps, and reliable square channel membrane valve particle filters.

Few technologies exist for bonding PDMS to plastics, notably CVD processes<sup>9,10</sup> or silane/silicate coatings.<sup>11,12</sup> Also, data on bond strength in aqueous and chemically harsh environments is not available for the published processes. A bonding process which can demonstrate bonds on low temperature plastics with long term hydrolytic stability is critical for the creation of plastic devices with active membranes. This process would enable active microfluidic devices inside dimensionally stable systems, merging the functionality of PDMS with established plastic mass fabrication technologies.

## Bonding technologies

Bonding between PDMS and plastics for fluidics requires interfaces which can handle high pressure and harsh chemical environments. Typical pressures for total valve closure lie between 5 and 15 psi. Of all possible properties of bond strength, hydrolytic stability is particularly important for reliability since cell growth, chemical synthesis, and protein crystallization, to name a few, all rely on aqueous environments with varying chemistries.

While direct bonding between PMMA and PDMS has been explored,<sup>13</sup> results indicated that interfaces only withstood 2.5 psi before failure. Bond strength can be improved through an intermediate layer, such as a deposited film of glass. Two major methods have been attempted for intermediate layer deposition, direct deposition of glass onto the plastic surface<sup>14</sup> and organofunctional-silane deposition.<sup>12,15</sup>

Direct glass deposition processes are high temperature or plasma activated, which can lead to plastic substrate breakdown. In addition, direct glass deposition onto plastic substrates leads to bonds which hydrolyze readily upon exposure to moisture. The idea of using an intermediate coating containing an inorganic oxide or an organo-functional-silane to improve bond characteristics between organic and inorganic substrates is also not new. In fact, multiple primer compositions for improving adhesion already exist and are sold commercially, with one specifically for Sylgard 184 under the name Dow Corning 92-023 Primer, which contains a titanium alkoxide and allyltrimethoxysilane. However, bond chemistry between this primer and organic surfaces is non-ideal due to oxygen coupled bonds and the lack of long-term hydrolytic stability in aqueous environments, with the majority of the primer consisting of a titanium alkoxide, which readily absorbs water molecules.<sup>16</sup>

More hydrolytically stable silane bonding systems have been explored for plastics, namely APTES to polycarbonate (PC) and PMMA surfaces to improve the adhesion of sol-gel coatings.<sup>12</sup> It was shown that PC surfaces react with amine groups of amino-propyltriethoxysilane (APTES) to form amide bonds on the

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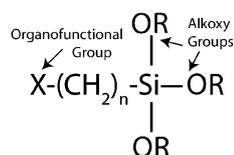
surface directly. Since amide bonds are hydrolytically stable over a wide pH range, from  $-1$  to greater than  $15$ , amine functional silanes are excellent candidates for surface coatings. Bonding of these coatings to PDMS have also been demonstrated,<sup>15</sup> but hydrolytic stability was not tested. Identifying the processes which cause hydrolytic failure in silane coatings will aid in developing silane compositions and process conditions necessary to ensure hydrolytic resistance.

## Silanes and bond failure

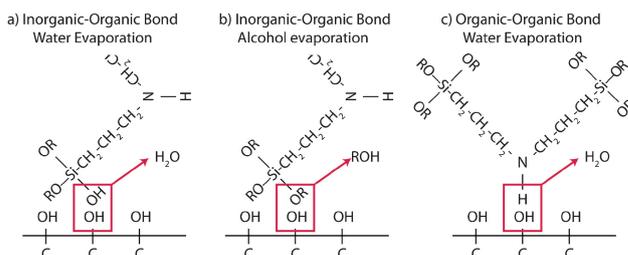
To understand the mechanisms for hydrolysis induced bond failure, an overview of silanes is necessary. An organofunctional silane is a silicon atom with at least one bond to carbon to enable organic functionality as shown in Fig. 1.

The inorganic side of the silane molecule consists of a silicon atom bound to alkoxy groups through Si–O–C linkages. Commercially, the hydrolytic instability of these bound alkoxy groups allows silanes to hydrolyze in the presence of water, converting the bound alkoxy groups to hydroxyl groups while liberating alcohol molecules. These hydrolyzed silanes can then be used in sol-gel processing, condensing onto hydroxyl containing surfaces or with each other to form substrate bound films. Since the silane matrix looks similar to glass, it is an excellent candidate for plasma bonding to PDMS.

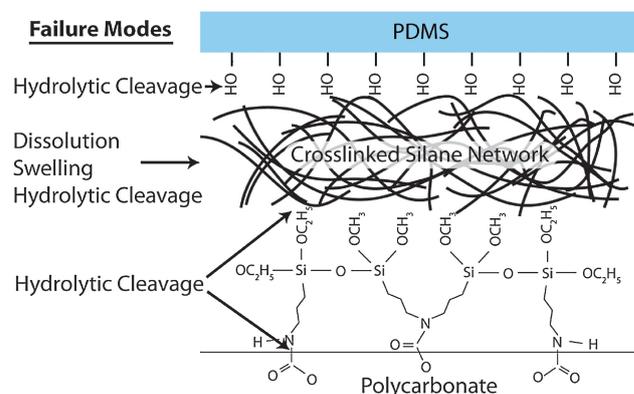
While amine functional silanes have been demonstrated to react directly with certain substrates such as PC and PMMA, prolonged treatment times necessary to generate a reasonable surface bond density as well as substrate selective chemistry make such a process not generally useful.<sup>12</sup> As such, surface activation such as plasma or chemical treatments will be required. In general, these activated organic substrates will contain bound hydroxyl, carboxyl, or other ionic groups which promote hydrogen or ionic bonding of silanes to the organic surface. For activated organic substrates, silane alkoxy group hydrolysis into silanols poses a major problem. While bonding between the silanol group and surface hydroxyl groups is desired for coupling silanes to glass or oxides, bonds formed with organic substrates generate Si–O–C bonds, which are hydrolytically unstable (Fig. 2a). These are the same bonds formed between the silicon molecule and its original alkoxy group, which are meant to hydrolyze readily in water. Any contact with water after bond formation will result in Si–O–C bond hydrolysis and ultimately bond failure. Furthermore, Si–O–C bonds have also been found to form directly between alkoxy groups such as methoxy and surface hydroxyl groups *via* alcoholysis<sup>17</sup> (Fig. 2b). In order to achieve hydrolytically stable bonds between silanes and organic surfaces, bonds must be formed through reactions between the organofunctional groups (nitrogen containing) of the silane molecules and the organic surface (Fig. 2c). Two



**Fig. 1** Chemical structure of a typical silane molecule. A carbon–silicon bond allows organic functional groups to be covalently linked to silicon.



**Fig. 2** Different methods of bond formation between organofunctional silanes and organic substrates. Inorganic–organic bond formation can occur through water (a) or alcohol (b) evaporation, generating Si–O–C bonds. Organic–organic bond formation can also occur through water evaporation (c).



**Fig. 3** Different bond failure mechanisms for silane bonding between organic substrates and PDMS. The PDMS–silane interface, the PC–silane interface, and the silane network are all vulnerable to hydrolysis.

bonding experiments will show that this bond mechanism can be increased by attaching sterically bulky groups to the silicon atom, inhibiting alcoholysis and hydrolysis.

In addition to the organic bond between the organofunctional-silane and the organic surface, other processes contribute to bond stability. Hydrolytic bond failure can occur at three locations in the bonding structure, at the PC–silane interface, at the PDMS–silane interface, and in the silane network itself as shown in Fig. 3. While direct interface hydrolysis is unlikely due to the stability of the amide bond, any hydrophilic groups at the interface can act as nucleation sites for water condensation, allowing the silane network near the interface to be plasticized and weakened.<sup>17</sup> A similar process can occur at the PDMS–silane interface but with the possibility of hydrolysis directly at the interface in addition to the weakening of the silane network. For the silane network itself, high crosslink density can provide a major increase in resistance. However, networks formed by typical silanes, containing three silanol groups, tend to be cyclic, decreasing their resistance to dissolution.<sup>17,18</sup> Addressing failure mechanisms in all three locations is necessary to ensure hydrolytic stability.

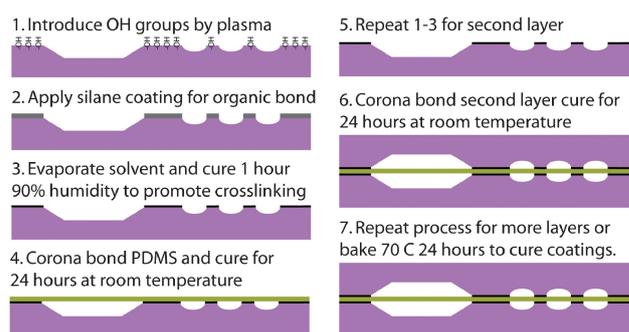
## Materials and methods

Isopropanol and titanium butoxide catalyst were purchased from Sigma Aldrich. Silane molecules amino-propyl-triethoxy-silane

(APTES), bis-trimethoxy-silyl-propyl-amine (BTMSPA), bis-triethoxy-silyl-propyl-amine (BTESPA), and bis-triethoxy-silyl-ethane (BTESE) were purchased from Gelest Inc. Preparation of silane solutions involved mixing 5% weight silane in isopropanol. Transesterification of BTMSPA into BTISPA products was prepared by mixing 5% weight silane solutions in isopropanol with 0.5% weight tetrabutyl titanate (TBT) and aging in ambient conditions for a minimum of 2 weeks.<sup>†</sup> While partial transesterification rather than complete replacement of methoxy with isopropoxy groups results, hydrolytic resistance is still improved.<sup>19</sup> Transesterification without TBT as a catalyst also proceeds, but takes significantly longer. Hydroxyl modified APTES (APTHS) was prepared by mixing 5% weight APTES in water and aging for 1 hour, generating a clear solution. Hydroxyl modified BTMSPA (BTHSPA) was prepared following manufacturer directions, by mixing a solution of 95% ethanol and 5% water adjusted to pH 5 with acetic acid and then adding 5% weight BTMSPA into the solution. Due to the instability of this solution, coatings were carefully applied before precipitation. Glass coatings were PECVD deposited on PC to 200 nm thickness.

PC samples purchased from McMaster Carr under the trade-name Makrolon were first machined using a mill to create test structures. Samples were then cleaned with isopropanol followed by mild corona discharge (5 to 15 seconds) to promote surface activation. Prolonged activation with corona discharge or activation with an oxygen plasma chamber was not used due to noticeable plastic and silane degradation and over-generation of hydrophilic groups. Mixed silane solutions were then wiped onto the corona activated surface with a cуетip and the solvent was allowed to evaporate. For “monolayer” coatings, the coated surfaces were again rinsed thoroughly with isopropanol after initial coating to remove any unbound silane molecules from the surface. A second silane coating consisting of BTESE was then optionally applied to form the crosslinked over-coating. After allowing for solvent evaporation, coated surfaces were placed into a high humidity environment (>90%) at 70 °C for 30 minutes to 1 hour to cure the coating. After curing, the layers were exposed to corona again, and bonded to a corona activated cured PDMS layer. The PDMS layer is prepared by spin coating PDMS onto a 3M high temperature transparency (PP2950) and baking at 70 °C for 4 hours. Bonded samples are cured at room temperature for 24 hours to ensure full siloxane bond formation without thermal stress induced delamination. Ambient cure is necessary since the initial bonds formed between the PDMS and silane layer can be separated.<sup>20</sup> Subsequent layers are then coated and bonded with the same procedure. The chip is then baked at 70 °C for 24 hours to accelerate hydrophobic recovery. A detailed illustration of the bonding process is given in Fig. 4.

<sup>†</sup> Solutions aged for longer times gave better results, and it is suggested that partial polymerization of silane molecules due to contact with water occurs. Partial polymerization in solution likely increases overall crosslink density after coating. It is also speculated that if polymerization is required, direct addition of water to the solution can reduce aging times, provided that the water concentration is kept low enough not to cause gelation. While we have seen that adding water to BTMSPA solutions causes gelation, transesterified solutions are much more stable, making this a possible alternative to aging.



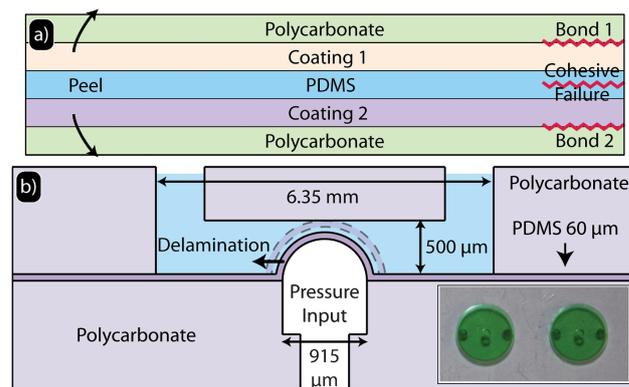
**Fig. 4** Fabrication process for bonding PC to PDMS using silane coatings. Curing and annealing steps are intentionally prolonged to ensure bond formation and hydrophobic recovery.

While curing and annealing steps can be shortened significantly, 24 hours ensured bond formation without complications.

Acid and base testing was performed using 10 M HCl and 10 M NaOH subsequently diluted to reach different pH values.

## Results and discussion

To test the effectiveness of the silanes for coupling PC to PDMS, peel test and blister test structures were used as shown in Fig. 5. For peel tests, PC-PDMS-PC stacks were bonded utilizing two different coating compositions on either side of the PDMS membrane as shown in Fig. 5a. Peel tests were performed by pulling apart the PC pieces and observing failure location. For blister tests, PDMS membranes are bonded between a layer of PC with 915  $\mu\text{m}$  diameter holes and a layer of PC with 16  $\mu\text{L}$  fluid reservoirs. This blister test structure simulates a microfluidic valve deflecting into an aqueous environment. As is typical for peristaltic valves, the critical bond interface between the PDMS membrane and the PC is separated from the fluid by the membrane. This enables testing bond strength as seen in the device, where liquids must diffuse through the PDMS to reach the bond interface of the actuation layer. Interface bond strength was first measured in air to determine bond strength. Wet



**Fig. 5** (a) Schematic of the bond stack used for peel tests. PC layers are bonded to a PDMS membrane using silane coatings on either side. (b) Schematic of the aqueous blister test structure used to test hydrolytic bond failure. Suspended PDMS membranes were 60  $\mu\text{m}$  thick and 915  $\mu\text{m}$  in diameter. A picture of a fabricated blister test structure with the wells loaded with green dye is shown in the inset.

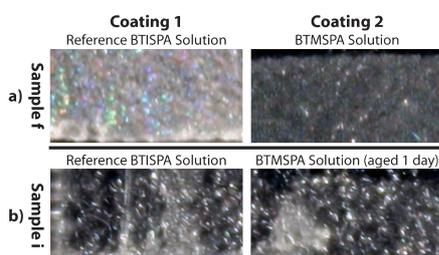
strength was then tested under different conditions to determine the effects of interface and silane chemistry on hydrolytic resistance. Finally, peristaltic pumps are fabricated and tested for long term reliability in acidic, basic, and neutral environments.

### PC–silane interface bond strength

In order to determine bond strength at the PC–silane interface, differential measurements of dry bond strength for different coating compositions are compared. In general, coating 1 is a reference coating consisting of BTISPA (BTMSPA aged for 2 weeks) which is known to have strong adhesion. Possible failures occur either at the PC–silane interfaces, or within the PDMS, since the plasma bonded interface between the coating and PDMS is not expected to fail in dry environments. Cohesive failure within the PDMS would indicate that bond strength is greater than the tensile strength of PDMS, or 1000 psi.

Large alkoxy end groups on silane molecules are critical to achieving high bond strength. Small end groups, such as methoxy for BTMSPA, react directly with surface hydroxyl groups to form bonds *via* alcoholysis.<sup>17</sup> As a result, a majority of weaker Si–O–C bonds are formed in comparison to silanes with larger alkoxy end groups. Sterically reducing alcoholysis by replacing methoxy groups with larger alkoxy groups will preferentially select for organofunctional bonding at the interface when silane coatings are applied. To demonstrate this process, a peel test between a newly mixed solution of BTMSPA in isopropanol and the reference BTISPA (Fig. 6a) is compared to a peel test for the same BTMSPA solution aged for 1 day and the reference BTISPA (Fig. 6b). While very difficult to peel, the BTMSPA coating from a new solution completely delaminates, as can be seen from the rainbow appearance indicating the BTMSPA coating is attached to the PDMS. In contrast, the BTMSPA coating aged in isopropanol for 1 day fails cohesively within the PDMS. This is an indication that interface bond chemistry is altered by isopropoxy transesterification of BTMSPA.

Similar peel tests were performed for a variety of coatings containing BTMSPA with exchanged end groups as well as for PECVD SiO<sub>2</sub> coatings. From the results shown in Table 1, cohesive failure occurs for coatings as alkoxy end groups become larger, with the minimal alkoxy group being ethoxy for cohesive



**Fig. 6** (a) A peel test (Table 1f) between newly mixed BTMSPA in isopropanol and a reference solution of BTISPA (BTMSPA aged for 2 weeks). The BTMSPA layer is completely removed from the bottom PC surface and bonded to the PDMS giving a rainbow appearance. (b) A peel test (Table 1i) with the same BTMSPA solution in isopropanol aged for 1 day and the reference BTISPA solution. Aging the BTMSPA solution for 1 day results in greatly improved bond strength. Peel tests result in cohesive failure and PDMS bonded on both PC sides.

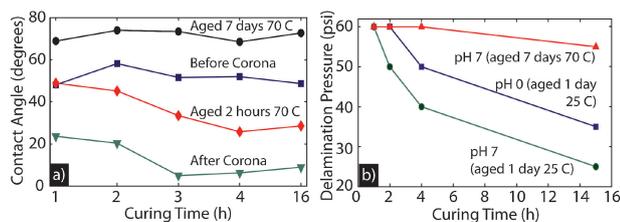
**Table 1** Summary of bond failures for differential peel tests. S is the sample type, B1 is bond 1 failure, B2 is bond 2 failure, and C is cohesive failure as given in Fig. 5a. Stronger coatings are listed as coating 1 and the weaker coating as coating 2. Delamination at bond 2 is apparent for all coatings with small end groups on the silane molecule. Failure at bond 2 for BTESE for sample (g) and success for sample (h) shows that bond strength is contributed by the amine functional group

	S	Coating 1 (end group)		Coating 2 (end group)		Failure		
		B1	B2	C				
Increasing End Group Size →	a	BTESPA (Ethoxy)	BTMSPA (Methoxy)			X		
	b	BTISPA (Isopropoxy)	PECVD SiO <sub>2</sub>			X		
	c	BTISPA (Isopropoxy)	APTHS (Hydroxyl)			X		
	d	BTISPA (Isopropoxy)	APTES (Ethoxy)					X
	e	BTISPA (Isopropoxy)	BTHSPA (Hydroxyl)			X		
	f	BTISPA (Isopropoxy)	BTMSPA (Methoxy)			X		
	g	BTISPA (Isopropoxy)	BTESE (Ethoxy)			X		
	h	BTISPA (Isopropoxy)	BTESPA (Ethoxy)					X
	i	BTISPA (Isopropoxy)	BTISPA (Isopropoxy)					X

failure. Tests comparing the bond strength of a non-functional silane BTESE (Table 1 sample (g)) *versus* its functional equivalent BTESPA (Table 1 sample (h)) also confirm the amine contribution to bond strength when large alkoxy groups are present. Bond failures for PECVD glass coatings, hydrolyzed silane coatings, and methoxy coatings (Table 1 samples (b), (e), (f)) demonstrate the reduced strength of Si–O–C bonds. Upon exposure of methoxy, hydroxyl, and SiO<sub>2</sub> coatings to water at 70 °C for 2 hours, complete delamination occurs at pressures less than 45 psi (data not shown), below the membrane rupture pressure of 60 psi. These failures demonstrate the hydrolytic instability associated with Si–O–C bonds at the interface. For operation of valves in aqueous solutions, coatings using silanes with larger end groups are necessary to increase the probability of interface amide bond formation.

### Interface hydrophobicity

The PDMS–silane interface is also vulnerable to hydrolytic failure. The rate of hydrophobic recovery from corona treatment in relation to curing time can be seen from contact angle measurements shown in Fig. 7a. After aging for 2 hours at 70 °C, samples exposed to corona treatment with longer curing times recovered their hydrophobicity slower. This hydrophobic recovery is correlated with interface hydrolytic resistance in Fig. 7b by measuring the delamination pressure *versus* curing time before corona treatment. Bonds with longer hydrophobic recovery result in lower delamination pressures when exposed to a 2 hour aqueous bake at 70 °C. In agreement with previous work,<sup>17</sup> acidic conditions are more resistant than neutral conditions, demonstrating that failure is caused by hydrolysis of Si–O–Si bonds. All silane coated surfaces eventually recover their hydrophobicity as well as improve their hydrolytic resistance, as demonstrated by both the contact angle recovery and the delamination recovery after baking bonded samples for one week at 70 °C. Interestingly, for the coating which was cured for 15 hours before bonding, 1 week of hydrophobic recovery still did not result in recovered hydrolytic resistance. This could be an indication that the film has not recovered, or a small degree of

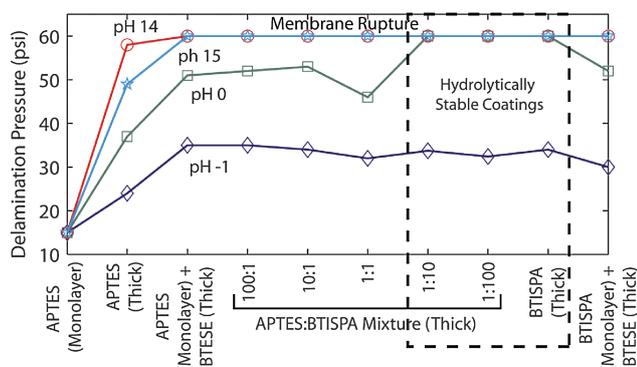


**Fig. 7** (a) Water contact angles before and after corona treatment of cured silane layers. Hydrophobic recovery is slower for samples with prolonged curing times. (b) Delamination pressure of blisters after a 2 hour water bake at 70 °C. Samples are bonded with corona treatment to PDMS after specified silane curing times. Delamination pressure decreases for samples bonded after longer curing times, but improves after aging bonded structures for 1 week at 70 °C. Similar behaviors of contact angle and delamination pressure suggest that interface hydrophobicity plays a major role in hydrolytic resistance.

hydrophilicity was permanently introduced. To prevent premature device failure, corona treatment must be initiated before the silane layer is fully cured and bonded chips should be aged until full hydrophobic recovery is achieved.

### Crosslink density and hydrolytic resistance

To determine the effect of bis-silanes on hydrolytic resistance, coatings utilizing different ratios of large alkoxy end group bis and regular silanes were explored. Monolayer coatings are not resistant to any aqueous conditions, most likely due to the inability to recover from corona treatment induced hydrophilicity. For thick coatings, all coatings containing bis-silanes have improved hydrolytic stability as shown in Fig. 8. As the concentration of BTISPA to APTES in the coating solution is increased, hydrolytic resistance improves over a wider pH range. This behavior saturates to hydrolytically stable bonds over a range of pH 0 to pH 15 when BTISPA is the majority of the mixture. Increased hydrolytic resistance can be attributed to the greater crosslink density for bis-silanes.<sup>17,21</sup> Samples which fail only at pH -1 are strongly suggestive of amide bond formation, since Si-O-C bonds would likely delaminate at more mild pH. To further demonstrate the importance of bis-silane addition, two step coatings consisting of APTES or BTISPA as the organic-inorganic bonding layer and BTESE as the crosslink



**Fig. 8** Plot of the delamination pressure *versus* primer type at pH extremes. Dotted area shows coatings that were stable from pH 0 to pH 15. Optimal hydrolytic stability occurs when coatings contain a majority of BTISPA, with failure only occurring at pH -1.

layer also show improved hydrolytic resistance *versus* APTES coatings. This suggests that two step coatings can be used when bis-silanes with appropriate organic functionality are not available.

### Criteria for hydrolytic stability

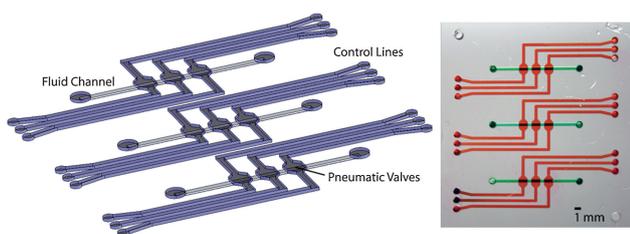
Bond strength tests reveal three major conditions for hydrolytically stable bond formation. First, dry peel tests demonstrate that strong organo-silane bonding to corona activated organic substrates such as PC require bonding from the organo-functional side of the silane molecule. This is accomplished by using silanes with bulky alkoxy groups bound to the silicon atoms, such as ethoxy or isopropoxy, to inhibit siloxane bond formation and promote organic bond formation. Second, hydrophobicity at the bond interface helps prevent bond hydrolysis and failure by preventing nucleation sites for water condensation at the interface. Corona bonding before the silane network is fully cured or post-baking at elevated temperature allows free hydrophilic groups to crosslink or diffuse away from the interface. Lastly, silane crosslink density is important for stability of the crosslinked network. Increased crosslink density is achieved through the use of bis-silanes which contain six available silicon bonds in comparison to three on regular silanes.

These three conditions are met following the fabrication process in Fig. 4 and utilizing a coating solution of 5% wt BTISPA in isopropanol with 0.5% wt TBT. Bonds from this coating are stable up to membrane rupture at 60 psi from pH 0 through pH 15. Interestingly, while NaOH even at concentrations as low as 1 M etched PC on the liquid side of the device during blister testing, the silane-PDMS layer protected the valve interface from similar attack, even at 10 M NaOH concentrations. Therefore, PC-silane-PDMS stacks could be used for improved resistance to NaOH solutions.

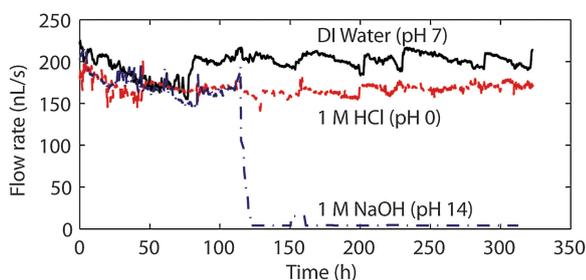
### Reliability testing

This process allows for bonding an arbitrary number of plastic layers separated by PDMS membranes, making multiple active layers in a single device possible. Since bonds are stable to high pressure, direct integration of manifolds and fluidic interfaces are also possible. To test the reliability in a working microfluidic system, a test chip consisting of three valve peristaltic pumps is fabricated as shown in Fig. 9. External lines are connected with PTFE tubing and epoxy to prevent chemical reactions with interface materials.

Reliability testing is performed by monitoring flow rate for each pump over the course of 2 weeks continuous operation at room temperature and 1 M HCl (pH 0), DI water (pH 7), and 1 M NaOH (pH 14). Higher concentrations of acid and base were not attempted since bond experiments showed that 10 M HCl resulted in interface bond failure and 10 M NaOH readily etched PC. The pumps were cycled with 5 states, (OOX, XOX, XOO, XXO, OXX), where X is a closed valve and O is an open valve, at a cycle period of 500 ms and a pressure of 18 psi to generate one unit of flow. Flow rates were measured by weighing the collected outflow with a scale for every 50 injection cycles. The plot of average flow rate for 1000 cycles *versus* time shown in Fig. 10 demonstrates peristaltic pump reliability in high molarity acidic



**Fig. 9** Schematic and picture of the test device fabricated in PC utilizing a 60  $\mu\text{m}$  PDMS membrane to provide pressure based actuation valves. Control lines are 500  $\mu\text{m}$  wide and 250  $\mu\text{m}$  high. The fluid channel is 125 to 150  $\mu\text{m}$  deep with a radius of curvature of 400  $\mu\text{m}$  with a 1.6 mm valve length. Variation in depth results from machining inaccuracies.



**Fig. 10** Plot of the flow rate *versus* time for three different peristaltic pumps flowing different pH solutions at 18 psi. Pumping rate is 1 cycle every 500 ms. Marginal decrease in flow rate over the course of the experiment demonstrates long term bond reliability.

and basic conditions for 2 weeks. Variations in actual flow rates are caused by stagnant bubbles introduced through valve pressurization. While DI water and 1 M HCl are stable for 2 weeks, NaOH at 1 M leads to device failure after 115 hours. As observed for blister tests, this failure occurs at the fluid layer PC–silane interface and has no effect on the control layer bond interface. Failure could result from either dissolution of the silane in contact with NaOH, or etching of the PC. Therefore, other plastic materials or measures to reduce direct contact between NaOH solutions and the PC–silane interface are necessary if long term exposure to NaOH is required.

## Conclusion

Migration from PDMS to plastics for microfluidics requires integration of flexible membranes into plastic devices for valve functionality. Organo-functional silanes provide a class of molecules capable of forming reliable bonds between plastics and silicon containing elastomers for valve applications. However, for bonds to be stable to hydrolysis, bond chemistry, interface hydrophobicity, and silane crosslink density must be addressed to prevent hydrolytic attack and premature valve failure. For a generally useful bonding process, dependence of bond strength on substrate and silane chemistry should be reduced. To achieve this generality, the developed bonding process uses corona treatment to introduce reactive groups on plastic surfaces and sterically hindered functional silanes to increase the probability of forming organic bonds with those reactive groups. While not shown, the same process has also been applied to PMMA and

polystyrene with similar results, suggesting that the bonding process could be applied to a variety of different plastics. By optimizing the hydrolytic stability for silane coatings on PC surfaces, we have shown that plastic–PDMS devices consisting of peristaltic pumps can be fabricated and operated at 18 psi in 1 M NaOH, with failure after 115 hours, and in 1 M HCl and DI water with no failure after 2 weeks. These time scales are compatible with many single use microfluidic experiments such as PCR, cell culture, and particle/cell manipulation. This process enables a variety of new devices which can take advantage of both the rigidity offered by plastics and the flexibility offered by elastomers.

## Acknowledgements

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