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Interface-Engineered Solid-Liquid Polymer Systems

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ABSTRACT

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This thesis explores the optimization and design of novel materials by engineering interfaces to impart novel mechanisms to polymer composites and multi-phase materials. By taking advantage of chemical and mechanical interactions it is possible to create materials with novel properties and unique mechanisms such as self-stiffening, self-healing, and adhesion. These properties arise due to large electronegativity differences which are repeated throughout the polymer chains which in turn give rise to strong macroscopic effects. The addition of a dynamic interface, an interface which can move and adapt under varying stress conditions, further enhances the unique properties of these materials. The composites discussed in this thesis were synthesized using a variety of techniques including thermal sonication/chemical synthesis, and mechanical synthesis. These novel composites were characterized using a myriad of techniques such as dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray computerized tomography (CT), in-situ scanning electron microscopy-based (SEM) mechanical testing, tensile testing (ADMET frame), SEM, transmission electron microscopy (TEM), contact angle (CA), optical microscopy, and qualitative testing.
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<td>Polydimethyl siloxane</td>
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<td>PTFE</td>
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Chapter 1

Introduction

In the past, composite creation has focused on the use of fiber reinforcement, particle reinforcement, as well as the addition of multiple fillers\textsuperscript{1-3}. However, many of these approaches look at building stronger materials from a macroscopic point of view, going from the macroscale and letting the nanoscale interactions sort each other out.

Recently, there has been a large shift away from these methods and towards the use of interfaces to enhance materials\textsuperscript{4,5}. These methods attempt to use surface groups and functionalization to enhance the interfacial strength of the material. Surprisingly, work by Style et al. has shown that the use of liquid inclusions can strengthen materials\textsuperscript{6}. This goes against the general rule of mixtures and Eshelby theory which states that a mixture of two phases in equal parts should yield a material with proportional strength. Liquids are considered to have a Young’s modulus of zero, hence, any material mixed with a liquid should have a lower
Young's modulus. Style et al. showed the opposite of this tends to happen. Due to strong surface tension interactions, the liquid filler increases the strength of the overall composite. As the material with the liquid filler is compressed or pulled the liquid will resist the deformation and increase the resistance to that stress. Thus, the liquids' natural desire to remain in its lowest energy state, a sphere, increases the overall strength of the material. The equation that describes the overall relation is as follows:

\[ E_c = E_m V_m + E_p V_p \]

Equation 1.1 – Rule of Mixtures.

In the above equation, \( E_m \) refers to the elastic modulus of the matrix and \( V_m \) is the volume fraction of the matrix whereas \( E_p \) and \( V_p \) refer to the elastic modulus and volume fraction of the filler, respectively. While both matrix and filler substantially affect the properties of materials, interface plays an equally important role. Most composite interfaces are solid-solid, boundaries between two solid components, while liquid-solid interfaces are much more rare and interesting. Solid liquid interfaces give rise to novel stress mitigation properties due to the liquid phase and give rise to properties such as adaptability within materials. By using liquid fillers and interfaces it is possible to synthesize novel composites that display an array of unique behaviors including self-stiffening.

Self-stiffening behavior is a new type of behavior that has only recently started being discussed by authors such as Carey et al.\textsuperscript{7} and Agrawal et al.\textsuperscript{8} This
behavior is particularly interesting since the materials tend to become stiffer upon constant external stresses. This type of behavior has been shown in composites with polydimethylsiloxane (PDMS) as well as others containing liquid crystal elastomers (LCEs)\textsuperscript{7,8}. However, this behavior is hypothesized to arise in response to re-orientation or elastic effects, both of which may be equally true. Thus, the synthesis of new systems that exhibit this behavior is rather complex.

1.1. Polymer Synthesis

There are many ways to synthesize polymers ranging from extrusion to solvothermal or purely mechanical methods. Each method has its own drawback, however, in this section I will focus on solvothermal and mechanical methods of synthesis.

Solvothermal synthesis is the use of solvents, generally theta solvents, to dissolve the polymer/composite and once a homogenous mixture is formed the polymer/composite is cast onto a surface and then a thermal anneal is applied to remove the excess solvent. One of the main drawbacks of this type of methods is that it can lead to delamination if the drying process is not done correctly. This happens due to the presence of excess solvent and is especially critical in aerospace applications where conditions can cause critical failure of the material. To avoid this problem, researchers employ thermogravimetric analysis (TGA) to check for remaining solvent. This is done by taking a piece of the polymer/composite and running it through a thermal sweep at a slow rate (<10 °C/min). The thermal sweep
needs to reach a temperature higher than the boiling point of the solvent that was used. Thus, the TGA will measure the change in weight due to the loss of the solvent and it will be able to tell you if the drying process was successful or not.

Although solvothermal synthesis seems simple, there are a few key informed decisions that need to be made so the process can be successful. When making polymer blends, mixtures of 2 or more polymers, it is critical that the chosen solvent dissolves both polymers. Additionally, some polymers cannot be easily dissolved in solvents and thus cannot be used with this method. It is also important to make sure that the polymer is miscible in the solvent, as well as miscible with the other phases used in the mixture.

Another important method to discuss is mechanical mixing. This can be achieved by using a screw extruder (melt mixing) or by hand, in some cases. The advantage of this method is that the drawbacks of using solvents will no longer be an issue. In addition, this method is very straightforward and can be applied to many different polymers and composites. Physical mixing (by hand) does not work with many different materials and can have several drawbacks including inhomogeneity and aggregations, depending on mixing times and percentages. Thus, when mixing things by hand it is important to carefully characterize the final product for consistency. On the other hand, using a screw extruder is very simple, however, it generally requires using temperature to melt one of the components and add a secondary phase. This is akin to melt mixing and is a commonly used technique both in research and industry.
1.1.1. Polyvinylidene fluoride (PVDF)

Polyvinylidene fluoride (PVDF) is a polymer made up of C, F, and H atoms, \([\text{C}_2\text{H}_2\text{F}_2]^n\). The polymer has four known phases: \(\alpha\), \(\beta\), \(\gamma\), and \(\delta\). There are no structural differences between these phases, however, the orientation differences lead to vastly different piezo, pyro, and ferroelectric properties. These properties are generally more prevalent in the \(\beta\)-phase of the polymer. Generally, the polymer is received in \(\alpha\)-phase, however, it can be converted to \(\beta\)-phase in several ways including strain, and solvent processing. By straining the PVDF sample enough, it is possible to cause the molecular chain to re-orient and turn into \(\beta\)-phase. Additionally, by dissolving the PVDF in dimethyl formamide (DMF) the polymer chain will re-orient due to the charge differences and change into \(\beta\)-phase.

To fully use the piezoelectric properties of the material it also needs to undergo polling. The polling process is complex and made lead to breakdown if not done properly. Polling orients all the polymer dipoles in the same direction. Without this step the piezoelectric effect is not very noticeable due to the dipoles negating each other because of their random orientation. In this work, I didn’t focus on the piezo, pyro, or ferroelectric properties of the polymer but tried to use the inherent dipoles as a starting point to create several simple, yet novel polymer systems.

1.1.2. Polytetrafluoro ethylene (PTFE)

Polytetrafluoro ethylene (PTFE) is more commonly referred to as Teflon®. PTFE has many everyday uses as coatings in various industries, most notably on
cookware. Many different researchers use this material due to its chemical stability and lubrication properties. The polymer has a backbone made of C atoms surrounded by F atoms. The general chemical formula for the monomer is \([C_2F_4]_n\), where \(n\) refers to the number of monomers.

This polymer is extremely interesting due to its robust mechanical and chemical properties. PTFE exhibits very high melting temperatures, thus making melt mixing and mechanical mixing difficult. Additionally, it is also resistant to many solvents making any solvothermal synthesis difficult. However, the material exhibits a very high Young’s modulus and generally robust mechanical properties. Although PTFE has many attractive characteristics, its uses in composites is very limited.

1.1.3. Polydimethyl siloxane (PDMS)

Polydimethyl siloxane (PDMS, \([C_2H_6OSi]_n\)) is a silicone based polymer which comes in liquid form, however, can be crosslinked into a solid. In liquid form this polymer has one of the most flexible macromolecular chains of any polymer. Thus, if used in liquid form, this polymer should easily re-arrange itself. The cured version of this polymer is generally referred to as Sylgard 184®. The material uses a 1:10 ratio for full curing and undergoes a hydrosilation reaction to crosslink. A schematic
(Fig. 1) showing the hydrosilation reaction can be seen below.

![Chemical structure diagram](image)

Figure 1: PDMS Crosslinking. This figure is a schematic showing the crosslinking of PDMS through hydrosilation. As the crosslinker and monomer interact Si-C-H is removed and PDMS forms a crosslinked network.

As the crosslinker and monomer interact Si-C-H gets removed and the creates a crosslinked network. By varying the amount of crosslinker the mechanical and optical properties of the PDMS can be tuned. Adding less crosslinker leads to an excess of Si-H, whereas adding more crosslinker creates excess Si-C=C. This changes the properties of the material drastically leading to a Young’s Modulus that can range anywhere from 0.5 MPa to 3.5 MPa, depending on crosslinker ratio (more crosslinker means higher modulus). The chemical changes were quantified using Raman spectroscopy which showed a large difference in peak intensities. By calculating the Si-H peak intensity and then taking the ratio of the Si-H intensity to the Si-C=C it was possible to quantify the crosslinking within the material. The
Raman showed excess crosslinker in the 1:5 PDMS and excess base in the 1:20. These chemical differences are also expected to affect the surface chemistry as shown in Fig. 2. Thus, the overall properties of the PDMS can be easily tuned and varied.

Figure 2: Raman Analysis. This figure shows Raman spectroscopy data of various ratios of crosslinker:base of Sylgard 184® PDMS. As can be seen the intensity of the peak varies, largely due to the change in the ratio. The ratio of Si-H to Si-C=C for each ratio is highlighted in blue.
1.2. Interfaces and Material Design

This thesis will focus on using polymers to create novel composites and blends that each have unique properties. The main approach for doing this is two-fold: use dipole interactions to enhance the cohesive strength and properties of the material, use liquid phases and inclusions to lead to novel mechanical properties and create a dynamic interface. Previously, a lot of composite research focused on reinforcing phases that were fibers, particles, or other solid inclusions. This leads to a static interface (i.e. does not adapt to changes under external stimuli) which causes the material to be passive. Recently, there has been a shift towards research in active materials and dynamic interfaces. As previously mentioned, Style et al. showed that Eshelby’s theory does not fit liquid inclusions and general mixing rules are also invalid in these cases. Thus, composites with liquid phases make up a unique section of materials. Additionally, because dipole interactions are distance dependent they can be continuously re-used because they never permanently disappear. Blends composed of PVDF/PTFE and PDMS have not been thoroughly explored and have been generally ignored, especially using liquid PDMS. The general thought is that by using liquid PDMS the overall strength of the material is lower than using another solid phase. Additionally, it is believed that these materials do not mix well which leads to phase separation. Although there are papers using separate layers of PVDF and crosslinked PDMS together, they are not blended together.
By using a very mobile polymer chain, such as PDMS, it can re-organize into the lowest energy state, which would maximize the effect of the dipole interactions due to the attraction between the H and F atoms. This allows the combinations of PVDF/PTFE and PDMS to remain stable over long periods of time and exhibit unique properties. The H-F dipole interactions repeat at least two times for each combination of PVDF+PDMS monomers and at least four times in the case of PTFE/PDMS. Due to the sheer number of monomers in polymer chains, the dipoles repeat and give rise to large scale interactions due to the summation of their effects in the blends.

To prove the feasibility of the initial concept, a solvothermal synthesis of PVDF+PDMS was attempted. The synthesis yielded a novel composite, dubbed the Self-Adaptive Composite (SAC), which exhibited unique properties. By tuning the liquid content in the solution, I synthesized micelles (like water balloons) filled with ~60% PDMS. This secondary synthesis was used as reinforcement in a crosslinked PDMS matrix to understand the effects of liquid phases in a solid system. The wt. % of micelles was varied to understand how liquid content affects the overall stiffness of the composite.

To prove the dependence of these interactions on dipoles I varied between PVDF (2 F atoms/monomer) and PTFE (4 F atoms/monomer). By using these two polymers in different blends, there should be a stark contrast with variation of Fluorine content. To elucidate the specific effects of extra dipoles I synthesized two blends, using PTFE and PVDF, respectively. The first blend was a mixture of PVDF
and PDMS, in equal ratios, which showed unique adhesive properties. In addition, I synthesized a secondary mixture, also in equal ratios, of PTFE and PDMS. Although both PTFE and PDMS are lubricants, the mixing of the two yielded a gel with adhesive properties.

The following chapters describe the techniques used to analyze the fillers, blends, and novel materials that were synthesized. The data provides a lot of background on the importance of dipole interactions and interfaces in composites and blends. The uses and applications of these novel materials as well as the implications of this data will be discussed in the final chapter.
Dynamic Interfaces and the Synthesis of Novel Solid-Liquid Composites

2.1. Importance of Interfaces

This paper references the paper in *ACS Applied Materials and Interfaces* titled “A Solid-Liquid Self-Adaptive Polymeric Composite”\(^9\)

As previously stated, the interface between materials is critical to the properties of the composite. As such, we synthesized a material that would include a dynamic interface. The interface was designed to take advantage of large electronegativity differences, in this case between F and H. This difference allows the new material to be much more cohesive while still gaining the benefits of the incompressible liquid phase.
The addition of liquid fillers into a solid matrix is generally thought to weaken the overall stiffness of the whole. Recognizing the importance of stiffness to materials and structures especially load bearing ones, there has been tremendous efforts to improve on the stiffness of materials. A large percentage of research has focused on composite materials especially polymeric ones due to the advantages offered compared to conventional materials. Stiffness is a critical property which determines the response of a material to deformation and load transfer effectiveness. Many techniques for the improvement of stiffness in composite materials have been proposed. Earlier attempts included the addition of particles into the polymer matrix to improve the stiffness. Zuiderduin and his colleagues were able to show an improvement of stiffness of up-to 46% by addition of 19% CaCO$_3$ particles in a polypropylene matrix. At low strains, CaCO$_3$ particles adhere to the matrix with no debonding hence the improvement observed. Due to the low aspect ratio of particles in the micro size, recently, nanoparticles have been used widely used to enhance the stiffness of composites. A wide range of nanoparticles have been proposed; silica, nanoclay, aluminum oxide, carbon nanotubes (single and multi-wall), graphene oxide, graphene nanoplatelets, nanocellulose etc.

Most nanoparticles improve composite stiffness; however, the improvement is only marginal. Addition of nanoparticles into the polymer is riddled with many drawbacks. When the amount of nanoparticles exceeds a certain value, it results in agglomeration which tends to lower the strength of the composites. Further, there is still a big challenge in effective dispersion of nanoparticles into the polymer. In
addition, most of the nanoparticles must be functionalized to provide stronger interfacial bonding with the polymers. Finally, nanoparticles have an effect of increasing the viscosity of the polymer thereby limiting its use e.g. in vacuum assisted transfer molding\textsuperscript{24}. Which rely heavily on the viscosity of the resin.

2.2. Solvothermal Synthesis of a Novel Solid-Liquid Blend

To synthesize this new material equal amounts (weights) of alpha phase PVDF (Alfa Aesar, melt viscosity of 23,500-29,500 poise at 230 °C) and hydroxy terminated PDMS (Sigma Aldrich, viscosity of 18,000 – 22,000 cSt) were added to tetrahydrofuran (THF). These components were mixed using tip sonication (VCX 750, Sonics & Materials, Inc.) and magnetic stirring simultaneously. The mixture was sonicated until at least 50 % of the solvent was evaporated and then left to evaporate at room temperature for 2 days. Finally, the sample went through a heat treatment at 95 °C in a vacuum oven overnight. Then, the blend was taken out and left to cool at room temperature.

2.3. Properties and Mechanisms of a Dynamic Material

Recently, there has been a push to look for more novel ways of increasing stiffness of composites. A survey of literature shows this to be an active area with interesting results. Hierarchical structures are being touted as the best system to improve the stiffness of a materials without sacrificing other properties\textsuperscript{13,14}. Even
with higher improved stiffness using these hierarchical structures, the process and methodology which goes into their preparation is complex and cumbersome. In some instances, repeatability or scaling up the processes to make them faster and more efficient has been the biggest obstacle. In this work, we report a simple one step in situ method of achieving a self-stiffening polymer blend by utilizing a liquid and solid phase simultaneously (Self-Stiffening Two Phase System-SS2PS). The liquid part of the blend consists of polydimethylsiloxane (PDMS) while the solid part consists of poly(vinylidene fluoride)(PVDF). We utilized the high fluorine content and large Young modulus (3 GPa) of poly(vinylidene fluoride) to enhance the PDMS mechanical properties. The large electronegativity of fluorine atoms delocalizes the electron distribution of neighboring atoms generating dipole and dipole induced moments, which are responsible for complex dipolar interactions. PVDF may initiate a dipole driven polymer entanglement between the PDMS and PVDF chains, which may enhance self-stiffening. To maximize the high viscosity fluid component and the fluorine content a blend containing 50% PDMS in liquid form were obtained. This fluid content is much higher than any other composites that include a fluid media (which generally have less than 10 wt. % fluid). We chose tetrahydrofuran (THF) as a solvent to mix the two polymers in a 50 by 50 wt. %. The complete synthesis is described in the methodology section of this work.

To explore the structure of SS2PS various imaging tools were used: SEM, FIB, nano-indentation, EDS, and in-situ SEM tensile testing. SEM micrographs show that SS2PS has a structure like that of a “sugar cube” and is extremely porous (see Fig.
3a-c). The inset in Fig. 3a, which shows SS2PS under an optical microscope, reveals a strong reflectance, which indicates the presence of a viscoelastic fluid phase.

Figure 3: Characterization of the quasi-solid nanocomposite. a), Image of quasi-solid nanocomposite. The right inset is the quasi-solid nanocomposite under optical microscope. b), and c) Scanning electron microscope (SEM) images of the bulk quasi-solid nanocomposite. The solid is composed of many spheres in a viscoelastic fluid as seen above. d), and e), SEM images of the quasi-solid nanocomposite after a focused ion beam (FIB) cut the sphere thus revealing a complicated substructure. f) Schematic of the different regions in the composite, g), h), and i) EDS of small area of the cross section of the sphere after FIB cut. The results show that the substructure is made up of concentrated Fluorine areas surrounded by a Silicon medium.
To further investigate this, nano-indentation testing was performed on SS2PS. The tests revealed that the spheres that compose SS2PS can re-orient themselves in the fluid phase (see Fig. 4). Additionally, the fluid phase is a viscoelastic fluid characterized by the “beads on a string” (BOAS) structure seen when pulling back from the sphere surface in Fig. 4e. Fig 4a-f were taken during nano-indentation testing before and after applying pressure, respectively, which revealed the blend can re-arrange the spheres under pressure and that the fluid acts as a binder, which supports the spheres. Fig. 4g-h provide a schematic for the re-arrangement of the spheres under pressure. To view the cross-section of the spheres FIB imaging was employed. The FIB revealed the presence of two distinct phases as seen in Figs. 3d-e, however, EDS was necessary to identify them. The EDS was performed on a small area inside the cross section of the sphere as seen in Fig. 3g. The EDS identified a high fluorine (F) concentration in the dark grey area, as seen in Fig. 3i, and a silicon (Si) rich region in the lighter areas, as seen in Fig. 3h. The structure of SS2PS is fully described by Fig. 3f, where the viscoelastic (PDMS-rich) fluid region is seen in red and the PVDF-rich region is in yellow. Fig. 3f shows that the solid spheres sit and are slightly coated by a viscoelastic media (of mostly PDMS). Extrapolating from the EDS data, the inside of the sphere (seen in Fig. 3e) has an interconnected PVDF-rich network inside bounded by a PDMS-rich fluid phase. The contents of the sphere are held together by a PVDF-rich shell that encompasses the area as seen in Fig. 3d. Thus, the overall structure of the blend can be categorized from inside to outside starting with the PVDF network composed of
spheres and dendrites inside the spheres (Fig. 3e), which is surrounded by a softer PDMS network (Fig. 3e), which is held together by a PVDF shell (Fig. 3d). This structure is repeated and held together by a viscoelastic fluid (as seen in Fig. 3f and Fig. 4) and composes the bulk blend seen in Fig. 3a.

Figure 4: Sphere re-organizations within the composite. a),d) Shows an SEM image of a sphere in the composite prior to indentation. b),e) Shows the re-orientation of the sphere under loading. The re-organization is an effect attributed to the viscous fluid
interface. c),f) Shows recovery after unloading. g),h) Provide a visual representation of the re-organization process when the material undergoes loading. The inset in e) shows the beads on a string (BOAS) effect which is characteristic of viscoelastic fluids.

To understand the interactions in the blend, SS2PS was analyzed using thermogravimetric analysis (TGA) (as seen in Fig. 5a and 5b). The TGA analysis was done in argon at a heating rate of 10 °C/min up to 1000 °C using a Q600 TGA from TA Instruments. SS2PS is expected to present two degradation peaks due to its similarity to PS-PDMS blend, which is immiscible\textsuperscript{27}. The TGA data, however, shows one peak indicating that there are interactions within the system. Additionally, SS2PS shows an enhancement of the thermal stability from pure PVDF due to the addition of PDMS. The remaining mass of PVDF after degradation was 33\% of the original weight of the polymer, however, pristine PDMS degraded completely. It would be expected that in a mixture composed of half PDMS and half PVDF only 16.5\% PVDF should be left after the thermal analysis, however, 20\% of the initial mass of SS2PS remains (which can be seen in the theoretical simulation in Figs. 3a and 3b). The remaining mass is 3.5\% higher than expected and cannot be accounted for by experimental error (which are of the order of 0.1\%). This disparity exists due to an interaction within SS2PS and can be more clearly seen by using a Lorentzian fit, or by analyzing the departure from the theoretical predictions. The difference between the theoretical mix and SS2PS is represented by the orange line in Fig. 5a and is as high as 40\%, which also indicates the presence of interactions within the blend. For the pristine PVDF the derivative of the TGA signal can be fitted by two
overlapping Lorentzians, characterized by $T_{i1}^{PVDF}=435\pm1$ °C and $T_{i2}^{PVDF}=448\pm1$ °C and by their corresponding Lorentzians widths $W_{i1}^{PVDF}=6\pm1$ °C and $W_{i2}^{PVDF}=9\pm1$ °C. The ratio of the amplitudes of these Lorentzians ($I_{1}^{PVDF}:I_{2}^{PVDF}$) is equal to 0.63. The derivative of the TGA data for PDMS is a stretched and broad Lorentzian characterized by $T_{i}^{PDMS}=500 \pm 5$ °C. In the case of SS2PS, the derivative of the TGA dependence is a narrow Lorentzian located $T_{i}^{SS2PS}= 451 \pm 1$ °C, with a width $W_{i}^{SS2PS}= 5.5 \pm 1$ °C. The increased thermal stability of PVDF upon the addition of PDMS, the differences between the theoretical mix and blend, and the changes in remaining mass all suggest the presence of strong interactions within the blend.
Figure 5: Spectroscopic characterization of the quasi-solid nanocomposite. TGA results of the PVDF, PDMS, a theoretical mixture of PVDF and PDMS, and SS2PS (weight vs. temperature a)) and the derivative of weight versus temperature (b). There is a difference of approximately 40% in the degradation behavior between the
composite and theoretical mixture; thus implying strong interactions. Raman results of the PVDF, PDMS and SS2PS for Raman shifts ranging between 100 and 1000 cm\(^{-1}\) (c), 1000 and 1500 cm\(^{-1}\) (d) and 2800 and 3100 cm\(^{-1}\) (e). The Raman correlates with the XRD data and shows characteristic peaks of alpha phase PVDF and PDMS. X-ray Diffraction (XRD) results of the composite and raw components can be seen in (f) and show the peaks of both homopolymers in the composite.

Active modes in Raman spectroscopy reflect changes in polarizability, directly connected to dipole-dipole and dipole induced interactions\(^{28}\). As noticed from Figs. 3c-3e, both PVDF and PDMS exhibit Raman peaks. The most important Raman peaks are shown in Figs. 3c-3e. For Raman shifts ranging between 80 cm\(^{-1}\) and 750 cm\(^{-1}\), the Raman spectrum of SS2PS depicts the competition between the Raman peaks of the homopolymers (PDMS and PVDF). The most intense peaks have been noticed at 411 cm\(^{-1}\) and 610 cm\(^{-1}\) (assigned to CF\(_2\) rocking and wagging/bending in PVDF, respectively) and at 487 cm\(^{-1}\) and 709 cm\(^{-1}\) (assigned to Si-O-Si symmetrical stretch and Si-C symmetrical stretch in PDMS, respectively). No significant changes in position, width, or intensity were noticed for these peaks. In the domain of 750 cm\(^{-1}\) to 1250 cm\(^{-1}\), the Raman spectrum of SS2PS is dominated by PVDF. A moderate broadening of the peaks located at 838 cm\(^{-1}\) and 1197 cm\(^{-1}\), assigned to CH\(_2\) rocking and twisting, respectively, is noticed. Between 1250 cm\(^{-1}\) and 1500 cm\(^{-1}\), PDMS shows a single intense and broad peak located at about 1366 cm\(^{-1}\), which may be associated to Si-C\(_6\)H\(_5\) vibrations which were shifted towards lower wavelengths. This peak is broadened beyond detection in the Raman spectrum of the blend. While the Raman peaks of SS2PS in this range of wavelengths
are controlled by the PVDF component and reflect CH$_2$ and CH$_3$ related vibrations, a general broadening is evident. In the range 2750 cm$^{-1}$ to 3200 cm$^{-1}$, there is a medium intensity peak at 2906 cm$^{-1}$ and a weak intensity peak at 2964 cm$^{-1}$ assigned to CH$_3$ stretching in PDMS. A peak located at 2981 cm$^{-1}$ and assigned to CH$_2$ vibrations in PVDF is also noticeable and broadened in the Raman spectra of the blend.

Raman spectroscopy indicates that the crystal structure of α-PVDF is not affected by the synthesis process. The observed broadening and small shifts of the Raman lines supports the possibility of electronic interactions between Si-C$_6$H$_5$ units and CH$_2$ or/and CH$_3$ groups from PVDF. In polymeric materials, the mechanical strain affects the positions and widths of Raman peaks. For example, uniaxially stretched polyethylene shows an increase in the width of Raman peaks upon stretching, which may be accompanied by a displacement of the Raman peak position towards a smaller wavelength. This enunciates the existence of interactions among the components of the blend, which are responsible for local strains, evidenced by the broadening in the Raman peaks.

Peaks in the 2900 cm$^{-1}$ – 3000 cm$^{-1}$ (seen in Fig. 5e) region indicate dipole interactions as previously studied by Jiang and colleagues$^{29}$. Additionally, peak broadening in the 1000 to 1500 cm$^{-1}$ range (the region dominated by PVDF peaks) and lowered intensity suggest interactions between the two components of SS2PS. Shifts in PVDF peaks, such as the peak present at 3022 cm$^{-1}$ in PVDF which was
shifted to 2988 cm\(^{-1}\) in SS2PS, provide further evidence for the presence of interactions in the blend. Characteristic PDMS peaks related to Si-O and Si-C stretches can be seen at 487 cm\(^{-1}\) and 709 cm\(^{-1}\), respectively. Additionally, the presence of characteristic \(\alpha\)-PVDF peaks (such as 2981 cm\(^{-1}\)) indicates that the \(\alpha\)-PVDF did not change phase after creating the blend.

The X-ray diffraction (XRD) data complements the Raman results and also provides more evidence for the interactions within this blend. The broad peak centered at 12\(^{\circ}\) in Fig. 5f corresponds to liquid PDMS and confirms the presence of the fluid throughout the blend. The WAXS spectrum is consistent with \(\alpha\)-PVDF, in agreement with the Raman data previously discussed. The peak positions are not affected (within experimental error) by the addition of PDMS, suggesting that the dimensions and symmetry of the unit lattice are not modified. However, it is noticed from Fig. 5f that the peaks of SS2PS are wider than the peaks of PVDF. This change in width may reflect either smaller crystallite sizes or strong stresses on the PVDF crystal which indicate interactions at the lattice level (such changes would not be expected in polymer blends).

To understand the effect of the interactions seen with in-situ testing, XRD, and Raman; Dynamic Mechanical Analysis (DMA) was performed on the system. The testing was done using a DMA Q800 from TA Instruments. Dynamic tests were performed using a fixed displacement of 30 \(\mu\)m (correlates to 1.1% strain) in compression at a constant frequency of 5 Hz. The samples were measured and
weighed before and after testing to verify that there was no mass loss in the blend and quantify changes in dimensions due to the testing. The mechanical analysis looked into $\tan \delta$, and stiffness. $\tan \delta$ was analyzed and used to describe the behavior of SS2PS. Since $\tan \delta$ is the ratio of loss to storage modulus it can describe the behavior of materials as viscoelastic ($\tan \delta$ of 1), solid ($\tan \delta$ close to 0), or fluid ($\tan \delta$ reaching infinity)\textsuperscript{31}. Stiffness is the force per change in length of the tested material and thus relies on dimensions.

Figure 6: Mechanical behavior of the quasi-solid nanocomposite. a) Theoretical data showing effect of compression cycles on Coulomb interactions. The decreasing trend implies a constant increase in interactions and decreasing potential energy. b) DMA data showing strain (black) and stiffness (blue) as a function of stress at a set amplitude of 30 microns (~1.1% strain). The material exhibits a 70-fold stiffness increase. c) Shows the $\tan \delta$ and stiffness at ~-140°C. The almost constant stiffness implies the stiffening is due to interactions between the liquid and solid phase as well
as re-organization. d) Is a schematic showing the re-organization process that leads to stiffening (due to densification) in tandem with increased Coulomb interactions.

SS2PS exhibits over 7250.5% self-stiffening, higher than any other recorded material. As previously stated, self-stiffening has never been larger than 90%\(^8\) in compression, or \(\sim 400\%\)\(^{32}\) in shear loading of polymer solutions. As seen in Fig. 6b the self-stiffening is so strong that the fixed displacement, represented by the black line, cannot maintain its original value, and must decrease to half its original value to keep up with the increase in stiffness. The closure of the pores can be extrapolated from the changes in dimensions of SS2PS, exhibiting a reduction in volume of 58.8%. This reduction in volume translates into a 30.1% increase in density which indicates a decrease in the distance between spheres and a filling of the pores. Additional proof that the self-stiffening is due to the interactions between the viscous phase and solid phase can be seen in the low temperature dynamic testing in Fig. 6c which indicates that at temperatures below the \(T_g\) of PDMS and PVDF there is very little self-stiffening (<2%) and the tan \(\delta\) indicates a value of 0.06 which is close to that of a solid plastic. This implies that self-stiffening is a function of the mobility of the system and interactions between PVDF and PDMS. This extreme self-stiffening is made up of three factors: the closure of the pores of the blend and the re-organization of the spherical structures (as seen in Fig. 6c), interactions between the rigid spheres in the system\(^{33}\), and atomistic dipole interactions. The interactions between spherical structures in polymers has been
previously studied by O’Connell and his colleagues\textsuperscript{34} which supports the three part theory proposed above.

Further evidence for the three-part hypothesis, namely the dipole interactions was gathered using theoretical modeling. By building up a system representing the inside of the SS2PS spheres and having it undergo compressive cyclic loading the effects of the DMA testing can be mimicked. The first compression showed a decrease in Coulomb interaction of 6000 kcal/mol (as seen in Fig. 6a). Upon recovery, the Coulomb interaction increased by 2000 kcal/mol and then decreased 3000 kcal/mol on the next cycle. This decreasing trend is constant throughout the compressive cycles which indicates an increasing interaction with cycles. This corroborates the previous results seen in the DMA and supports the three-part hypothesis.

The unique properties of the blend (such as self-stiffening and reorganization) can be attributed to the material structure which gives rise to many interesting features and most specifically an adaptive interface. The spheres have the ability to re-organize when exposed to external stresses (as seen in Fig. 6c) and are the main factor in the materials’ unique properties. This re-organization provides a distinct advantage because it allows the spheres in the material to carry all the load and is drastically different than the interface in materials with fillers. Most reinforced polymers, and even polymers in a hard matrix, fall prey to interface cracking or have to deal with low strain bearing interfaces\textsuperscript{35}. These interfaces limit
the material load bearing capacity, however, by having a viscoelastic interface these problems can be minimized. Additionally, this material is extremely porous, with a density half of what would be expected of such a blend (0.6 g/cm$^3$ compared to a theoretical density of 1.37 g/cm$^3$). The density is much lower than other conventional light-weight materials, except graphene aerogel (seen in Fig. 7a)\textsuperscript{36}. A graph comparing the material densities as well as the change in stiffness can be seen in Fig. 7a. This shows that this material exhibits large self-stiffening compared to other conventional materials such as PDMS-CNT, LCEs, and actin fiber networks.

![Figure 7: Material Comparison](image)

Figure 7: Material Comparison: a) Shows the comparison between densities of different materials. SS2PS has lower density than other conventional reinforced materials such as polymers and ceramic filler (P+B) and exhibits only slightly larger density than graphene aerogel\textsuperscript{37,36,38–40}. b) Is a visualization of the stiffening behavior. Stiffening is more than 10 times stronger than any other previously recorded material\textsuperscript{7,8,41}. 
As previously stated the blend has an uncanny ability to re-arrange itself under stress. This is due to the viscoelastic PDMS fluid interface, additionally, this fluid acts as a binder between the solid spheres. The spheres in the fluid are very hard to deform and still retain similar diameters after mechanical testing (about 46.6 microns). To test the tensile properties of SS2PS, testing was done using a 2N load cell micro-tensile setup inside a SEM. A notch was created in the sample and the blend was stretched until a crack appeared and propagated through 70% of SS2PS after which the blend was returned to its original dimensions. SEM showing the repetitive cycles can be seen in Fig. 8. After unloading there are regions of viscoelastic fluid acting like an elastic binder to hold the two sides together (as seen in Fig. 8c). The viscoelastic regions are outlined in a dashed red rectangle. This provides further proof that SS2PS spheres are encompassed by a viscoelastic fluid that acts as a binder and allows the re-arrangement and recovery of the material thus preventing interface failure.

![Figure 8](image-url)  
*Figure 8: In-situ Mechanical Testing. a) SEM image of SS2PS at the beginning of a load-unload cycle with a notch made to view crack propagation. b) Crack propagation as load-unload is happening. c) Shows the sample after unloading.*
2.4. Importance and Novelty of Dynamic Polymer Blends

This section demonstrated the synthesis of a brand-new polymer blend with a hierarchical structure and intriguing mechanical properties. The blend also differs from traditional polymer blends and composites due to the presence of both a viscoelastic fluid and solid phase, as well as a viscoelastic interface, making it a unique composite. It shows increases of over 70-fold in stiffness, much higher than conventional materials with similar properties. The self-stiffening effect is a result of atomistic level dipole interactions, pore closure and re-organization, as well as interactions between the solid spheres. Thermal analysis exhibits increased thermal stability, and a large deviation from the theoretical model which indicates strong interactions within the blend. Raman and XRD analysis both indicate the presence of both components in the blend as well as interactions on the lattice level. The blend has a unique structure composed of both viscoelastic fluid and solid components which gives rise to its unique behavior. In addition, the material also shows the ability to recover due to the presence of the viscoelastic phase. However, as the next chapter shows, due to the design of this material there are many different possible blends that can be made for a myriad of uses.
Chapter 3

Reinforcement Through Liquid Inclusions

3.1. Transition to Using Liquid as Reinforcement

This paper references the paper in *Advanced Materials Interfaces* titled “Structural Reinforcement Through Liquid Encapsulation”\(^42\)

Using the previous work as a benchmark, we looked at altering the wt. % of liquid PDMS to solid PVDF. By doing this, we synthesized novel micelles that are like water balloons. They have a hard outer PVDF shell and a liquid PDMS center which, theoretically, allows them to absorb large amounts of energy.

In contrast to conventional composite materials design, liquid structural reinforcement in solid materials has not attracted a lot of attention from researchers. Generally, liquid fillers have been mostly used in self-healing composites\(^{43–47}\) and have more recently been used to create conductive networks\(^{48,49}\) and thermal networks\(^{50}\), however, there is not much research looking
into the use of liquid polymeric fillers as mechanical reinforcement. As previously
mentioned, work by Style et al. has shown that liquid inclusions do not follow
general Eshelby theory\textsuperscript{6}. Thus, using this as a starting point we attempted to create a
novel material that included liquid micelles. These micelles were 62% liquid PDMS
with a solid polymer shell of PVDF which made up the other 38% of the
composition. The micelle was then introduced into a Sylgard 184\textregistered PDMS matrix. By
using these liquid reinforcements, we can create a similar dynamic interface as
when using the 1:1 liquid PDMS to solid PVDF system. This interface should also
exhibit similar self-stiffening behavior as previously shown. In addition, we can still
maintain the general advantages of the F-H interactions shown in previous work.

These materials are meant to represent a shift towards composite that more
closely mimic nature. The use of liquids is prevalent throughout the human body, as
we are 80% liquid. Thus, by using liquids we believe it is possible to mimic and
synthesize materials that are both novel and unique.

One of the most important factors when designing a material, aside from the
interface, is the strain transfer within the different phases of the composite. One
such example is the pull-out behavior seen in carbon nanotube (CNT)-based
composites. Pull-out leads to premature failure, thus showing the material is unable
to make full use of the strength of the CNTs. Thus, a serious effort has been made to
engineer composites to enhance the interfaces between fillers and the matrix, thus
leading to better strain transfer. Surface modification, as well as the addition of
surface binders, and designing specifically shaped reinforcements have been some of the main ways that have been used to synthesize materials with higher interfacial and load bearing strength. However, when using liquids as reinforcements parameters such as viscosity become critical due to its effect on both strain transfer and overall shape of the filler. This can dramatically change the overall strain transfer properties of the material. The uses of liquids to strengthen solids has generally been disregarded since it is assumed that composites using liquids than to be weaker. However, in the previous chapter, we have shown that using dynamic liquid interfaces can dramatically change strain transfer and lead to adaptive materials.

3.2. Using Liquid Phases for Reinforcement

Generally, PVDF and PDMS have been thought of as immiscible and have not been directly mixed. Most researchers show them being used in separate layers, but never fully blended. By using the previously explained dipole interaction mechanism we plan to show that the same theory holds true in all areas of material synthesis, including reinforcement.

PDMS is one of the most flexible polymers, whereas PVDF has a very high Young's modulus, thus lending a large amount of mechanical strength to the spheres. Since adding another phase to the system would make it more complex,
we chose to use Sylgard 184® PDMS because it is like the PDMS already present in the system, however, can be crosslinked into a solid.

To make the system, we took alpha phase PVDF (Alfa Aesar, 23,500–29,500 poise) and dissolved it in THF (tetrahydrofuran) while undergoing magnetic stirring. The solution was monitored until it reached homogenization (approximately 3 hours). Afterwards, hydroxyl terminated PDMS (Sigma-Aldrich, 18,000-22,000 cSt) was added to the PVDF solution. The solution underwent further stirring for an additional hour. Afterwards, the mixture was placed in a fume hood and simultaneously tip sonicated and magnetically stirred until all solvent was removed (approximately 24 hours). The final ratio of PDMS to PVDF was 62:38 wt. %, based on initial material weights (20.4786 g PVDF with 33.577 g PDMS). The synthesis beaker containing the material was left to dry overnight for 24 hours. To fully remove the solvent, the as-obtained composite was heat-treated above the boiling point of THF (100°C) for 24 hours.

To incorporate the spheres/micelles into the system we used Sylgard 184® (Dow Corning) and added 20 wt. % and 50 wt. % spheres, respectively, into Part A of the two part Sylgard 184®. Afterwards, the crosslinker was added to match the suggested 1:10 ratio. The samples were cured inside a vacuum oven at 60°C. The vacuum was necessary to eliminate any air bubbles in the mixture. The hydroxyl
terminated PDMS did not cure using the same crosslinker and thus the innermost part of the spheres remained liquid even after crosslinking.

Figure 9a shows a schematic of the process for the synthesis of PDMS/PVDF spheres. The spheres had an average size between 30 and 40 microns. To carefully examine the overall structure of the material we employed focused ion beam (FIB), scanning electron microscopy (SEM), and transmission electron microscopy. The FIB measurements were done using an FEI Helios SEM/FIB. While the SEM was done using FEI Quanta 400 ESEM at scanning voltage of 15 to 20 kV. Transmission electron microscopy (TEM) was performed with a JEOL 2100 field emission gun. As seen in Fig. 9b, SEM imaging of a cluster of spheres confirms homogeneity in both size and shape. A single sphere can be seen in Fig. 9c, taken using FIB. After ion milling a section of the sphere (Fig. 9d), the liquid can be seen flowing out (Fig. 9e). The shell thickness of the spheres/micelles varied with size, with most spheres exhibiting a shell thickness of approximately 1/20th of the radii. TEM imaging has shown shell thickness down to 15 nm, for spheres of ~300 nm in radius (Fig. 9f). FIB of larger spheres confirms the radius to thickness relationship, as well as clearly shows how the liquid oozes out. The spheres range in size from 300 nm up to 30 μm. Using SEM images as a benchmark, it can be observed that ~80-90 % of particles range from 10-30 μm in size. Using theoretical models, we stabilized the structure of PDMS and PVDF into a sphere. The graphical representation of the spheres can be seen in Fig. 9g. Theoretical modeling showed that the mixture of PVDF and PDMS stabilized into a structure consisting of a rigid PVDF shell and a liquid PDMS center. These results
agree with the experimental data. The core shell structure was also previously shown in the previous PVDF+PDMS blend shown in this thesis.

Figure 9: Morphology of the liquid spheres. a) Schematic of the synthesis process. b) SEM of a sphere cluster; c) FIB of a single sphere, d) the sphere after an incision, e) and finally the liquid flowing and spreading out of the incision. f) TEM image of a 0.5 µm burst sphere where the wall is calculated to be 15 nm and there is a clear contrast between the outer solid shell and liquid polymeric phase inside the sphere. g) Obtained simulated structural model and its cross-section. Mixing PDMS/PVDF
results in a structure where the PVDF composes a rigid outer layer encapsulated a liquid PDMS phase.

To understand the mechanics in the spheres themselves we measured the mechanical properties of both the single spheres, a mat of the spheres, and the reinforced composite. The spheres were measured using an *in-situ* SEM mechanical compressive test. To test the mat and reinforced composite we used DMA. The results were also verified using DFT and MD simulations.

All DMA measurements were done using a DMA Q800 from TA Instruments. To measure the spheres alone, they were placed onto the compressive DMA clamp and arranged in a rectangular shape. The area that the spheres took up was measured and used by the instrument in the calculations of the properties. Thus, the overall DMA test should give a good average of the properties of the spheres. The load-unload cycles for the spheres were done at 0.15 N, 0.5 N, and 1 N at a rate of 0.15 N/min for the first two cycles then 0.1 N/min for the final cycle. On the other hand, for the reinforced composite the loading was done at 1 N, 2 N, 5 N, 10 N, and 15 N at a constant rate of 0.5 N/min. All isothermal measurements were performed at a frequency of 5 Hz, a temperature of 30°C, and with a 20 μm oscillation amplitude. In additional testing, the force was ramped at a rate of 0.5 N/min up to 18 N.

The DMA testing of the sphere mat, at room temperature, showed that the material retained high stiffness over several cycles (Fig. 10a). Load-unload data showed secondary features, which can be attributed to slip and re-arrangement
within the mat. The overall stiffness of the mat exhibit a constant rise with subsequent loading cycles, most likely due to constant re-organization within the mat to a more tightly packed formation. Additionally, upon release of the load the mat would return to equilibrium, thus signifying that no plastic deformation took place. This also suggests that the overall load was equally distributed throughout the mat. Surprisingly, the overall stiffness of the spheres was 12 kN/m, much larger than expected for a liquid-containing sphere. This is most likely due to the ability of the spheres to transfer strain to the liquid phase, thus increasing the overall stability. The ability to efficiently dissipate the energy added without permanent deformation to the system is encouraging for the creation of future two-phase systems.

To investigate the mechanics of an individual sphere more closely, we performed in-situ testing using a 30 µm flat punch SEM PicoIndenter (Hysitron Inc.). The load versus depth profile of the uniaxial compression of the sphere is shown in Fig. 10b. The green plot (Deformation 1) shows the sphere being deformed up to 7000 µN, prior to plastic deformation, then release. The second plot (Deformation 2), shown in red, shows the behavior of the sphere until critical failure (burst). The calculated elastic modulus, obtained from the slope of the curve in the elastic region, is 354 kPa. SEM images showing the deformation throughout the deformation cycle can be seen in Fig. 10c.

The deformation of the sphere can be generally characterized using a two spring model. By assuming the sphere acts like two springs with different stiffnesses
in series, one for the shell and one for the liquid, the system can be more easily understood (Fig. 10e). If the spring constant of the shell is $K_s$ and the liquid phase is $K_L$, both springs should experience the same pressure ($P$), since the force is applied uniaxially. We can assume that the total strain in the system is $\varepsilon_{\text{total}} = \varepsilon_s + \varepsilon_L$. Additionally, the stiffness of the liquid ($K_L = P/\varepsilon_L$) should be much lower than that of the solid ($K_s = P/\varepsilon_s$). Thus, the strain in the liquid will be much higher than that observed in the solid which will cause the system to deform to accommodate the larger strains. Hence, most of the strain that would go to the shell goes to the liquid phase which results in the deformation of the sphere to an elliptical shape which protects the shell from premature failure (Fig. 10e). Generally, in composites made up of a single solid phase (static interface), interfacial failure due to modulus mismatch is extremely common. However, this can be avoided by using liquid-solid system since the liquid can accommodate large strains without interfacial cracking by deforming and absorbing energy. Additionally, the sphere returns to its original shape after 10 seconds without any permanent deformation. This time will vary depending on the polymers and their relaxation time as well as the applied load. The forces behind this recovery is the fact that a sphere is a much more energetically favorable shape than an ellipse, thus facilitating the recovery (Fig. 10e).

The sphere was compressed until failure in the second loading cycle (deformation 2). The sphere yielded at 8000 $\mu$N, which corresponds to a stress of $\sim 12$ MPa. The sphere undergoes shell fracture at 11500 $\mu$N, corresponding to a stress of 16.3 MPa and a strain of 80%. The area under the force-displacement curve indicates
the energy that went into the system, which in this case is 0.2 J. Fig. 10d shows a time lapse of the behavior of the sphere up until failure (Fig. 10d). The sphere exhibits plastic deformation after yield and crack initiation begins in the direction orthogonal to loading. This is indicated in the schematic insets in Fig. 10d. The liquid phase can be seen flowing out in the final image of Fig. 10d.

Figure 10: Mechanical behavior of a single PDMS/PVDF sphere. a) Sphere stiffness values as a function of time at regimes of 0.2 N, 0.5 N, and 1 N, as obtained from load-
unload testing using a DMA Q800. The inset in shows the spheres after their mechanical testing. b) Shows the load versus depth curve of the in-situ SEM testing of a single sphere. The images below c) correspond to the in-situ testing of the spheres. Shows the spheres prior to load and the spheres after loading. d) Shows a time lapse of the behavior of the spheres once pressure is applied and once they eventually burst and then the pressure is removed. e) Unique behavior of solid-liquid sphere observed in current work.

To study dynamic response under mechanical deformation, the spheres were subject to compression by an external piston using a harmonic motion. Up to 3 complete oscillations with a period of 200 ps were considered. Due to computational limitations, a small sphere of 10 nm was used for compression, while keeping the fraction of solid to liquid the same as that in the experiments.

For the rest of the simulations, the polymers were described using a Compass force field\textsuperscript{54} for the bonded terms and Buckingham potential\textsuperscript{55,56} to describe long-range interactions. All the parameters are described in the references\textsuperscript{57-59}. A typical structure obtained from MD simulations is shown in Fig. 9g (external view and cross section). These structures were obtained considering an initial configuration of spheres of PVDF (outer shell) and PDMS (inner phase).

Thus, we carried out fully atomistic molecular dynamics (MD) simulations\textsuperscript{55,56,58-61}. We investigated the structural and dynamic properties of composites made up of a mixture of PVDF and PDMS polymer chains. Two cases were considered; (i) a composite composed of a mixture of PDMS and PVDF in equal amounts (in weight) and initially randomly distributed; and (ii) a two-phase system composed of a hollow
sphere made of PVDF and filled by PDMS. During the compression cycle of the mixture we analyzed the Coulomb interactions between PVDF and PDMS. More specifically, we analyzed the interactions between the fluorine atoms, from PVDF, with the hydrogen atoms, from PDMS (see structures displayed in Fig. 11a). At the compression stage of the first cycle, the polymer chains are densified (are placed in closer contact) and the energy contribution associated with the Coulomb interactions decreases to ~6000 kcal/mol (Fig. 11b). When the piston returns in the next cycle, due to its periodic motion, this energy changes, from -6000 to around -4000 kcal/mol and stabilizes through the next cycle. During the second compression cycle, the Coulombic energy drops from -4000 to -7000 kcal/mol, indicating that the F – H interactions increase, because of the structural rearrangement of the composite induced by the piston movements, followed by a new structural stability plateau with energy around -5000 kcal/mol. After the third compression cycle, the minimum energy stabilizes around -7000 kcal/mol when the piston is compressing the system and around -5200 kcal/mol when the pressure is released. The corresponding von Mises stress and hydrostatic pressure values are presented in Fig. 11c-d, respectively.

From the MD simulations, we observed the formation of spheres with the external shell composed mostly of PVDF, with encapsulated PDMS (Fig. 11e-f), which is consistent with the experimental observations (Fig. 9). To test these sphere structural stabilities and whether the used model can describe a two-phase system, we carried out an MD within an NVT ensemble with the constant temperature of 300 K. With no external forces acting on the system, the spheres remained stable for up to 2 ns. Due
to the liquid behavior of the PDMS, it can deform to fulfill the hollow space in the center of the sphere. Additionally, it is noticeable that the PDMS can occupy some holes present in the PVDF shell structure. The hydrostatic pressure in the material was also modeled and showed that the PVDF-PDMS mix withstood up to 500 atm of pressure in each cycle (Fig. 11d). The Coulomb energy evolution showed that the interaction between PDMS and PVDS during the compression process becomes stronger (Fig. 11d). Thus, one mechanism that may improve the PVDF cluster formation is the Coulomb interaction between the two phases of the composite. We also modeled the von Mises stresses in the material whilst undergoing compression and it showed irreversible stresses deformations being built into the material with each cycle and a maximum stress of 11000 atm (Fig. 11c). The material did not exhibit instant recovery but a viscoelastic relaxation to a new equilibrium point (~8000 atm). The general features (shape and pattern) of the stress curves from these simulations are very like those from the experimental studies. Additionally, the hydrostatic pressure patterns presented in Fig. 11d reinforces our failure hypothesis discussed in the in-situ measurements.
Figure 11: Theoretical modeling of PVDF+PDMS spheres. a) Optimized structural model of PVDF and PDMS chains. The most important atoms (F and H) and distances for the Coulombic interactions are also clearly marked; b) variation of the Coulombic energy (blue curve) as a function of the simulation time. The corresponding piston positions in indicated in the red curve; c) von Mises stress values in the spheres as a function of simulation time and d) hydrostatic pressure values experienced by the sphere as a function of the simulation time; e) Structural two-phase sphere model and the correspond atomic strain values for the uncompressed (left) and compressed
(right) stages, respectively; f) Pressure values experienced by the two-phase sphere model as a function of the applied compression (strain). A corresponding quantitative stress-strain plot can be seen in g).

To gather further insight in the interpretation of the in-situ results, we have also carried out a molecular dynamics simulations of the compression (squeeze) of a single sphere and calculated its corresponding stress-strain curve. Our results show that as the sphere moves from a stable configuration (Fig. 11e) and starts to become compressed (Fig. 11f) most of the strain is transferred to its liquid center (Fig. 11f). At a strain of 30%, we observe the formation of a crack at the surface orthogonal to loading direction very like that of the experimental observation. Although the size and loading rates are different in the experiments and the simulation due to computational limits, we are still able to capture the deformation of the solid liquid system. The section of the sphere during loading shows most of the strain is absorbed by the liquid and expands in all three directions. After yielding, the surface solid cracks, the liquid does not move out of the solid shell due to interfacial interactions and the surface tension forces. In conventional reinforced (with good interface) composites, with hard reinforcements (high modulus), load transfers from the matrix to the reinforcement and fails as the interface or matrix yields. Due to mismatch in the strain of the matrix and reinforcement, cracks initiate at either the interface or in the matrix and fractures subsequently. In liquid reinforced composites, the spheres deform and load transfers from the solid to the soft liquid (negligible modulus) and results in an increase in stiffness due to the incompressibility of the liquid phase. As the loading increases the interface changes and due to viscosity, the liquid changes its
shape and fits the surface. Due to such a high interface matching of solid and liquid, the spheres deform almost 80% before yielding. The atomic interaction at the interface and high viscosity of the liquid does not allow the liquid phase to pass through the cracks and can continue loading. No de-mixing was observed for the cases we considered. We also investigated different starting configurations and the results were not sensitive to the initial configurations.

We embedded the spheres in PDMS (a two-part Sylgard 184®) using the procedure described at the beginning of this chapter. The inset in Fig. 12a shows the PDMS composite samples with spheres (first 3 vials) and the pure PDMS control (rightmost clear vial). Generally, the behavior of the neat spheres and the composite including the spheres is extremely similar. However, by placing them in the PDMS matrix it will take more energy to cause them to deform. Thus, it is expected that the composite should take much larger loads than the spheres alone. The mechanical data are in agreement with previous stiffening results seen by Bartlett et al. Fig 4a-b shows the reinforced PDMS matrix under strain, in SEM. The SEM images shows strain lines moving towards the spheres where they come to a stop. This indicates that the spheres can act as a point of deflection (i.e. it takes more energy for the crack to continue thus causing it to blunt). The strain lines are highlighted in the inset of Fig. 12b. Here, the crack lines try to change directions as they reach the spheres thus giving proof to our previous statement. A large amount of energy is required for a crack to change direction; thus, it can be inferred that the presence of the spheres enhance the overall durability of the matrix. Hence, it follows that, for a crack to fully
go through the reinforced material it would have to change direction several times thus increasing the failure point of the composite by a lot. Additionally, the liquid phase of the spheres also adds more energy dissipation properties and durability to the system. Proof for this can be seen in Fig. 12c-f. The sphere-reinforced PDMS composite showed an increase in stiffness of 32.4% and 72.3% for 20 wt. % and 50 wt. % loading, respectively (see Fig. 12d). Considering the amount of liquid going into the system, it is surprising that the overall stiffness increases by such a large amount. We also modeled the behavior of the material in response to a force ramp (Fig. 12e). Although both pure PDMS and the reinforced composite showed similar trends, as the sphere content increased so did the maximum stiffness. However, there is remarkable change in material behavior under static loading (Fig. 12d). As the material was constantly cycled (5 Hz) the stiffness exhibited a unique increase only seen in a few other materials. The stiffening behavior, or self-stiffening as described by others\textsuperscript{7,9,62}, is amplified as more spheres are added to the system. This behavior is mostly seen in isothermal static loading over a myriad of cycles, much like we see here. The behavior has been linked to incomplete curing or sometimes structural re-arrangement. However, in the reinforced composite, self-stiffening arises due to the pushback of the liquid phase as it attempts to maintain its spherical shape against the applied force. As seen with other liquids, spheres represent the lowest energy state and thus trying to change the shape requires surpassing an energy barrier. Thus, whilst being deformed it pushes back causing a rise in stiffness until there is enough energy to cause failure or change the shape dramatically. In addition to this effect it is also
important to remember that the shells also add a degree of stiffness to the overall system. At higher loadings, the PVDF shells could interact with each other thus exhibiting another increase in stiffness. This behavior might also be seen at large strains as the location of the spheres is displaced. Self-stiffening is not seen in pure PDMS and only exhibits at larger wt. % of spheres. Thus, we can postulate that the self-stiffening is not due to curing since our control was cured under the same conditions as the composites. By calculating the overall change in stiffness in each sample a positive linear relationship can be seen between the wt. % of spheres and the amount of exhibited stiffening (Fig. 12f). The bar graph emphasizes the linear trend which is also supported by the fact that the 20 wt. % sample since almost exactly halfway between the pure PDMS and the 50 wt. % sample. This means that we should be able to tune the stiffness to whatever values we want between the two points. To better understand the mechanical behavior as a function of temperature we set up a temperature ramp test in the DMA. PDMS showed a steady increase in stiffness with temperatures up to 200\(^{\circ}\)C. However, after the spheres are added the behavior shows a drastic change and a dip at about 150\(^{\circ}\)C (Fig. 12c). This is due to the melting of the PVDF and the loss of structure, which causes the stiffness to drop dramatically. This is confirmed by the difference in the drops observed between the 20 wt. % sample and the 50 wt. % sample.
Figure 12: Testing and imaging of sphere-reinforced PDMS composites. a) Images of different solutions of PDMS as an inset (rightmost clear bottle) and SEM images of PDMS with the sphere reinforcement. b) Shows a detailed SEM image of the stress lines around the PDMS sphere and deflection of cracks that happens with the spheres present in the composite. c) Shows the behavior of pure PDMS (blue) and PDMS with 20 wt. % PVDF encapsulated PDMS (red) and 50 wt. % PVDF encapsulated PDMS (green) as a function of temperature. d) Shows the stiffness as a function of time in an isothermal test (same coloring scheme and wt. % as Fig. 12c) with dynamic compressive cycling. Finally, e) shows the response of the composites and pure PDMS to a compressive force ramp (inset in figure) and f) showing the effect that liquid has on the stiffness of the PDMS matrix with increasing wt. % of polymer encapsulated liquid.

3.3. Summary on the Effects of Liquid Reinforcement

In summary, the synthesis a new PVDF+PDMS composite that contains liquid PDMS and surrounded by shell of solid PVDF has been reported. The material exhibits an interesting mechanical behavior and shows promise as a reinforcing agent even while containing nearly 60 % liquid. The in-situ mechanical testing shows unique deformation behavior. Molecular models reinforce the mechanical analysis and show the same dynamics as seen in the experimental results. Also, the simulation shows interface between solid-liquid plays an important role in strain accommodation, load bearing capacity and fracture behavior. Moreover, the simulations show that some of the novel properties of the reinforced PDMS are strongly dependent on the level of Coulomb interactions, which can be exploited to tune the stiffness of this new class of materials. The novel spheres/micelles made up of solid-liquid components can be used as reinforcement and exhibit self-stiffening and improvement in mechanical
properties. Thus, we have shown that even as fillers the use of a liquid phase can be very beneficial. Additionally, by highlighting the loading we have also shown that this effect is strong and gives rise to novel behavior. This novel self-stiffening behavior is a relatively novel behavior and, as seen in this part of the thesis, one way to impart it to a material is to use liquid reinforcement.
Chapter 4

Interface-Based PVDF + PDMS Adhesive Blends

4.1. Switching from a Solid Polymer Matrix to a Liquid Matrix

This thesis has explored the possibility of using solid polymer matrices with liquid reinforcements, however, using a liquid matrix with solid filler should yield materials with novel properties. Since polymer chains are repeated monomer units these F-H interactions should play a much larger role in this type of composites due to the high chain flexibility of the liquid phase. This type of material should exhibit completely different properties than purely solid or purely liquid materials and could have many applications ranging from medical to packaging.

Examples of liquid matrices that containing solid particles include starch based solutions. These solutions are particularly interesting due to their non-Newtonian behavior. Additionally, these types of mixtures tend to mimic nature due to their enhanced viscosity and may end up being the synthetic version of tree frog mucus, which allows them to adhere to many different places.
Frequently, nature is used as source of inspiration for researchers in the development of new functional materials\textsuperscript{63,64}. Among all bio-mimetic materials, particular interest has been paid to soft temporary adhesive materials due to their potential applications in consumer products: biomedical, robotics, and device packaging\textsuperscript{65–67}. Materials based on geckos and spiders\textsuperscript{68,69} are some of the earliest examples of adhesive materials which have been further improved through the addition of nanomaterials and enhanced processing\textsuperscript{70,71}. In all of them, the core mechanism is based on intermolecular forces that arise from van der Waals and hydrogen bonding interactions\textsuperscript{72,73}. Generally, the dispersive force exceeds the other types of interactions in ambient conditions but does not have significant resistance whilst submerged in water\textsuperscript{73,74}. Great effort has been expended on the synthesis of adhesive materials inspired by mussels, due to their ability to work underwater\textsuperscript{75}. In general, these materials rely on chemical bond formations with the substrate, which are unaffected by water\textsuperscript{75}. However, one of the drawbacks of this approach is the large variation in bond strength with different substrates. As an alternative, researchers have yet again found inspiration in nature, specifically in the adhesion behavior of the tree frog, leading to the development of novel environmentally independent (in air or underwater) sticky materials\textsuperscript{76}.

The main mechanism of tree-frog adhesion is a combination of complex geometry coupled with the discharge of a viscous fluid. Generally, the geometry is composed of a hexagonal array of nano-pillars distributed randomly within the
array and filled with a viscous fluid\textsuperscript{77}. Several experimental and theoretical studies suggested contributions from capillary forces, friction, and viscous forces to the wet adhesion mechanism\textsuperscript{78}. The draining effect associated with the channel structures allows the frogs to expel the fluid out of the contact layer and achieve high frictional forces. There have been recent reports suggesting the role played by a second phase fluid added to sticky matrices\textsuperscript{79,80}. Cheung \textit{et al.}\textsuperscript{81} demonstrated a simple method to enhance adhesion by depositing a thin layer of silicon oil into an array of biomimetic fibres. Meanwhile, Patil \textit{et al.}\textsuperscript{82} coated a layer of liquid PDMS with low cross-linker content on an array of micro-posts and found enhanced adhesion with limited magnitude of deformation as well as less cohesive separation. All these approaches, however, involve complex fabrication processes and do not fully reproduce the versatility of the tree frog gripping mechanism.

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limited magnitude of deformation as well as less cohesive separation. All these
approaches however involve complex fabrication processes and stabilizing solid-
liquid interfaces.

4.2. Mechanical Synthesis of a Dynamic Solid-Liquid Polymer

Blend

The PVDF-PDMS blend was made through mechanical dispersion of 50 wt. %
PDMS and 50 wt. % PVDF, done under ambient conditions. The constant addition
of PVDF into the system showed an optical shift from the clear nature of PDMS to
an opaque white gel. The blend exhibited a markedly different consistency than the
PDMS indicating a change in the system. This is quite different than the blend made
in THF, since there was absolutely no solvent added and no sonication. Thus,
thermal effects that would lead to changes in properties can be largely ignored. The
properties and structure of the blend were analyzed using microscopy (SEM and
Optical), spectroscopy (Raman and FTIR), as well as mechanical (load-unload
compressive DMA test) and thermal testing (TGA). Additionally, switching from a
PVDF matrix to a PDMS matrix completely changes the properties of the overall
blend. To characterize the existing bonds and the interactions within the blend, we
used Raman and Fourier Transform Infrared (FTIR) spectroscopy. Raman measurements were carried out using a Bruker Senterra confocal microscope operating at 785 nm.

Imaging was done using scanning electron microscopy (SEM) (FEI Quanta ESEM FEG) and a goniometer (Rime-Hart). Raman was done using a Bruker Senterra Raman at 785 nm in ambient conditions. Thermal measurements were done using a TA Instruments Q500 TGA. FTIR was done using a Bruker. XPS was done using a PHI Quantera XPS. XRD was done using a Discovery 8 Bruker XRD. For the mechanical tests we used Dynamic Mechanical Analysis (DMA). For the load-unload procedure in compression, we considered three cycles with a maximum force of 0.01 N, 0.05 N, and 0.1 N respectively. Using a blend made of PVDF and PDMS, which has a gel-like consistency, we create a thick layer and performed the load-unload testing. This kind of test allow us to understand how adhesion behaves both when adhering and upon separation from a surface.

We carried out Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA)\textsuperscript{85} and Perdew-Burke-Ernzenhof (PBE)\textsuperscript{86} for exchange-correlation functional in the calculations of the electronic properties of PDMS and PVDF. The calculations were carried out using the code OpenMX, which employs a formalism based in pseudo-atomic orbitals (PAO)\textsuperscript{87} and norm-conserving pseudopotentials\textsuperscript{88,89}. For the elements carbon, oxygen and silicon we considered two s-orbitals, two p-orbitals and one d-orbital (s2p2d1) as a PAO
basis set to expand the electronic wave function. For hydrogen and fluorine ones the considered basis set were s2p1 and s4p4d4f3, respectively. For energy cutoff and energy convergence tolerances we used 125 and 1.0×10⁻⁶ Hartree, respectively. We carried out geometry optimization and the final geometry was considered optimize when the maximum force in the system is below 1.0 × 10⁻⁴ Ha/Bohr. The van der Waals interactions were included through the scheme proposed by Grime et al.⁸⁵.

The MD calculations were carried out using LAMMPS⁹⁰ software. The bonded interactions (bond, angle, and dihedral terms) were described by COMPASS⁵⁴ force field, and the parameters optimized to describe the PDMS⁵⁹ and PDVF⁵⁸ structures. The atoms belonging to the SiO₂ slabs were kept frozen during the simulations. To simulate the loading procedure, a mixture of PDVF and PDMS was placed in between two SiO₂ slabs. The bottom slab was kept fixed and the upper one had all atoms displaced by a constant rate of 1.5x10⁻⁴ Ang/fs, approximating to the bottom one. The unloading procedure was performed using the same rate, but in the opposite direction.

**4.3. Mechanics of Dynamic Polymer-based Adhesive**

In this work, we report a chemical reaction free, scalable approach to create a two-phase (solid/liquid) polymer adhesive material (repeatedly stick to different materials, independent of environment, does not require curing time) achieved by
combining two inexpensive commercial polymers (PDMS and PVDF). At the macroscopic level isolated PDMS is a transparent liquid, whereas PVDF is a white powder. The solid-liquid composite is results from the simple mechanical dispersion of the PVDF into PDMS, as shown in Fig. 13a. Just combining these two polymers the resulting material is no longer solid or liquid but has a gel-like consistency and a translucent colour (shown in Fig. 13b, see the coating of adhesive on glass covering right owl eye) and Fig. 13d-e illustrate the gel consistency. The structural characterization at the microscopic level and subsequent proof of the PVDF dispersion into PDMS was obtained by optical and scanning electron microscopy (SEM) (Fig. 13c-f). The images show well dispersed blister-like appearance of solid PVDF spheres (~200 nm diameter) embedded into liquid PDMS. The material also shows structural and chemical stability over long periods of time (no segregation or degradation were observed in samples aged up to several months).
Figure 13: Structural characterization of the material resulting from combining (mechanical dispersion) of PVDF and PDMS. a) Molecular model composed of PVDF rigid spheres (in red) embedded into the liquid PDMS phase (in yellow). b) Digital image of a glass sheet coated with the adhesive showing the translucent material. c) SEM image showing the PVDF spheres immersed into the PDMS medium. d) Side view and e) top view of the processed adhesive. f) Optical image of the adhesive depicting the uniform dispersion of solid PVDF (black) into liquid PDMS (white).

Diversified spectroscopy analyses (Raman, Fourier Transform Infrared (FT-IR) and X-Ray Diffraction (XRD)) reveal that the signatures belonging to isolated PVDF and PDMS are preserved after mixing (Fig. 14a-b). The Thermogravimetric Analysis (TGA) of the adhesive shows degradation occurred at \( (461 \pm 1) \)°C and a small broad peak can be observed at \( (439 \pm 1) \)°C (Fig. 14b). The onset of degradation was shifted in relation to neat PVDF, which can be attributed to the interactions between the two polymers.
Figure 14: PVDF+PDMS Raman and TGA Characterization. a) Raman characterization of PVDF, PDMS, and the blend. b) TGA analysis showing PVDF, PDMS, and the mixture. The orange line represents the degradation curve of PDMS whereas red signifies the PVDF and black is the mixture of PDMS and PVDF. Additionally, blue is the derived weight loss of the mixture, purple is the PVDF weight loss, and grey is the PDMS weight loss.

These results indicate that no chemical reaction between the polymers occurred during the process (two phase system remains and no new phase forms). To gain insight about the PDMS/PVDF interface, we carried out Density Functional Theory (DFT) calculations. DFT was used to analyze how the relative orientation between PDMS and PVDF chains affect the adhesive stability. The DFT study was carried out considering PDMS and PVDF short chains (Fig. 15a-b).
Figure 15: Dipole interaction between PVDF and PDMS polymers. a) PDMS and b) PVDF chains considered in the DFT calculations. Taking the chain length as reference (x-direction) the upper region is formed mostly by hydrogen, while the bottom one is formed by oxygen (fluorine) for PDMS (PVDF) c), d) and e) show the electronic
density for the three most stable configurations. f) interaction energy (in eV) for all the considered configurations. To allow a direct comparison between the electronic densities, all of them were plotted with the same isosurface value.

The interaction energy is calculated for different configurations (Fig. 16a-f).
Figure 16: Different theoretical configurations. a-f) Shows the different configurations that were used in theoretical energy calculations between polymer chains. Configurations 3, 5, and 6 are the most stable interactions.

The interaction energy is defined as the difference between the total energy of the interacting chains ($E_{PDMS+PVDF}$) and the total energy for the isolated ones ($E_{PDMS}$, $E_{PVDF}$ for PDMS and PVDF, respectively):

$$ E_{TOT} = E_{PDMS+PVDF} - (E_{PDMS} + E_{PVDF}) $$

Equation 4.1 – Energy Relation for PDMS+PVDF

In Fig. 15c-e we show the three most stable configurations, in terms of interaction energies (Fig. 15f). The electronic cloud chain anisotropy can explain these large differences. The results show that the interaction energy is strongly dependent on the relative orientation between the chains, which resembles the lock and key effect present in similar molecular systems $^{91}$.

The electronic density for configuration 3 (Fig. 15c) shows a substantial overlap between the chains, when compared with other considered configurations (e.g. configurations 5 and 6, Fig. 15d-e). Electronic density overlap is evidence of strong interactions (e.g. hydrogen bonding)$^{92}$ between PDMS and PVDF, especially in configuration 3. For the other configurations, the overlap is less pronounced and indicates a weaker interaction such as adsorption $^{93}$. Energetic comparison for all the considered configurations showed a preferential orientation and the strength of the interaction (~1.0 eV) comparable to the ones encountered in ion HF system
These results have important implications to explain the adhesive properties, as discussed below.

To characterize the adhesive properties, cyclic compressive measurements (loading-unloading) with 0.01, 0.05 and 0.10 N were performed (Fig. 17a). During adhesive loading (compression) the stiffness increases and during unloading (release) the stiffness does not drop, which is a signature of adhesion. In order to quantify the strength of the adhesive, a 180 degree peeling test (as schematically shown in the inset of Fig. 17b) was performed using two copper sheets. The shear stress versus strain plot (Fig. 17b) shows linear stress region until 2% strain and reaches a maximum value (ultimate strength) around 0.11 MPa (Fig. 17b).
Figure 17: Mechanical testing of the adhesive. a) cyclic test of compression (loading) and tensile (unloading). The loading/unloading stages are indicated by dotted red lines. The black solid and dotted blue curves indicate the load and stiffness variation in time, respectively. Inset shows schematic of the loading setup. b) Adhesive shear test (180-degree peel test) of two copper samples put into contact using the adhesive. Inset shows schematic of the loading conditions. c) Optical imaging shows two glass sheets stick together by the adhesive (before) and the formation of strings during separation (after). d) SEM image after separation highlighting a single string. e-g) Snapshot from MD simulation mimicking the loading/unloading adhesive cycle. e) initial stage, f) maximum loading and g) intermediate unloading stage showing the string formation. h) the force profile experienced by the adhesive during the load (positive force) and unload (negative force). The red points indicate the force at specific time of the simulation and the blue curve it the fit of these points. i) high magnification SEM image, j) and AFM image with line profile of strings after adhesive detachment.

To understand the morphology changes during adhesion, two glass slides were adhered together (before and after shown in Fig. 17c). The glass slides are then separated and the process is monitored using an optical microscope. As the slides are separated, the adhesive exhibits severe plastic extensions and stringing (Fig. 17c - after). This behavior is observed in most adhesives. The SEM image of the separated slides (Fig. 17d), also confirms the presence of stringing. Higher magnification images (Fig. 17e) show the presence of strain lines running across their surfaces of the strings. These strain lines indicate adhesive stress accommodation, which is a consequence of PVDF spheres acting as anchor points in PDMS. The same behavior cannot be seen in isolated PDMS (Fig. 18).
Figure 18: SEM of PDMS. The figure shows the SEM of PDMS. This shows the stress lines created by the gold coating on the PDMS post sputtering.

Further evidence of anchoring effect was obtained through Atomic Force Microscopy (AFM). AFM height profile (Fig. 17f) revealed a peak of 200 nm (corresponds to PVDF size) followed by steps around it. The steps correspond to the strain lines due to anchoring of PVDF, which were also seen in the SEM images.

DFT results showed that there are significant interaction energy differences, which could be in the origin of the anchoring effect. To address this issue with DFT methods is computer prohibitive (size system and simulation time). One possibility is to use classical Molecular Dynamics (MD) for large enough system to mimic the PDMS/PVDF structures. Using this approach, it is possible to address the adhesive behavior from atomistic level. We have carried out MD simulation using classical force field \(^{60,96-98}\) (see methodology section for further information). The used model system (Fig. 17g) consists of PVDF spheres (in red) embedded into the PDMS
medium (in yellow) placed in between two slabs of amorphous silicon oxide (SiO$_2$). To simulate the load stage, the distance between the slabs is decreased at a constant rate until to attain a significant deformation (54%) (Fig. 17h). During the adhesive compression, the liquid phase allows the solid spheres to easily flow towards the slabs, thus increasing the contact area. The unload stage is performed using the same loading rate but along the opposite direction (Fig. 17i). In this stage, it is possible to observe the onset of string formation between the slabs, which are consistent with experimental observations (Fig. 17d). The net force along the direction of the sheet displacement is recorded during the load/unload cycle. We can identify an asymmetric behavior (Fig. 17j), with maximum force for the loading stage (corresponding the instant from 0 to 200 ps) $\sim$12 nN and for the unloading stage (corresponding the instant from 200 to 400 ps) $\sim$25 nN. The force experienced during the unloading stage is around two times higher than the maximum force in the loading stage, which characterize an adhesive regime.

The combined analysis of experiments and simulations allow us to have a clear understanding of the adhesive mechanism. Although individually PDMS and PVDF do not present adhesive behavior, but after mechanical dispersion the product exhibit adhesive behavior. During the loading PVDF interacts stronger than PDMS with the contact surface, while during the unloading due to the strong interaction between the PDMS and PVDF we have an anchor effect that is the origin of the adhesive behavior and string formation.
Our adhesive can work on a broad range of different materials (and mismatched combinations of them), such as, organic, inorganic, metal and oxide (Fig. 19a-d). For all cases, standard weights were used to determine the maximum shear strength required for separation. We have explored the application of the adhesive in sticking bio-materials, such as, chicken and pig skins (Fig. 19c-d). The measured adhesive shear stresses of few of these materials are also shown in Fig. 19e. The co-existence of liquid and solid phases can explain this universal-like adhesion. The liquid can take the shape (roughness of the surface) of the interface creating an almost perfect interface whilst the size of the nanoparticles allows an almost homogeneous distribution, thus creating a strong interfacial interaction.
Figure 19: Adhesion on different materials and in different environments. Representative examples of adhesion on different substrates a) glass/paper, b) metal/glass, c) chicken skin and d) pig skin. e) Adhesive shear strength for different materials interfaces. f) Contact angle values of water droplet on glass, paper, aluminum and plastic coated with adhesive. g) Stiffness versus time under loading and unloading cycle of adhesive submerged with different fraction of water in a submerged clamp (shown in the inset). Demonstration of adhesion behavior of two transparent glass sheets inside water h) initial state of two separated glass sheets. i-j) adhered glass sheets viewed from different directions.

To evaluate the adhesion behavior of the composite in liquid media (water and oil), a cycling loading and unloading test in submerged condition is performed (Fig.
The submerged clamp volume is filled with different fraction of water and compressed and then pulled. The adhesive behavior is similar in both wet and dry conditions (water and oil, as well). PDMS and PVDF are both hydrophobic materials. We tested the adhesive wettability to see if the mechanical dispersion changes this characteristic. The results (standard contact angle measurements) showed that the adhesive is still hydrophobic (Fig. 19f). The adhesive can even work under water, as illustrated in Fig. 19h-i.

4.4. Unique Properties and Applications

In summary, we report a bio-inspired, chemical free (with no curing time required), easily scalable, new class of adhesive, made by simple mechanical dispersion of PVDF (solid) into PDMS (liquid). The material can be utilized universally and repeatable under different ambient conditions, even under liquids. These results represent a significant advance in achieving amphibious adhesive and can lead to new pathways for designing new universal adhesives, like the ones exhibited by some of the biological systems in nature.
Chapter 5

Optimized Polymeric Adhesives:
Shifting Towards PTFE and PDMS

5.1. Exploring other Dynamic Interfaces

To further explore the strength of the F-H interface we synthesized a different version of the adhesive by replacing the PVDF with polytetrafluoroethylene (PTFE). By replacing PVDF the polymer chains have access to two more F atoms per monomer. These F atoms will help enhance the strength and cohesion of the material. Thus, this part of the thesis sets up a methodology for synthesizing novel adhesives based on novel liquid-solid polymer blends using strong electronegative differences.

Newer and simpler ways to generate adhesion in various materials have been the subject of several recent studies\cite{99,100}. Several approaches have been used to achieve this including patterning, cross-linking, surface modification, and chemical synthesis\cite{73,101–104}. One of the most recent examples of adhesion can be seen from Yuk
et al.\textsuperscript{103}, where the authors surface functionalized hydrogels to allow them to readily stick to porous surfaces. Additional examples of adhesion include mussel inspired adhesives and gecko-patterned materials. Mussel-derived proteins and 3,4-dihydroxyphenylalanine (DOPA) cross-linkers are recent methods used to synthesize water resistant adhesives\textsuperscript{66,73,74,103}. Research focused on patterning materials to create strong adhesive materials have shown impressive results, yet face scalability issues\textsuperscript{77,105}. Many polymer adhesives rely on cross-linking, or \textit{in-situ} polymerization which can lead to unexpected changes in material properties\textsuperscript{99}. Adhesives derived from these methods can also suffer from: substrate limitations, environmental limitations, long curing times, toxicity, and lack of recyclability. Furthermore, instant curing adhesives have become an area of great interest to avoid the drawbacks associated with the curing process. These instant adhesives are separated into several categories based on their curing process: chemical curing, photo-curing (light activated), thermal-curing (temperature activated), and most recently low-voltage curing\textsuperscript{106}. Although each one of these methods can instantly cure adhesives the curing is permanent and irreversible. In reaction to this, researchers such as Lawrence \textit{et al.}\textsuperscript{107} proposed the use of ionic-bonding to create semi-reversible adhesives. To this day, the search for a versatile biocompatible adhesive with the ability to work in any humidity level, show reversibility, and have a myriad of substrate choices is an ongoing focus. As previously stated, such an adhesive is extremely useful for biomedical, underwater, as well as energy applications.
5.2. Synthesizing an Optimized Adhesive System

Much like the PVDF-PDMS blend, equal weight of hydroxyl terminated PDMS (Sigma Aldrich 18,000-22,000 cSt) and PTFE (DuPont Zonyl 1000 MP submicron particles) were measured out using a scale and then mixed (by hand) until a homogenous mixture was obtained. The substrates used for adhesion were cut to the dimensions of a glass slide and the adhesion area was roughly 15 mm by 25 mm (except for Si due to size restriction where we adjusted for the area in the overall stress calculation, \( \sigma = F/A \)).

Qualitative tests were performed using standardized weights. The materials were qualitatively tested by taping weights and holding at 90° for several minutes as shown in the supplemental material. This was performed both in air and fully submersed in water for both shear and tensile modes.

Qualitative torsion tests were performed using a spin coater and applying a layer of glue onto a 10 g weight with a 15.83 mm diameter. The adhered weight was spun at various speeds up to 500 rpm. The speed was incremented by \(~50\) rpm and held for 30 seconds to assure that the weight did not prematurely separate. The weight was held at a constant distance from the center of the spincoater to ensure that the torsion forces did not change. The underwater testing was performed by pouring water over the contact area then adhering the weight and underwent the same procedure as the dry samples. DMA testing was performed at 0.1 N/min and
0.001 N/min for pure PDMS, 25% PTFE+PDMS and 50% PTFE+PDMS. The testing was performed in force controlled mode in tensile using samples made of copper foil (overall size ~ 18 mm x 6 mm, length x width). The testing was performed at standard room temperature and pressure. The tensile testing was performed using an ADMET eXpert 7600 setup with a steel wire to pull at 90°. The steel wire was attached to a hook that was directly welded into the upper metal substrate used in the adhesion. The pulling was performed at a rate of 5 mm/min. We tested both adhesion between two metal substrates and adhesion between a plastic and aluminum substrate. For the adhesion between mismatched substrates we replaced the bottom aluminum piece with a piece of plastic and repeated the same procedure. The procedure was repeated several times without re-application of the adhesives and without touching the adhesive surface. The procedure was also repeated after smoothing out the adhesive surface in between runs, but after failure. In-situ testing was performed at Hysitron Inc. PI85 indenter attached inside 3D VERSA with field emission gun. FTIR was performed at the Army Research Laboratory. (Thermo Nicolet Nexus 670) using an averaging of 16 scans per spectrum with a resolution of 4 cm⁻¹. The material was spread between salt crystal wafers and scanned with varying PTFE:PDMS ratios. TGA was performed using a TGA 500. The procedure was performed in air up to 800°C at a rate of 10°C/min.

When trying to produce high quality CT scans, the sample preparation can be as critical as the scanning process. The sample was mixed and applied onto a 25 mm
by 25 mm glass slide, an identical slide was pressed against the sample and then pulled apart, taking care to not add any sliding or rotation to this process. The glass slide was then mounted into the Zeiss Xradia 510 Versa so that at 0° the source and detector would be at a normal to the plane of the glass slide. To enhance phase contrast for edge detection, the source and detector were brought in as close to the sample as possible, without collision during its rotation from 0 – 360 °. The recipe was set to 80kV, 7W, 4X objective, no filter, 0.5 second exposure with 8601 projections and multiple references. All CT measurements and analysis was done at the Adelphi Laboratory Center (ALC).

All mechanical properties are computed using classical molecular dynamics (MD) with its numerical implementation in the large-scale atomic/molecular massively parallel simulator \(^{90}\) (LAMMPS), using: 1) the parameterizations of the Reax Force Field (ReaxFF) described below, 2) a timestep of 0.25 femtoseconds, and the 3) Nosé-Hoover thermostat at room temperature.

The ReaxFF C/O/H/Si/F force field parameters used in this work are a combination of the carbon-parameters from Srinivasan et al. \(^{108}\) which were extended to C/H/O interactions by training against the DFT-data described by Chenoweth and co-workers \(^{109}\). The Si/C interaction parameters were trained against the DFT-training set described in the PDMS/ReaxFF work \(^{110}\). The new C-F bond and affiliated angle and dihedral terms were trained against DFT-data derived from a Zdol-
monomer (Fig. 20a) and from \((\text{H}_3\text{C})_2\text{CF}_2, \text{C}_4\text{F}_{10}\) and \(\text{F}_2\) molecules. All DFT calculations were performed at the B3LYP/6-311G** level. Figures 20b-d compare the ReaxFF and DFT results for the bond, angle and dihedral scans for the training set molecules. Overall, the ReaxFF performance is a good match to the DFT-data. The ReaxFF bond energies are typically a little lower than the DFT-numbers – but as such provide a better match to experimental bond energies. For the C-O-C angle in Zdol, ReaxFF obtains a shallow secondary minimum at around 90 degrees – this is probably due to the formation of a weak C---C bond across the C-O-C angle; this could potentially be repaired by increasing the C-C-O angle parameter force constants. However, this secondary minimum is quite shallow (about 1 kcal/mol) and as such is not expected to significantly affect C-O-C angle behavior during MD-simulations. In Fig. 20d, we only show the dihedral angle cases with meaningful rotational barriers; we also performed DFT analyses for the C-O-C-O and C-C-O-C dihedrals in Zdol and found very small rotational barriers (< 0.5 kcal/mol) – and these small barriers are reproduced by ReaxFF.
Figure 20: ReaxFF Parameters. a) Zdol monomer structure with backbone numbering as used in the ReaxFF force field development. b) ReaxFF and DFT energies for bond compression/extension energies in Zdol (H₃C)₂CF₂ and in F₂ molecules for F-F bond. The C-C bond data (see related inset) is for the C₂-C₃ bond (see numbering in Figure 20a), the C-O bond data (see related inset) is for the C₃-O₄ bond, the C-H bond data (see related inset) is for the C₂-H bond, the C-F bond data (see related inset) is for the C-F bond in (H₃C)₂CF₂ and the F-F bond data (see related inset) is for the F-F bond in F₂. c) ReaxFF and DFT energies for valence angle opening/closing energies in Zdol. The C-C-F angle data (see related inset) is for the C₂-C₃-F angle, the C-O-C angle data (see related inset) is for the C₃-O₄-C₅ angle, the F-C-O angle data (see related inset) is for the F-C₃-O₄ angle, the F-C-F angle data (see related inset) is for the F-C₃-F angle and the O-C-H angle data (see related inset) is for the O₁-C₂-H angle. d) ReaxFF and DFT energies for dihedral angles in Zdol (O-C-C-F and F-C-o-C) and in F₃C-CF₂-CF₂-CF₃ (C-C-C-C). The O-C-C-F dihedral data (see related inset) is for the C₅-O₆-C₇-F dihedral angle (see numbering in Supplemental Figure 20a) and the F-C-O-C dihedral angle data (see related inset) is for the F-C₅-O₄-C₃ dihedral angle.

Single units of hydroxyl-terminated PDMS, OH-[Si(CH₃)₂O]ₙ-H, and PTFE, (C₂F₄)ₘ, with n = 410 and m = 512, were prepared using the molecule editor Avogadro(51), equilibrated in a canonical ensemble (NVT), in a 150 Å × 150 Å × 150 Å simulation box with fixed boundary conditions, for 40 picoseconds. The equilibrated PDMS and PTFE units (see Fig. 4A) were inserted into two 100 Å × 100 Å × 100 Å simulation boxes with periodic boundary conditions. The PDMS+PTFE box contained three PDMS units and one PTFE unit while the PDMS box contained three PDMS units. Both boxes were squeezed by roughly 20% in a microcanonical ensemble (NVE) for 5 picoseconds and equilibrated first in a canonical ensemble (NVT) for 5 picoseconds to ensure an even distribution of particles in the box and then in an isothermal-isobaric ensemble (NPT) for 5 picoseconds to relax the
simulation box. This series of equilibration processes resulted in a 51 Å × 51 Å × 51 Å PDMS+PTFE (4FPS) simulation box with a mass density of ~1.8 g/cc and a 20 Å × 20 Å × 20 Å PDMS simulation box with a mass density of ~0.97 g/cc (see Fig. 4A). Further, a 1 × 1 × 2 4FPS supercell was then sandwiched between two identical 76 Å × 108 Å × 11 Å bulk Si (100) substrates into two configurations: A configuration (Si/4FPS/Si) with the 4FPS supercell lying on the surface of the substrate and a configuration (Si/4FPS+H₂O/Si) with the 4FPS supercell ~5 Å away from the surface of the substrate (see Fig. 5). Water molecules, H₂O, were added into the second configuration in the space between the substrates and the 4FPS supercell as well as all around the 4FPS supercell until they reached the density of ~1 g/cc. They were then equilibrated in a canonical ensemble (NVT) for 30 picoseconds (with periodic boundary conditions) to ensure proper chemical interactions with the substrate and the mixture.

The computation of the stress-strain relationships on the above 4FPS, PDMS, Si/4FPS/Si, and Si/4FPS+H₂O/Si models proceeded by: 1) further equilibrating the respective structures in an isothermal-isobaric ensemble (NPT) while compressing them by 22 %, 22%, 30% and 33% respectively for 5 picoseconds and 2) stretching them back by 25 %, 25%, 33%, 35% respectively for 5 picoseconds. As the box compression/tension or loading/unloading occurred uni-axially (in the x, y, and z direction) and bi-axially (in both x and y directions), the respective stresses and strains at every step were computed.
MDA MB 231 cells were cultured in a 96 well plate. 2000 cells were seeded in each well. The specified amount of glue was dissolved in the cell culture media by mechanical mixing. Various concentrations were then added to the cells in culture. The cells were incubated for 24 hours and 48 hours. After the incubation time the media was aspirated and the wells were washed with PBS before adding the MTT reagent. The cells were incubated with the MTT reagent for 2 hours before adding DMSO as the stop solution. The absorbance was then measured in a plate reader. There was no significant cell death observed at concentration as high as 1mg. The experiment was repeated with higher concentrations (5mg, 10mg) of the material. However, no significant toxicity or cell death was observed.
HEK 293T-GFP (Embryonic kidney normal cell line)  MDA-MB-231-GFP (Breast cancer cell line)

![Images of HEK 293T-GFP and MDA-MB-231-GFP cells]

**c**

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HEK 293T-GFP (Embryonic kidney normal cell line)

![Images of HEK 293T-GFP cells at different time points]
Figure 21: MTT Assay for Cell Viability. a) HEK 293T cells grown on a culture dish coated with the glue b) MDA-MB-231 cells grown on a culture dish coated with 4FPS c) Percentage cell viability obtained by MTT assay on MDA-MB-231 cells with different concentrations of the glue, calculated relative to the control at 24 hrs. Anticancer drug Doxorubicine (DOX 2µM) is used as the positive control. d-f) HEK 293 T cells showing good cell growth on a tissue culture grade dish coated with a uniform layer of the glue.

To study the growth of the cells on the glue, it was well spread uniformly on the cell culture dish. This was incubated with the media for a day before adding the cells. The study was conducted on GFP labelled human embryonic cell line HEK 293T and GFP labelled breast cancer cell line MDA MB 231. No proliferation defects were seen.
Figure 22: Mixture of 4FPS with Antibiotics. Optical image of mixture of 4FPS with antibiotics of different concentration. It clearly showing a homogenous mixture.
5.3. Characterization and Analysis

We chose hydroxyl terminated PDMS (poly dimethylsiloxane, liquid phase) and PTFE (poly tetrafluoroethylene, solid phase) as the prototype system to demonstrate the novel adhesion concept\textsuperscript{112-114}. The large amount of fluorine in the PTFE polymer is capable of generating an induced dipole-moment in neighboring atoms\textsuperscript{115,116}. PTFE and PDMS are immiscible, however, the mixture has not shown separation over extended time periods (>6 months). Raw PTFE (DuPont Zonyl 1000 MP) is a powder made up of spherical shape particles and hence has a large surface area. As mixing occurs, the PDMS organizes preferentially around PTFE spheres (Fig. 23a and d). The molecular-level dipole interactions can give rise to macro-scale adhesive properties and are bolstered by the previously discussed jamming effects expected between liquid PDMS and PTFE spheres. During shear/torsion the PTFE can interact with the PDMS through dipole interactions and resist deformation. The resistance to deformation is expected to rise with deformation rate (Fig. 23a). Additionally, during tension the spheres can hold each other in place (jamming) and will not move because of the surrounding dipoles (Fig. 23b). The new material is characterized using scanning electron microscopy (SEM), \textit{in-situ} mechanical testing attached with SEM, X-ray tomography, dynamic mechanical analysis (DMA), thermo-
gravimetric analysis (TGA), Fourier-transform infrared (FTIR), and qualitative methods using standard weights. The idea of building unique adhesive behavior based on molecular interaction is verified using MD simulation with help of new ReaxFF reactive force field description (supplementary information Fig. 20).

Figure 23: Proposed Mechanism and SEM Imaging of Failure Modes. The proposed failure mechanisms for shear a) and tensile b) modes show the interactions at play while failure is happening. The dipole interactions prevent initial failure and give a large amount of resistance. The schematics are confirmed through SEM imaging where tensile failure c) shows the stress lines due to pull out in the inset as well as the voids left from pulling out the PTFE. Additionally, the second inset in c) shows the different mixtures of the polymers and the change from clear PDMS to a white mixture. The dipole interactions are schematically emphasized in d) and apply to the shear failure seen in e). The stress lines have also been highlighted in e) and they can also clearly be seen around all the PTFE which act as anchoring points.
SEM analysis of 4FPS (1:1 PTFE to PDMS ratio) showed that the material is homogenous and shows a polka dot like pattern (Fig. 30c-e). To the naked eye, the material looks like a white gel, whereas, PDMS is clear and PTFE is a white powder (inset in Fig. 23c). SEM images after tensile failure (Fig. 23c) show that the PTFE tends to pull out of the matrix and this is further supported by the stress lines that can be seen around the pull-out area as emphasized in the inset in Fig. 23c. In comparison, shear failure under SEM (shown in Fig. 23e) shows stress lines developing around the PTFE particle which indicates that the PTFE acts as anchoring points (inset in Fig. 23e) for the adhesive.

In-situ SEM mechanical measurements showed stringing within 4FPS (molecules bridging the gap across the substrates after attempting to detach from the material (Fig. 24b and inset in Fig. 24b)\textsuperscript{117}. The in-situ tensile mechanical measurement is shown in a series of SEM images that correspond to compressive pre-loading, loading (in tension), and unloading (Fig. 24a, b, and c respectively). The in-situ load-displacement curve shows full recovery after each cycle but some distinct abnormalities are present in the first cycle (Fig. 24d-e). Generally, such load drops represent sudden changes in material behavior such as loss of contact area. Although loss of contact is a possibility in this type of test it cannot be seen in either the images in Fig. 24a-c. Thus, we postulate that the local maxima and sudden drops seen in the in-situ measurements are most likely because of jamming effects since they tend to dissipate once a critical load is reached through re-organization (these effects are highlighted in red in Fig. 24d). Jamming is known to occur as a buildup of stress
(exhibited by the local maxim at a depth of ~2000 nm) and then release (represented by the valley following the peak at ~2000 nm) through rearrangement which is strikingly similar to what in-situ data suggests\textsuperscript{118}. After rearrangement the stress will normalize and the trend will continue until jamming re-occurs (as seen at ~3000 nm)\textsuperscript{119–121}. These effects did not happen in subsequent cycles which support the idea that these abnormalities disappear after re-organization (Fig. 24e). The material does not exhibit any residual strains and shows highly recoverable cyclic behavior which indicates no loss of adhesion even after several cycles. This is complemented by the liquid phase which prevents crack formation and propagation due to the mobility of the PDMS polymer chains.
Figure 24: *In-situ* testing and characterization of PDMS+PTFE. The *in-situ* testing images were set up to show the initial a) loaded b) and unloaded c) states of the PDMS+PTFE (4FPS). The stress areas from the tensile loading were clearly outlined in b) and the stringing effect can be seen in the inset in b). Stress-strain curves showing the initial cycle d) and multiple cycles e) are present and have key features highlighted. The loading and unloading is clearly marked in e) and the jamming can be seen in d). A schematic of the effects of loading on the material can be seen in f) and shows how the material goes from a relaxed state I and undergoes re-orientation in II while under compression. When the material is under tensile load (III) jamming and anchoring take place and there is a stress gradient which is emphasized by the colored outlines around the spheres (red is high stress and yellow is medium stress). Final failure is seen in part IV where the material finally separates. X-ray computerized tomography (CT) of an overall mass of 4FPS is shown in g) and then bisected in h) to reveal the inner structure of the mixture. In these images, blue shows the PDMS regions whereas the yellow marks the PTFE regions. Further zooming in on the inner structure shows strain/flow lines, emphasized by red arrows, in both i) and j). A re-color, j), of the same image shows the agglomeration and initiation of jamming of PTFE particles in line with the direction of the stress/flow. By zooming in on the interface k), the PTFE particles can be seen arranging near the substrate in both 2D slices l-n) but also in the 3D side view p). The dashed red line marks the end of the substrate in both the 2D slices l-n) and 3D side view p). The 2D slice l) shows both the PDMS (blue) and PTFE (yellow) regions colored accordingly, whereas m) only highlights the PTFE region, and n) show the raw grayscale slice. A 3D overview with both colored and grayscale versions of the image is shown in o), whereas a side view is shown in p). In the 3D side-view, the PTFE is arranging along the interfaces with the substrate, which has been highlighted using a dashed red line.

A proposed schematic explaining the load-displacement behavior of the material can be seen in Fig. 24f. The material consists of dispersed solid spheres and liquid around it, and starts in an initial state (I). During compression/mixing (in secondary state (II)) the material keeps re-orienting until reaching the lowest energy arrangement (i.e. with low distance between spheres). As the solid-liquid composite is being unloaded (separated), it begins to exhibit stress concentrations at interface, while the solid spheres try to keep themselves together and cause jamming to prevent separation. The stresses are expected to be much higher as the spheres are closer to
the source of the tensile force as displayed by the outlines around the spheres. The final phase of the testing would be complete failure and would lead to separation between the two substrates (IV) as seen in the SEM images (Fig. 23e). SEM images for the initial stress-strain cycle representing pre-loading, loading, and unloading can be seen in Fig. 24a-c, respectively. The in-situ mechanical data further supports the mechanism, showing the effects of tensile stresses on the glue during adhesion as seen in supplementary information Fig. 25a-e.
Figure 25: *In-situ* Characterization. a) Shows *in-situ* pulling of 4FPS. Upon zooming in, b) shows a closer image of the glue during strain. Further zooming, c) reveals the spherical PTFE embedded in the PDMS and as the adhesive is pulled from c-f) strain lines begin to appear. These strain lines have been specifically highlighted in e) and f) and show the re-orientation discussed in the paper and serve as experimental proof for the proposed adhesion mechanism seen in Fig. 24f as well as the general tensile behavior of the adhesive proposed in Fig. 23b.
Although jamming is difficult to experimentally show and characterize, we employed X-ray computerized tomography (CT) to tentatively visualize the effect in the mixture. Two glass slides were adhered and separated using 4FPS, afterwards, the 4FPS was imaged using CT. The data is showed in Fig. 24g-p. The imaged data was shown both in grayscale as well as using colored regions of interest, blue for PDMS and yellow for PDMS. The overall 3D structure of the 4FPS (Fig. 24g) shows aggregations and surface stress lines, the agglomerations near the surface are an initial indicator of possible jamming. Once bisected, the material shows inner stress lines (Fig. 24h). Zooming in shows agglomerations of PTFE around the stress lines indicating jamming in that area (Fig. 24i-j). The arrows seen in Fig. 2i show the direction of stress and Fig. 24j shows the PTFE particles in yellow which were identified based on their intensity in relation to the PDMS phase. Jamming could also take place at the interface, thus Fig. 24k-p show the interface of the 4FPS with the glass substrate. An overall 2D slice of the material is shown in Fig. 24k. Zooming in on an area close to the substrate shows PTFE extremely close to the surface (Fig. 24l-n), thus lending strength to our hypothesis that PTFE can act as anchoring points. A 3D view of the top surface and side surface of 4FPS on the glass substrate can be seen in Fig. 24o and p, respectively. The 3D side views (Fig. 24p) clearly show the presence of many PTFE particles and agglomerates near the surface of the glass. Closer inspection of all the CT data also shows that these particles trend toward the peaks and is also further evidence in Fig. 26f-k. Additional CT scanning of the inner structure of the material are further show the agglomerations of the PTFE particles along the
stress lines and surfaces. This further supports the hypothesis that jamming can happen within the mixture since particles get closer towards the peak of the material.

The chemical structure of the material was analyzed using FTIR spectroscopy, as seen in supplementary information Fig. 26a. The spectrum clearly shows that there are no new chemical bonds formed through the mixing thus eliminating the possibility of covalent bonds. As we change concentration of PTFE, the CF₂ peaks appear and relative intensity of PDMS decreases (see supplementary information Fig. 26a). Thermogravimetric analysis (TGA), performed in air at 10°C/min, shows results supporting the spectroscopy observations as seen in supplementary information Fig. 26b. The material shows some molecular interactions since the onset of degradation shifts by ~80°C relative to raw PDMS. The two highlighted regions in supplementary information Fig. 26b correspond to regions that have the same degradation slopes (i.e. the blue region represents the region where the mixtures’ degradation slope is the same as that of PDMS, while the green region represents the region where the degradation slope matches the PTFE slope, revealing the composite has the same behavior as individual components. An additional Raman analysis was also performed and shown in supplementary information Fig. 26c.
Figure 26: Material Characterization. The material was also characterized through FTIR a) which shows the diminished peaks of the Si-O-Si vibrations and the increasing CF$_2$ vibrations arising from higher PTFE content. TGA studies b) show the degradation of the material and the highlighted areas represent similar slopes between the mixture and either the PTFE or PDMS (blue represents similar slope to PDMS whereas green represents a similar slope to PTFE). The overall Raman spectra can be seen in c), for varying wt. % of PTFE and PDMS. A closer analysis of the characteristic peaks of PDMS and PTFE can be seen in d). This shows that at low PTFE concentrations, the CF$_2$ vibrations are dampened. This dampening effect is graphed in e) by relating the weight ratio of PTFE and PDMS to the area under their characteristic peaks. A X-ray computerized tomography analysis of a 4FPS peak is shown in f-i). The same 2D slice was re-colored to clearly show the PTFE concentrations near the peak. A 3D image of the 4FPS seen in j-k) shows the material as it is bisected j) and after several slices k). It is clear that the PTFE particles get a lot closer near the peak.

Theoretically, it would be expected that the ratio of the main vibrational peaks for PTFE and PDMS should be the same as their relative weight percentage. However, there is an unexpected dampening in the CF$_2$ (733 cm$^{-1}$) molecular vibrations at low PTFE concentrations compared to the PDMS vibrations (711 cm$^{-1}$)$^{128,129}$. This is due to the outstanding chain flexibility of PDMS thus allowing the PDMS chain to diffuse within very small volumes, resulting in a very small separation between the H atoms of PDMS and the F atoms of PTFE. This intermolecular interaction between F and the H atoms of PDMS locks the PTFE chain in a molecularly jammed configuration. A drop of more than 50 % in the CF$_2$ signal upon the addition of 5 wt. % PDMS is shown in supplementary information Fig. 26d-e, thus further supporting the hypothesis of intermolecular interactions and jamming.
One of the most important properties of an adhesive or adhesive-like materials is their ability to be used with multiple substrates under varying environments. The ability to be used on multiple substrates underwater is very important, however, to understand this behavior, it is necessary to perform relevant tests such as contact angle and careful SEM measurements. Our observations show that once a drop of our 4FPS material is put on the surface of a copper sheet it spreads out over time, thus causing the contact angle to change (Fig. 27j-k). This is a specific advantage of the liquid phase of the mixture. Thanks to the high mobility of the PDMS chains, the material can freely enter pores and fill them thus allowing it to fully wet surfaces and enable good adhesion. Moreover, this material shows hydrophobic properties (Fig. 27l) which allow it to function under water while still being able to wet many different types of surfaces. The wettability of the material was further explored through SEM at the interface of the copper as well as SEM on paper. SEM images showed that 4FPS fully coats both copper (Fig. 27m) and paper (Fig. 27n), thus eliminating surface features and showing full penetration into the material. This is schematically explained in Fig. 27o. As gravitational forces press down onto the 4FPS droplet capillary forces work in tandem to allow it to penetrate and spread.

In addition, the testing shown in Fig. 27h-i were done using standardized weights and are pictures taken during the testing that relate to the bar graphs in Fig. 27a-b. The bar graphs tend to look similar due to the low divisions in standardized weights that were available. The materials qualitatively held the same weights in air
as in water. Adhesion was done under the same conditions and the area was accounted for in each instance. To calculate the stress values, we used the equation:

\[ \sigma = \frac{F}{A} \]

Equation 5.1 – General Stress Equation

Where \( F \) represents the force on the material, \( A \) is the area, and \( \sigma \) represents stress. Additionally, we ignored the role of buoyancy in submerged situations. Due to the hydrophobic nature of the material it tends to push out all water in the way and can adhere while fully submersed.
Figure 27: Mechanical Properties of PDMS+PTFE. Qualitative tensile a), shear b), and torsion c) testing using standard weights showing the adhesive strength both in air and in water. The loading can be clearly identified by the schematics in each figure. The inset in a) shows the tensile failure of glass before the failure of the adhesive after being submerged and exerted to a 500 g load. The inset in b) shows the sample sizes and adhesion areas used in shear and tensile. The DMA testing d) shows the effects of concentration on adhesion in lap shear (the blue (iii) represents PDMS, the red 25% PTFE in PDMS (ii), and the green represents 50 wt. % PTFE in PDMS (i)). The inset shows the differences between pure PDMS and a 50:50 wt. % ratio of PDMS:PTFE at 0.001 N/min and 0.1 N/min. Tensile testing using an ADMET system e) shows the difference between raw PDMS in adhesion between aluminum substrates and mismatched substrates (aluminum and plastic). The mismatched results are the green line (i) and the red line (ii), which show the adhesion of PDMS and 4FPS when adhering aluminum with plastic, respectively. Meanwhile, purple (iii) and blue (iv) represent adhesion between two aluminum blocks using PDMS and PDMS+PTFE, respectively. The difference between PDMS and 4FPS is emphasized in the figure and highlighted in the inset where dark blue represents the PDMS and grey represents the 4FPS. The shear f) and tensile failures g) were imaged and exhibit expected patterns for slip and pull out, respectively. The adhesive can be seen holding 2 kg in water h) and in air i). j) Shows the contact angle of the 4FPS onto a piece of Copper substrate. After ~5 seconds the glue spreads out and wets the whole surface as seen in k). The hydrophobicity of the material on copper is shown in l) by placing a drop of water onto a copper substrate that had 4 FPS on it. To clarify the wetting effect seen in the contact angle a copper surface had 4FPS put on it and then was imaged using SEM m). It is clearly shown that the copper surface was fully coated by the 4FPS material. Additionally, 4FPS was also placed on paper and examined under SEM n). By imaging an area that had no 4FPS (left of the dashed red line) and comparing with an area that has 4FPS (right of the dashed red line), it is observed that the mixture fully fills the empty space at the interface thus leading to stronger adhesion. This mechanism is schematically shown in o). As time passes the liquid polymer phase can relax and spread across the surface, thus filling all the available cracks and pores and promoting better adhesion and allowing it to work with a myriad of surfaces.

To ascertain the material’s strength on different substrates, with different loading types, and in different environments, we performed qualitative tests using
standard weights. These tests showed that 4FPS exhibits the highest strength in tensile loading (similar to 90° peel testing) (Fig. 27a). The material exhibited adhesion with a variety of substrates including: plastic, metal (Cu foil), paper, Si wafers, and glass. We also tested torsion loads (under high speed rotation) (Fig. 27c) and shear loads (similar to 180° adhesion) (in air and under water) as seen in Fig. 27b (the different materials and their adhesion areas can be seen in the inset in Fig. 27b). The adhesive strength was preserved both in air and under water for all materials. Furthermore, in the case of glass and aluminum, the glass broke while the bond remained intact (inset in Fig. 27a). The new material, 4FPS, can be seen easily holding 2 kg in tensile mode only using a 25.5 mm diameter adhered area both in air and under water (Fig. 27d-e). It is important to note that the thickness of the applied adhesive is about 0.01 mm, which makes holding this amount of weight more remarkable. The ability of the material to hold weight underwater is not surprising since both materials are hydrophobic. As water comes into contact, it is repelled by hydrophobic forces and if water is in the way of the adhesive bond, it will be pushed out as the substrates are adhered. It is also important to note that 4FPS was also able to glue atomically flat silicon wafers which imply that the material adheres regardless of surface roughness. To qualitatively test the strength of the material in torsion, a spin coater was used. The spin coater was set to different speeds and a 10 g weight was adhered to the surface. The adhered weight was spun for 30 seconds at each speed to ensure the adhesion was stable. The tests showed that 4FPS exhibited a
700% increase in adhesion over pure PDMS with no change in strength even in the presence of water (Fig. 27c).

To quantify the strength of the adhesive bonds we used DMA for shear measurements in tandem with tensile testing. Shear testing was performed using a force controlled method at a rate of 0.1 N/min and 0.001 N/min. The rate plays a very important role in the apparent strength of the material, as lower rates will yield lower strength. At 0.1 N/min, the adhesive showed a maximum strength of ~0.3 MPa (see Fig. 27f). This is an increase up to 548% over pure PDMS, that was also tested at 0.1 N/min (see Fig. 27f and the corresponding inset), with a shear strength of ~0.3 MPa. The material was also tested under a slower rate (0.001 N/min) and showed a 5,800% increase over pure PDMS that was tested at the same rate (see inset in Fig. 27f). The difference in rate is very clear and as the rate goes higher the strength is also expected to increase (shown in the inset in Fig. 27f). DMA results also showed a stark difference between having 25% PTFE and 50% PTFE in the sample (Fig. 30a). The material shows that even 25% PTFE content shows a nominal change, however, using 50% PTFE shows a 524% increase. This implies that fluorine in PTFE a large role in adhesive behavior. Moreover, the amount of jamming that can occur is directly related to the mass fraction of granules/spheres (more spheres, more jamming)\textsuperscript{118}. Although the shear strength of the material is not too high, it still matches the adhesion of shellfish-based adhesives onto aluminum which boast a strength of 0.3 MPa\textsuperscript{102,130–132}. Additionally, the material shows much higher adhesive strength than 3M Velcro (0.07 MPa) and similar strength to 3M double sided foam tape (0.28
MPa\(^{130}\). After testing, the failure pattern could clearly be seen in the remaining adhesive on the substrates (see Fig. 27g). The pattern shows aggregations of the material in the direction of failure. In the case of shear failure, the pattern (Fig. 27g) and the shear failure SEM images (Fig. 23d) indicate that failure most likely occurred due to PTFE spheres slipping past each other in the PDMS matrix.

To complement the DMA shear testing, tensile testing was performed using an ADMET testing system. The testing was performed by gluing a 25.5 mm aluminum disk onto a block and pulling at a rate of 5 mm/min (see Fig. 27i). The test was repeated for PDMS and using mismatched substrates (aluminum and plastic). The material showed a 3408 % increase over PDMS in loading mismatched materials and an 1814 % increase in loading aluminum samples (highlighted in the inset in Fig. 27i). The substrate surfaces play a lesser role in overall adhesion and reinforce our previous data (Si wafer adhesion data). To further emphasize this point, even mismatched substrates showed vastly improved adhesion using 4FPS in relation to PDMS. The strongest adhesion was apparent using aluminum and the failure mode can be seen in Fig. 27h. The ridges seen on the metal disk are apparent because of the mixture being pulled upwards by the tensile force which is supported by the SEM images seen in Fig. 23c. This failure mode is in clear contrast with the shear failure where slip played the largest part.
The multifold improvement in adhesive behavior of PDMS is proposed to be due to molecular interaction between solid-liquid. To verify our hypothesis, we employed molecular dynamics simulations with ReaxFF (force field parameters described in the computational details section). Uniaxial loading and unloading are schematically shown in Fig. 28f-h for PMDS and 4FPS. Their corresponding stress-strain relationships, depicted in Fig. 28a-c and Fig. 29, are quantitatively and qualitatively indicative of the adhesive tendencies of both PDMS and PTFE, which have also been shown experimentally. Indeed, besides the fact that a 20% compressed PDMS doesn’t recover under uniaxial tension (see insets in Fig. 28a-c) as opposed to the combination of PDMS and PTFE that does recover, 4FPS’s maximum stress at 20% compression is roughly 10 times PDMS’s maximum stress at 20% compression which denotes the superior adhesive capability of PDMS on PTFE which corroborates the in-situ SEM testing in Fig. 24d-e. Such a conclusion can also be drawn from the molecular perspective in Fig. 28f-h where the unloading phase after compression breaks PDMS atomic bonds, thus creating voids in the structure. In the case of the combination of PDMS and PTFE instead, the unloading phase displays a very strong bonding interface between PDMS and PTFE responsible for the two polymers sticking together even after 25% unloading tension. The superior adhesive potential of the combination of PDMS and PTFE is further confirmed by the biaxial shear stress-strain results in Fig. 28d where 4FPS stress at 17% strain is roughly 5 times PDMS stress at 17% strain thereby signifying that PDMS units stick to PTFE unit more than PDMS units stick to one another. The voids in PDMS final strain
structure (Fig. 28g) and the PDMS units sticking to the central PTFE (Fig. 28i) are illustrative of the aforementioned observation. In as much as the simulation processes described above do not involve any premade PDMS/PTFE crosslinks, the simultaneously strong and flexible PDMS/PTFE interfacial bonding is unlikely to come from non-polar covalent electron sharing between PTFE fluorine atoms and PDMS hydrogen atoms but rather from the very polar nature the fluorine-hydrogen dipole interaction at the interface. In fact, the very high F-H electronegativity difference (1.9) unmistakably creates a strong dipole interaction at the interface. Plus, fluorine being one the most electronegative elements and hydrogen being one of the most electropositive elements found in polymers, the chemical attraction between the two elements inevitably leans more towards PTFE fluorine atoms than towards PDMS hydrogen atoms. Interfacial PTFE fluorine atoms are therefore expected to attract interfacial PDMS hydrogen atoms thereby forming flexible but strong PTFE-PDMS interfacial glue responsible for the high adhesive properties of the mixture. This is consistent with our FTIR results, although there is no chemical bond formation, we still observe adhesive behavior. The direction of the polarization, from PDMS to PTFE, is confirmed in the 4FPS uniaxial and biaxial tensile stresses in Fig. 28h and 28i where while PTFE interfacial atoms tend to keep their equilibrium positions, PDMS interfacial atoms tend to stick to PTFE interfacial atoms despite the increasing amount of load in the opposite direction. Through uniaxial and shear mechanical testing, both simulations (Fig. 28b-e) and experiments (Fig. 27a-e and Fig. 24d-e) quantitatively and qualitatively show a superior adhesive nature of the mix of
PDMS and PTFE over PDMS alone. The very high electronegativity difference is deemed the primary cause of the reformable and strong interfacial bonding as evinced by the shear mechanical testing (Fig. 28e for simulations and Fig. 27a-e and Fig. 24d-e for experiments), the lack of evidence for covalent bonding in STM data, and the diametrically opposed polar nature of fluorine and hydrogen atoms.
Figure 28: Molecular dynamics simulations of PDMS: PTFE adhesion. a) Final PDMS simulation model (left), PDMS and PTFE simulation units (middle), and final PDMS+PxcTFE (4FPS) simulation model (right). Uniaxial stress-strain curves for compressive loading and tensile unloading in the: b) x-direction, c) y-direction, d) z-direction. e) Biaxial stress-strain curves for tensile unloading in x- and y-directions. Snapshots of simulation box in uniaxial compressive loading and tensile unloading for: f) PDMS, and h) 4FPS. Snapshots of simulation box in biaxial tensile unloading for: g) PDMS, and i) 4FPS.

To highlight the fact that the gluing mechanism proposed above doesn’t just work within the components of the mixture, but also between the mixture and an external material in presence and in absence of water, a comparable stress-strain relationship was computed on two structures obtained by sandwiching a chunk of the 4FPS mixture between two Si (100) substrates in presence and in absence of water (see Fig. 29). In fact, from initial stages where the 4FPS mixtures are respectively lying on the surface Si (100) and ~5 Å away from it, the loading stages are undertaken to ensure enough adhesion between the substrates and the 4FPS mixture (Fig. 29). The subsequent unloading stages both in presence (right side of the Fig. 29) and in absence of water (left side of Fig. 29) show that the adherence between the Si (100) substrates and the 4FPS mixture remains throughout the unloading process, thereby testifying to the gluing capability of the 4FPS mixture to the external material herewith examined. The Si (100)/4FPS interfaces at the end of the unloading stage, zoomed in at the bottom of Fig. 29, are evincive of the lingering interfacial bonding described above both in presence and in absence of water. Such a lingering interfacial bonding, occurring both within the components of the mixture and between the
mixture and the external material, ultimately constitutes the atomistic rendering of the jamming mechanism described above. It is worth noting that the stress-strain curve (central part of Fig. 29) quantifying the unloading and loading stages in the direction of the substrates (z-direction), doesn't show an appreciable difference between the 4FPS mixture alone and the 4FPS mixture immersed in water.
Figure 29: Molecular dynamics simulations of PDMS/PTFE mixture (4FPS) on Si (100) substrate in presence (right) and absence of water (left). With respect to initial stages, respective unloading stages show the PDMS/PTFE mixture sticking to Si
(100). Stress-strain ($\sigma_{zz}/\varepsilon_{zz}$) curves in the z-direction (center) confirm the gluing capability of the mixture to Si (100) in the presence and absence of water. The interfaces between Si (100) substrate and 4FPS in presence (bottom right) and absence (bottom left) of water are zoomed in to further elucidate the adhesive properties of the mixture.

The low temperature studies seen in Fig. 30b shows the material becomes more rigid with temperature and as the glass transition ($T_g$) of PDMS (-135°C) is reached. Moreover, the load-unload testing shown in Fig. 30f serves to corroborate the reversible nature of the adhesive.
Figure 30: Characterization and Comparison. a) Shows the difference between PTFE content from DMA tests at the rate of 0.1 N/min. b) Shows the effects of low temperature on the gel (50% PTFE, temperature range of RT to -40). The testing was done at a frequency of 5 Hz with an oscillation amplitude of 30 microns. c-e) Show SEM images of the composite at different magnifications which emphasize the polka-
dot like pattern and show the dispersion of the PTFE particles into the PDMS. f) Shows load-unload testing done in DMA on the samples and g) shows a general comparison of 4FPS with some other adhesives from lap shear testing. The values for Velcro and 3M double tape are from publications on their lap shear strength\textsuperscript{130}, and the mussel values were measured by other researchers\textsuperscript{102,130,131,133}.

Moreover, the testing shown in Fig. 29 was done using an ADMET tensile tester at a rate of 5 mm/min. These tests that PDMS alone does not have much adhesion, however, adding PTFE changes that dramatically. This mixture is very odd since it is composed of two lubricants that come together as an adhesive. The testing shown in Fig. 31 d and f was done consecutively and without changing the material. First the adhesive was placed on both sides of the aluminum substrates then the material was pulled until failure. The first run (shown in black) showed a strength of almost 50 N, however, on the second run after just re-adhering the materials without smoothening the adhesive surface the strength fell. The strength stayed at this lowered level for 6 runs. Interestingly, by smoothening out the adhesive surface after each failure it is possible to preserve the strength of the first run indefinitely. This shows that the material keeps its adhesive properties over several runs and that when smoothened it can maintain its maximum adhesion. This can be attributed to the increased interaction area created by smoothening out the adhesive which leads to higher adhesion.
Figure 31: ADMET Tensile Test Comparison. a) Shows tensile tests of adhesion of PDMS between two aluminum substrates, while b) shows PDMS adhesion between mismatched substrates (Aluminum-Plastic). c) Shows adhesion using PDMS versus 4FPS as well as the effect smoothing the surface has on 4FPS (4FPS Aluminum-Aluminum-Smoothened vs. 4FPS Aluminum-Aluminum). d) Shows 4FPS adhesion between metals with the surface of the adhesive being smoothened out in between runs. e) Shows the adhesion between mismatched materials while f) shows adhesion between aluminum substrates but without smoothing.

The overall strength of the material is characterized in Table 1. This shows that the material strength is not as large as other adhesives. Additionally, the observed failure modes were indicative of cohesive failure, hence, by further manipulating the interface we should be able to reach values much closer to the specified theoretical strength.

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<tbody>
<tr>
<td>Pressure Sensitive</td>
<td>0.01-0.07</td>
</tr>
<tr>
<td>Starch Based</td>
<td>0.07-0.7</td>
</tr>
<tr>
<td>Rubber Based</td>
<td>0.35-3.5</td>
</tr>
<tr>
<td>Polyvinylacetate (PVAc)</td>
<td>1.4-6.9</td>
</tr>
<tr>
<td>PVDF+PDMS</td>
<td>0.11</td>
</tr>
<tr>
<td>PTFE+PDMS</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 1: Comparison of Adhesive Strengths
5.4. Effect of Using PTFE and Afterword

In general, adhesive materials can be classified either by the main mechanism that explains their adhesion or by their main features or applications. Typically, the most important adhesion mechanisms are: 1) Chemical adhesion\textsuperscript{107,133}, which implies a chemical bond between the adhesive and the substrate, which can be either ionic or covalent. This is the strongest adhesion, however, requires time to cure and is irreversible. 2) Physical adhesion\textsuperscript{135,136}, which includes weaker interactions between the adhesive and the substrate such as van der Waals, hydrogen bonding, dipole-dipole, and dipole-dipole-induced interactions. Such adhesion is not as strong as chemical adhesion but presents a certain degree of reversibility. 3) Geometry-based adhesion\textsuperscript{105}, resulting from the entanglement/diffusion of adhesive molecules to the substrate. A classic example is represented by molecular interlocking, chain entanglements in polymeric materials, or sintering in ceramics. Gecko-like adhesives are frequently included under geometry based adhesives.

As mentioned by Majumder \textit{et al.}\textsuperscript{137}, most synthetic adhesives are strong but not reusable. Nature prefers using geometry rather than resorting to the brute force of chemical adhesion. This manuscript reports the synthesis and main physical properties of a novel reusable adhesive. The reversibility of the adhesion mechanism resides in the exploitation of physical and geometrical adhesion, a completely novel approach, rather than chemical adhesion. The proposed adhesive defines a unique category of reversible, instant adhesives that work in both humid and dry
environments, a combination of properties that we have not seen before. The adhesive, a mixture of one of the most flexible macromolecular chains (PDMS) with a rather rigid macromolecular chain (PTFE), whose strength most likely arises from the dipole-dipole induced interactions present due to the presence of electronegative fluorine atoms (PTFE). Thus, this novel adhesion mechanism is characterized by a combination between geometrical interlocking (which can be elegantly described by the jamming theory) and a dipole-dipole induced interaction between the two polymeric components of the adhesive. The 4FPS mixture consisting of two biocompatible polymer constituents can be useful adhesive for instant adhesion of injured parts (consisting of liquid) or devices (need multiple use). The cell viability is characterized with different cells as shown in Fig. 21. The adhesive can also be used as an antibiotic medium as shown in Fig. 22. Extending the current work, such adhesives can be explored as possible first aid essentials, with the ability to join, protect, and soothe injuries developed in a warzone, or even everyday sports.

Throughout this thesis, we have shown a new approach to synthesize unique and versatile solid-liquid based instant adhesives. The use of liquid polymers allows the polymer chains to easily re-arrange and create the strongest adhesive conformation while aiding in the contact between substrates. This methodology promotes adhesion through molecular-level dipole interactions which constantly repeat themselves and are enhanced by jamming. The methodology requires that one component have a highly electronegative element and the other to have a weak
electronegative element. We have shown that this works with both PVDF and PTFE, with varying strength (dependent on F content). The fluorine content dependence was shown both by altering the amount of PTFE in PDMS and showing PVDF based materials. Simulations show that pure PDMS cannot withstand uniaxial forces, whereas PTFE creates strong interfacial dipole interactions that solidify the mixture. Based on theoretical and experimental pieces of evidence, these adhesives should be categorized as interfacial adhesives, i.e., adhesives that rely on interfacial interactions to stick. These new adhesive addresses some of the key drawbacks of many adhesives by being re-usable, non-toxic, moisture independent, as well as bypassing curing through its novel instant adhesion pathway while still working with a myriad of substrates and avoiding the side reactions commonly related to covalently cross-linked adhesives. The procedure described in this paper can be used in tandem with other procedures such as patterning to synthesize even stronger adhesive materials. However the scalable synthetic approach we have used to create adhesives is distinctly different from methods such as patterning, cross-linking, surface modification, and chemical synthesis. This work can lead to new ways of thinking and enable the design of novel adhesives which can be useful for biomedical, robotic, and amphibious applications.
References


17. Chan, M., Lau, K., Wong, T., Ho, M. & Hui, D. Mechanism of reinforcement in a


33. O’Connell, P. A. & Mckenna, G. B. The stiffening of ultrathin polymer films in the rubbery regime: The relative contributions of membrane stress and


60. Sun, C. H. An ab Initio Force-Field Optimized for Condensed-Phase


93. Zhao, J., Buldum, A., Han, J. & Lu, J. P. Gas molecule adsorption in carbon nanotubes and nanotube bundles. **195**,


127. Mofokeng, J. P. & Luyt, A. S. Morphology and thermal degradation studies of melt-mixed poly(hydroxybutyrate-co-valerate) (PHBV)/poly(ε-caprolactone)
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Appendix A