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Investigating the Relationship of Molecular Attributes and Intrinsic Self-Healing Efficiency in PDMS Based Polymers with Application Towards Coatings in UAVs

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The intrinsic self-healing efficiency of polydimethylsiloxane (PDMS) based polymers is extensively evaluated through tensile testing. Three novel, intrinsically self-healing polymers composed of bis (aminopropyl) terminated PDMS units reacted with diisocyanates to form urea linkages were synthesized. By altering the molecular weight range of the aminopropyl terminated PDMS starting material, these polymers yield different mechanical properties. The self-healing efficiencies and moduli of these novel polymers are assessed via tensile testing to evaluate their overall strength and flexibility. Tensile testing involves stretching the polymer until it fractures, recording the force (N), time (s), and extension (mm) which can be used to calculate the stress and strain to determine the tensile strength and elastic modulus. The moduli of the samples are found to range from less than 0.1 to 43 MPa and are inversely proportional to the molecular mass of the PDMS linker within the polymer chain. Samples of the polymer are tested before and after being damaged to determine the percentage healing efficiency. Intrinsic self-healing efficiencies of up to 60% are observed at room temperature after 72 hours. The influence of PDMS molecular weight on self-healing capability and mechanical properties was identified, providing critical insights into the relationship between polymer structure and self-healing efficiency. A systematic investigation of the balance between hydrogen bonding capabilities and molecular mobility as a function of chain length offered guidance for designing self-healing polymers with varying functional groups and mechanical properties. Shear adhesion tests indicated the potential of these polymers as protective coatings for unmanned aerial vehicles (UAVs). Furthermore, the ability of these polymers to retain their mechanical properties and self-healing efficiency when upcycled highlighted their suitability for sustainable material development.

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I. Nomenclature

PDMS = Polydimethylsiloxane
UAVs = Unmanned Aerial Vehicles
IMFs = Intermolecular Forces
THF = Tetrahydrofuran
Mn = Number-Average Molecular Weight
MPa = Megapascals (a unit of pressure or stress)
FTIR = Fourier-Transform Infrared Spectroscopy
SHE = Self-Healing Efficiency
MPU = Methylenebis(phenyl isocyanate) (context-dependent, could refer to a specific polymer unit in this case)
IU = Isophorone Diisocyanate Urea (context-dependent, relates to polymer units with isophorone diisocyanate)
NSF = National Science Foundation
NASA = National Aeronautics and Space Administration

II. Introduction

Unmanned Aerial Vehicles (UAVs) are increasingly used in diverse and often challenging environments, from complex urban landscapes to remote and harsh natural settings. The risk of structural damage is considerably high under these conditions.[1] Self-healing materials can automatically repair damages incurred from collisions or harsh environmental exposure, thus maintaining the structural integrity of UAVs during mission-critical operations.[2] This capability not only enhances the safety and reliability of UAVs but also extends their operational lifespan and reduces maintenance costs and downtime. Given the expanding role of UAVs in critical applications, including search and rescue, surveillance, and logistics, the importance of such innovations cannot be overstated.[3] Self-healing technologies thus emerge not only as a means of safeguarding valuable equipment but also as an essential factor in ensuring the success and safety of the missions they undertake. [4]

The critical components of an intrinsic self-healing polymer involve a balance of interactions between polymer chains.[5] The reversible nature of hydrogen bonding interactions provides the intrinsic self-healing mechanism to allow the polymer chains to reconnect after being damaged.[6-7] This balance of weak and strong intermolecular forces (IMFs) makes the material robust while allowing the molecular mobility necessary for the self-healing mechanism to occur.[8] The strength of the IMFs can be tuned by incorporating functional groups capable of weak and strong hydrogen bonds. For this work, the polymer is synthesized from aminopropyl terminated polydimethylsiloxane (PDMS) and diisocyanate moieties. The diisocyanates are chosen to have both sterically hindered and unhindered structures so that a combination of strong and weak hydrogen bonds comes from the resulting urea functional groups. The polymer is formed from the reaction of the aminopropyl terminated PDMS with both MPU which is an aromatic based diisocyanate, and IU, which is an aliphatic based diisocyanate to give the urea linkages. Because the MPU, is flattened due to the aromatic rings, the two urea moieties in this segment are aligned and capable of engaging in four coordination points for the hydrogen bonding interactions. However, the IU segment is significantly more sterically hindered due to the cyclohexane ring and the urea moieties are not aligned so that all four hydrogens are not in the plane. Therefore, it is hypothesized that a maximum of two points of hydrogen bonding for the IU segments are possible between two chains of the polymer resulting in a weaker hydrogen bonding interaction. This combination of weak and strong hydrogen bonding provides the balance of elasticity and energy dissipation to provide a stretchable material with autonomous self-healing properties.[9-10]

We have previously reported a polyurea PDMS based polymer that exhibits good intrinsic self-healing properties.[11] Thin film polymer samples (~0.2 mm thickness) were prepared via electrospinning and then damaged by scratching the surface with a needle. These samples demonstrated healing efficiencies of 50% as measured via optical microscopy in 24 hours at room temperature. For thicker samples, optical microscopy proved less adept at determining self-healing efficiency over time as the three-dimensional healing of the damage could not be reproducibly measured. To obtain consistent and reliable healing assessment, this study reports the self-healing efficiency via tensile testing.[12-13] In this report, we investigate the mechanical properties and self-healing efficiencies of three polyurea PDMS based polymers which differ by the chain length of the bis(aminopropyl) terminated PDMS starting material.

III. Materials and Methods

Bis(3-aminpropyl) terminated poly(dimethylsiloxane), H2N-PDMS-NH2, Mn = 2500; Mn 850-900, Mn = ~5000, Triethylamine, anhydrous tetrahydrofuran (THF), methylenebis(phenyl isocyanate), isophorone diisocyanate, methanol was purchased from Sigma Aldrich and used as received.

Polymer Synthesis: To a flame dried 250 mL Schlenk flask under nitrogen was added bis(3-aminpropyl) terminated poly(dimethylsiloxane) **1c** (15.0 grams, M_n = 5000, 1 equiv) followed by anhydrous tetrahydrofuran (THF) (30 mL). The solution was cooled to 0 °C and triethylamine (0.40 mL, 1 equiv) was added. To a 100 mL flame dried round bottom flask was added Methylenebis(phenyl isocyanate), **2**, (0.30 grams, 0.4 equiv) and Isophorone diisocyanate, **3**, (0.40 grams, 1.6 equiv) followed by anhydrous THF (15 mL). The solution of diisocyanates was then added to the reaction mixture dropwise over a period of about 15 minutes. The reaction was allowed to slowly warm to room temperature and stir overnight. After 12-15 hours, the reaction is quenched with anhydrous methanol (0.5 mL, 10 equiv). The reaction was allowed to stir overnight then solvent was removed by rotary evaporation to give a solution of about 40% polymer in THF. The solution was poured into a silicone mold and cured at 100 °C for 2 hours under vacuum as illustrated in Figure 1. Samples were prepared in a 6 x 25 mm dog bone shaped mold to have the same length and width measurements. Approximately 1 mL of polymer solution was poured into the molds to provide polymer samples with a thickness of approximately 0.5-0.6 mm for tensile testing. The above procedure is for the synthesis of polymer **5c** but is representative for both **5a** and **5b**.

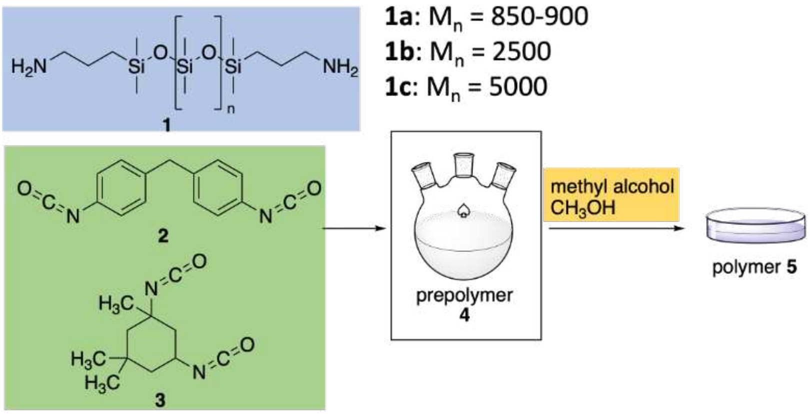

Figure 1. *Synthesis of self-healing polyurea PDMS based polymer.*

Upcycling Procedure: To samples of either **5a**, **5b**, or **5c** was added a volume of THF to give a 40% m/m polymer solution. The mixture was allowed to stir at room temperature for 2-3 hours before being added to the silicone molds to be cured at 60 °C under vacuum overnight.

Tensile Testing Experimental Setup: A force gauge attached to the tensile testing tower (as shown in Figure 2) was used to measure the force applied to each polymer sample. The polymers were loaded onto the tensile tester identically and each starting position was recorded. As each polymer is stretched, a continuous stream of recorded load (N), and time (s) was collected from the force gauge. From the collected data, the extension of the polymer was calculated for every 0.1s interval. This was done by converting the 45 mm/min loading rate into 0.075 mm/0.1s and recursively adding itself every 0.1s to precisely identify the position the polymer is at for every individual load measurement.

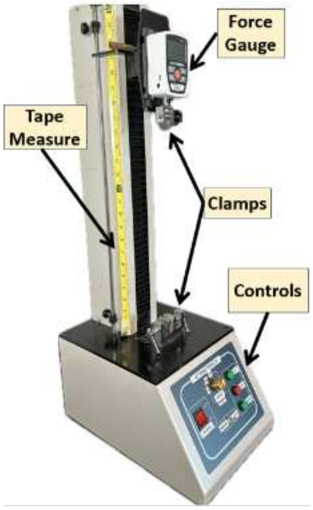

Figure 2. *Force gauge and tower setup for tensile testing.*

Calculating Healing Efficiency: Tensile stress is calculated by taking the load divided by the cross-sectional area of the polymer from Eq. (1). The cross-sectional area of the polymer is the rectangular portion of the dog bone shape. This is calculated to be the average thickness of the bone multiplied by the width of the rectangular portion of the sample. As shown in Eq. (2), the strain is calculated by using the change in length, or extension, divided by the original polymer length The self-healing efficiency of each polymer is determined by taking the recorded peak healed stress from the stress-strain curve and dividing it by the peak control stress as in Eq. (3). Figure 3 shows a sample being stretched for healing efficiency measurements.

$$Stress\ [MPa]: S = \frac{F}{A} \tag{1}$$

$$Strain\ [\%]: \varepsilon = \frac{\Delta L}{L_o} \tag{2}$$

$$Healing\ Efficiency\ [\%]: \frac{Peak\ healed\ stress}{Original\ peak\ stress} * 100\% \tag{3}$$

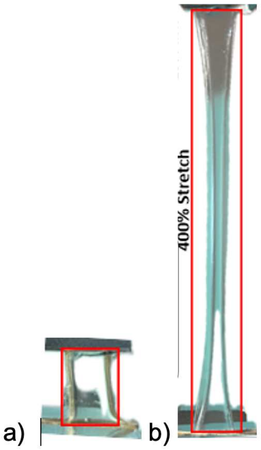

Figure 3. *Images of a) the beginning and b) during the tensile testing to find peak stress for self-healing efficiency calculations.*

IV. Results and Discussion

Fourier-transform infrared spectroscopy (FTIR): As the isocyanate functional group has a distinctive absorption around 2300 cm^{-1}, the absence of this peak in the polymer confirms that these moieties have reacted and are converted to the urea moieties within the polymer chain (see Figure 4).

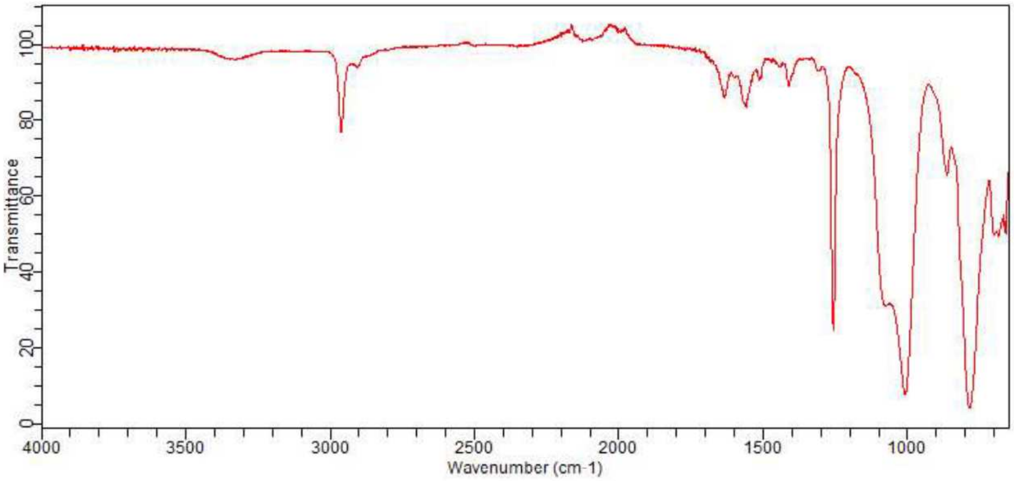

Figure 4. *FTIR for Polymer 5b*

Young's modulus calculations: The Young's moduli of the polymers used in this experiment ranged from 0.066 to 43 MPa. The most rigid material resulted from the use of the smallest bis(propylamino) terminated PMDS prepolymer (Mn = 850-900) to make polymer **5a** which had a Young's modulus of 43 MPa. As the prepolymer average molecular mass (and thereby chain length) increased, the Young's modulus value decreased significantly. When the starting prepolymer of Mn 2500 was used, the modulus of the polyurea polymer decreased by almost 100 fold resulting in a modulus of 0.42 MPa. Remarkably, when the starting prepolymer of Mn ~5000 was used, the resulting polymer was extremely soft with a modulus of over 600 times smaller than polymer **5a** and found to be 0.066 MPa. These results are summarized in Table 1.

Table 1. *Young's modulus for polymers* ***5a****,* ***5b****, and* ***5c***

Polymer	Average Molar Mass of starting PDMS polymer 1 (g/mol)	Young's modulus (MPa)	Normalized Modulus
5a	875	43	650
5b	2500	0.42	6.4
5c	5000	0.066	1

Figure 5 shows the stress-strain curves for Polymers **5a**, **5b**, and **5c** which correspond to starting PDMS polymer of Mn = 875, 2500, and 5000. Polymer **5a** exhibits extremely high tensile stress up to 14 MPa, yet it has a very low strain compared to the other polymers. Polymer **5b** is shown to have the largest strain of over 475% with a stress of over 3.5 MPa while polymer **5c** has the weakest mechanical properties with having hardly any stress under load and just over 275% strain. These tensile testing results demonstrate that the starting chain length of the PDMS portion of the polymer greatly influence the mechanical properties of the material.

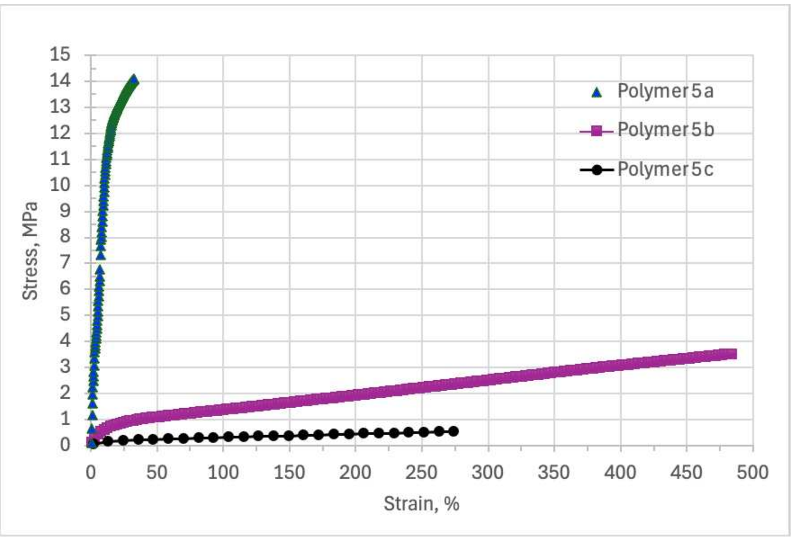

Figure 5. *Stress-Strain curve for polymers 5a, 5b, and 5c*

Self-healing efficiency (SHE) calculations: The SHE tests were performed on polymer samples that were sliced with a razor blade, the two pieces were then replaced to ensure that the surfaces made contact by visualization with optical microscopy (see Figure 6). The SHE measurements were performed on the samples after healing at room temperature for varying times: 24, 48, and 72 hours. Tensile testing was used to directly compare the ability of each of polymer to undergo intrinsic self-healing.

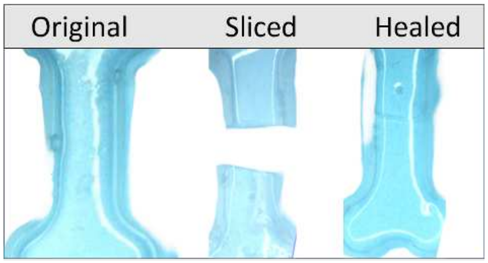

Figure 6. *Image showing process of damaging and healing of polymers*

Average data from 3-5 trials of each of the healed polymers pulled at 45 mm/min were used to determine the peak stress of the samples and compared to the peak stress of the original polymer to obtain the % SHE as shown in Eq. (3). These results are summarized in Table X for polymers at the different time intervals. Polymer **5a** did not demonstrate any intrinsic self-healing after 72 hours at room temperature. However, even at room temperature both polymers **5b** and **5c** show significant healing after 24 hrs. From entries 2-4, polymer **5b** shows a non-linear trend of self-healing reaching up to a SHE of 33% after 72 hours with a substantial increase in healing between 48 and 72 hours. Conversely, for polymer **5c** most of the healing is achieved prior to 48 hours with only a minimal gain after 72 hours.

Although all three polymers in this study share the structure of the urea bonds from the IU and MPU moieties alternating with the PMDS backbone and therefore the potential of both weak and strong hydrogen bonding between polymer chains exists, SHEs differ between these polymers. Our results are consistent with the inverse relationship between Young's modulus and self-healing efficiency which has been noted in the literature: as the rigidity of the material increases, the self-healing ability decreases.[14]

Table 2. *Self-healing efficiency results from tensile testing measurements for Polymers 5b and 5c*

Entry	Time Interval After Damage (hrs)	Peak Stress (MPa)	Self-Healing Efficiency (%)
Polymer 5b: from 1b (Mn = ~2500) at room temperature			
1	**0**	**1.8 (?)**	**--**
2	**24**	**0.41667**	**24**
3	**48**	**0.34925**	**20**
4	**72**	**0.58927**	**33**
Polymer 5c: from 1c (Mn = ~5000) at room temperature			
5	**0**	**0.55**	**--**
6	**24**	**0.22459**	**42**
7	**48**	**0.2963**	**55**
8	**72**	**0.3252**	**60**

Shear adhesion tests: Although polymers **5a**, **5b**, and **5c** do not have inherent adhesive properties, methods to make these polymers adhere to various surfaces were explored for the potential use of these polymers as coatings. It was found that hydrogen bond disrupting solvents such as ethanol, methanol, and acetone could be applied to the polymer to obtain strong adhesion to multiple surfaces including glass, paper, metal, and plastic. Some preliminary data to determine the strength of adhesion between the different polymers and a nylon-carbon fiber material 3D printed with Onyx filament[3] was obtained. A small amount of solvent, either ethanol or acetone, was applied to the surface of a rectangular piece of polymer which was then sandwiched between two pieces of 3D printed rectangles of the Onyx material. The pieces of filament were placed in the grips of the tensile testing instrument and force was applied until the pieces were separated from the polymer. Table 3 shows the results of this shear adhesion test. Polymer 5a has the greatest adhesion force with ethanol as the solvent to effect adhesion; it required over 44 N of force to pull the carbon fiber pieces apart. For polymers **5a** and **5b**, when ethanol was used as the adhering solvent, a force of ~1.5 times greater was required to separate the pieces than when acetone was used. However, polymer **5c** shows the weakest adhesion to the carbon fiber material and only a small difference in the amount of force to separate the pieces of carbon fiber was observed between the use of ethanol and acetone as adhering solvents.

Table 3. *Shear adhesion tests with polymers 5a, 5b, and 5c on carbon fiber filament.*

Polymer	Shear Force (N)	
	Ethanol	Acetone
5a (PDMS Mn 850-900)	**44.6**	**28.6**
5b (PDMS Mn ~2500)	**26.2**	**17.2**
5c (PDMS Mn ~5000)	**11.6**	**13.6**

V. Conclusion

Three sustainable polyurea PDMS based polymers have been synthesized and their mechanical properties, including determination of the Young's modulus, shear adhesion testing, and shape memory testing, have been investigated. Additionally, the room temperature self-healing efficiencies for each of the polymers has been evaluated via tensile testing. These results provide insight into the molecular properties necessary for developing a polymer to serve as a protective coating for UAVs. Future work in this research group will focus on balancing the functionality needed for efficient self-healing properties while optimizing mechanical properties necessary for the desired application.

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[3] Onyx filament: https://shop.markforged.com/shop/s/product/detail/01t1600000HG2aOAAT

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