The Interplay of Modulus, Strength, and Ductility in Adhesive Design Using Biomimetic Polymer Chemistry

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High-performance adhesives require mechanical properties tuned to demands of the surroundings. A mismatch in stiffness between substrate and adhesive leads to stress concentrations and fracture when the bonding is subjected to mechanical load. Balancing material strength versus ductility, as well as considering the relationship between adhesive modulus and substrate modulus, creates stronger joints. However, a detailed understanding of how these properties interplay is lacking. Here, a biomimetic terpolymer is altered systematically to identify regions of optimal bonding. Mechanical properties of these terpolymers are tailored by controlling the amount of a methyl methacrylate stiff monomer versus a similar monomer containing flexible poly(ethylene glycol) chains. Dopamine methacrylamide, the cross-linking monomer, is a catechol moiety analogous to 3,4-dihydroxyphenylalanine, a key component in the adhesive proteins of marine mussels. Bulk adhesion of this family of terpolymers is tested on metal and plastic substrates. Incorporating higher amounts of poly(ethylene glycol) into the terpolymer introduces flexibility and ductility. By taking a systematic approach to polymer design, the region in which material strength and ductility are balanced in relation to the substrate modulus is found, thereby yielding the most robust joints.

1. Introduction

Adhesives with different chemistries and varying forms have found widespread use in the automotive, aerospace, construction, and biomedical industries. The polymers involved are most often epoxy, polyurethane, or acrylics. Typical formulations include hot melt, rubber toughened, and pressure sensitive systems. Generally speaking, optimal bonding is needed for a range of substrates, joint geometries, and applications. Consider that a typical new car now uses 12 kg of adhesive, up from 5 kg a decade ago.[1] The newest generation of commercial airplanes such as the Boeing 787 and Airbus A350 contain more than 50% bonded carbon fiber structure, as opposed to the prior technology of riveted aluminum.[2] With adhesives being used in more places there is a growing demand for higher performance materials.

When designing an adhesive, the modulus (i.e., stiffness) of both the glue and the substrates being joined must be considered. If the modulus of these materials differs and the joint is subjected to mechanical load, the mismatch in stiffness generates interfacial stresses that can bring about bond failure.[3] In order to maintain bond integrity, a lower modulus adhesive should be used for bonding more flexible substrates such as rubber or soft skin (**Figure 1**A). A high modulus adhesive is preferred for stiff substrates including metal and hard bone (Figure 1B). This materials design consideration becomes more problematic when adhering dissimilar substrates of varying stiffness (Figure 1C).[3,4]

Several analytical models have shown that as the adhesive modulus becomes increasingly different from the modulus of the substrates being glued together, stress concentrations in the joint become more pronounced.[5–7] Only a limited number of experimental studies have explored what happens when the modulus of the adhesive is changed to match that of the substrates being bonded.[8,9] In one such example, commercial epoxides adhesives with different flexibilizers were investigated and then used to bond metals and plastics.[8] The elastic moduli of the adhesives (2.1–2607 MPa) and substrates (170–207000 MPa) varied significantly.[8] Generally, improved bond strengths were obtained when the lower modulus adhesives and substrates were paired together.[8] Likewise, higher modulus adhesives performed better on stiffer substrates. A separate report studied five commercially available modified acrylic-based resins on aluminum, steel, and plastics such as poly(methyl methacrylate) (PMMA) and poly(carbonate).[9] The elastic moduli of the cured adhesives were all similar to the moduli of the plastics (2–4 GPa). This study examined bonding similar and dissimilar substrates, finding that, due to the mismatch in properties, the bi-material systems often had lower strengths compared to the same-material system.[9]

Both of these studies[8,9] were carried out with commercial glues and various added modifiers or curing agents, potentially changing the adhesive chemistry somewhat. In terms

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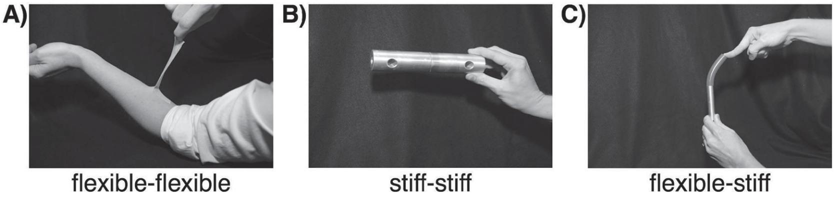


Figure 1. Adhesives are used to join substrates of varying stiffness. Bonding A) flexible skin, B) stiff aluminum, or C) flexible rubber to stiff aluminum will each have different requirements. The moduli of the adhesives should be chosen to match the moduli of the substrates in order to minimize stress concentrations.

of understanding and optimizing adhesive design, we can still benefit from a systematic study to explore the tuning of a polymeric adhesive to specific moduli, for matching with the moduli of the substrates. The ability to "dial in" polymer moduli for specific substrates could help solve problems such as rubber-to-metal bonding in motor mounts for the automotive industry, tendon-to-bone joinery for biomedical applications, and construction of aerospace vehicles.

An ability to match the adhesive and substrate moduli will improve joint performance. Also important are strength and ductility of adhesive materials.[10] In lap shear bond configurations, the points of highest stress are at the edges. Use of brittle adhesives makes this stress concentration even more pronounced.[11] Stiff adhesives with low ductility (i.e., percent elongation) foster crack propagation. A more flexible, ductile adhesive can undergo plastic deformation and extend to high elongation percentages, allowing the mechanical load to distribute throughout the joint in a more uniform manner. However, a problem emerges in that material ductility gains are typically incorporated at the expense of material strength.[12] A highly ductile adhesive is often a weak material and can only sustain minimal loads. Studies with different adhesive chemistries[13–19] and hybrid designs that use separated segments of stiff and flexible glues along the bondline[12,20,21] have shown that ductility does influence joint strength, yet the optimum balance between strength and ductility often remains unclear.

For decades, three traditional adhesive classes have been most prominent: acrylics, epoxies, and urethanes. An exciting fourth area of adhesive chemistry has been emerging recently. By looking to the oceans, we are learning how to design biomimetic materials. Marine mussels use adhesive plaques for sticking to rocks and other surfaces.[22–25] Close inspection of these plaques has revealed that they are made up of six different mussel foot proteins, all of which are relatively rich with 3,4-dihydroxyphenylalanine (DOPA).[26–28] This amino acid, in particular, provides mussels with an ability to obtain strong and versatile adhesion via surface binding and cross-linking. Taking glue directly from the animal is impractical due to the minimal amount produced. We turn to synthetic mimics such as polymers, incorporating various forms of the DOPA sidechain moiety. Although this field has expanded rapidly in the past five years,[29,30] we still do not have a good handle on how to transform these biomimetic systems into functional materials with high performance.

Our research group has carried out several studies with a simplified mimic of mussel adhesive proteins, poly[(3,4-dihydroxystyrene)-*co*-styrene]. By exploring changes to the polymer composition,[31] molecular weight,[32] and formulation (e.g., polymer concentration, cure time, cure temperature, and adding fillers) we have been able to, in some cases, obtain strengths higher than commercial products such as "Super Glue."[33] Modifications to this styrene-based system have also provided insight into a more compliant adhesive. Oligo(ethylene glycol) chains were added to poly[(3,4-dihydroxystyrene)-*co*-styrene] to yield poly{[3,4-dihydroxystyrene]-*co*-[4-vinylbenzyl{methyltetra(ethylene glycol)}]-*co*-styrene}.[34] When working with this system, we noticed that increasing oligo(ethylene glycol) content resulted in less brittle polymers. Although we may have been able to work with this polymer to gain insight into how to tune an adhesive to obtain different mechanical properties, the six-step synthesis became cumbersome. We have now turned to a methacrylate-based biomimetic polymer that can display a wide variety of moduli and be made in only two steps.

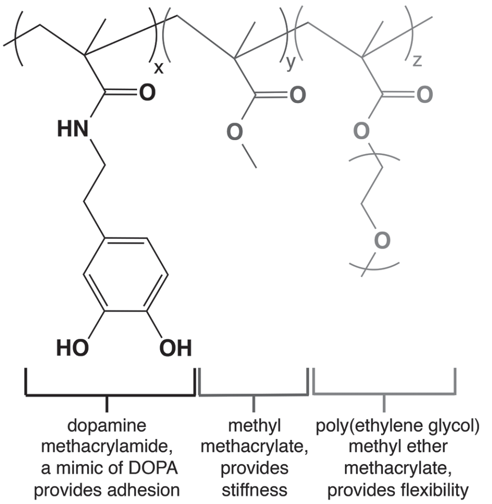
An ideal adhesive should have an optimum balance between strength and ductility, while also displaying a modulus similar to the substrates being bonded together. To the best of our knowledge, there are no published systematic data examining the interplay between strength, ductility, and modulus, within an adhesive material in relation to the modulus of the substrates being bonded together. Gaining insights on the interplay between these critical parameters will allow us to create the strongest adhesive joints possible.

Here, a family of biomimetic terpolymers were synthesized with varying amounts of methyl methacrylate and poly(ethylene glycol) methyl ether methacrylate (PEG), while keeping dopamine methacrylamide constant. Incorporation of the methyl methacrylate monomer brought about stiffness, whereas the PEG chains appended to an acrylate monomer promoted flexibility. The adhesive monomer was dopamine methacrylamide representing the DOPA of mussel proteins. Each of these polymers was then adhered to substrates of differing stiffness. Starting from a biomimetic design, we were able to systematically modify an adhesive and identify regions of maximum bonding performance. In the end, the highest performance bonds were found where the strength and ductility of the adhesive were complementary.

2. Results and Discussion

2.1. Polymer Design, Synthesis, and Characterization

A family of adhesive terpolymers with the structure shown in **Scheme 1** was obtained via radical polymerization. The dopamine methacrylamide adhesive monomer was prepared in bulk (≈10 g) following a published procedure.[35] When incorporating this compound into the backbone, ≈33 mol% was targeted given that an analogous composition showed the highest adhesion with poly[(3,4-dihydroxystyrene)-*co*-styrene].[31] The other monomers used here were commercially available poly(ethylene glycol) methyl ether methacrylate ($M_n \approx 300$ g mol^{-1}) and methyl methacrylate. Molecular weights above ≈5000 g mol^{-1} are necessary for obtaining bulk adhesion.[36] Consequently, molecular weights above this value were targeted.



Scheme 1. An adhesive random terpolymer that can be tuned to have specific mechanical properties by controlling the amount of methyl methacrylate versus poly(ethylene glycol) methyl ether methacrylate monomers.

Polymer characterization was carried out with proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (Figure S1, Supporting Information) and gel permeation chromatography (GPC) (**Table 1**). The final percentage of monomers in the backbone followed the initial feeds (Table S1, Supporting Information). The dopamine methacrylamide content ranged from ≈28 to 36 mol%, with methyl methacrylate and poly(ethylene glycol) methyl ether methacrylate (PEG) varying intentionally from ≈0 to 70 mol%. The number-average molecular weights (M_n) ranged from ≈6000 g mol^{-1} to ≈25 000 g mol^{-1} with polydispersity indices (PDIs) of 1.3–2.0 (Table 1).

Thermal characterization using differential scanning calorimetry (DSC) was met with limited success. The glass transition temperatures (T_g) for the 100% PMMA and 100% oligo(dopamine methacrylamide) homopolymers were ≈110 and ≈88 °C, respectively. For poly[(dopamine methacrylamide)$_{35\%}$-*co*-(methyl methacrylate)$_{65\%}$], the T_g was at ≈113 °C. Using DSC to identify glass transition temperatures became more complicated with PEG chains added to the polymers. The T_g of a poly[(ethylene glycol) methyl ether methacrylate] homopolymer has been reported to be −57 °C.[37] For all PEG-containing terpolymers here, a quite broad endothermic peak appeared from ≈−5 to ≈75 °C. Since a single peak was observed by DSC, random arrangement of the monomers in the backbone was quite likely. In an effort to gain more specific insights on the nature of these polymers, a melting temperature apparatus was used to locate potential thermal transitions. For poly{[dopamine methacrylamide]$_{28\%}$-*co*-[poly(ethylene glycol) methyl ether methacrylate]$_{72\%}$}, without methyl methacrylate, the sample was a viscous gel and could not be tested. At 0% PEG, 65% methyl methacrylate, and 35% dopamine methacrylamide, the sample started deforming at ≈140 °C. With 52% PEG, 16% methyl methacrylate, and 33% dopamine methacrylamide, this high PEG sample began deforming at 40 °C. Although not precise, these data do show that the incorporation of PEG into the polymers decreased the glass transition temperatures.

2.2. Adhesion Studies: Lap Shear

Eight polymers with similar amounts of dopamine methacrylamide (28% to 36%) and varying amounts of methyl methacrylate (0% to 65%) versus poly(ethylene glycol) methyl ether methacrylate (PEG) (0% to 72%) were synthesized and tested. No external cross-linking agents were added. Lap shear is one of the most common ways to evaluate bulk adhesion and was thus used here (Figure S2, Supporting Information).[38,39] Studies on both stiff (elastic modulus ≈69 GPa) and flexible (elastic modulus <1 GPa) substrates were conducted to better evaluate the effect of matching the substrate and adhesive moduli. Many of our prior studies have bonded aluminum substrates cleaned by the ASTM D2651 standard method. Consequently, lap shear adhesion studies here began with aluminum. Adhesion is defined as the maximum load at failure divided by the glue-covered substrate overlap area.

Past studies with a styrene-based polymer showed that oligo(ethylene glycol) chains could influence adhesion in some cases.[34] Up to ≈18 mol% oligo(ethylene glycol)-containing monomer could be copolymerized with styrene and 3,4-dihydroxystyrene without seeing any adhesion penalty, reaching ≈2.5 MPa on polished aluminum. With more than ≈18%

Table 1. Composition and molecular weight data for a family of poly{[dopamine methacrylamide]-*co*-[methyl methacrylate]-*co*-[poly(ethylene glycol) methyl ether methacrylate]} terpolymers.

dopamine methacrylamide [mol%]	methyl methacrylate [mol%]	poly(ethylene glycol) [mol%]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI
0	100	0	12 200	17 800	1.5
35	65	0	5900	8100	1.3
34	58	8	5300	7400	1.4
34	54	12	6100	8100	1.3
36	41	23	21 000	35 400	1.7
34	32	34	10 000	14 000	1.4
29	27	45	10 400	20 400	1.9
33	16	52	12 600	21 000	1.7
28	0	72	24 900	51 000	2.0

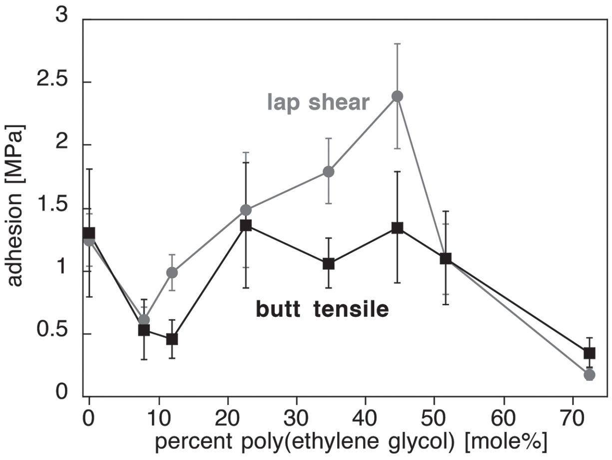


Figure 2. Lap shear and butt tensile adhesion of terpolymers containing ≈33 mol% dopamine methacrylamide and varying percentages of methyl methacrylate versus poly(ethylene glycol) methyl ether methacrylate on aluminum.

of the oligo(ethylene glycol) monomer, adhesion diminished significantly, down to ≈0.3 MPa at 35% oligo(ethylene glycol).

For the methacrylate-based polymer used in this current study, initial incorporation of PEG resulted in a slight decline in adhesion between 8 and 12 monomer percent. Interestingly, at loadings of 23% PEG, adhesion started to rise, reaching ≈1.5 MPa (**Figure 2**). The peak in adhesion at ≈2.4 MPa was obtained with 45% PEG in the backbone. At 72%, the highest loading of PEG, adhesion then decreased down to ≈0.2 MPa. Common commercial adhesives were tested on aluminum to obtain a comparison of bonding performances. Under similar conditions, poly(vinyl acetate) Elmer's Glue All adhered at ≈4 MPa, cyanoacrylate Krazy Glue at ≈7 MPa, and Loctite epoxy at ≈11 MPa.

If trying to obtain gains in strength by matching the modulus of the adhesive and the substrate, one might expect that the stiffest substrate (e.g., aluminum in this case) would bond best with the highest modulus adhesive examined. In other words, the 0% PEG polymer, poly[(dopamine methacrylamide)$_{35\%}$-*co*-(methyl methacrylate)$_{65\%}$], the left most point in Figure 2, might be the strongest bonding glue on aluminum. Yet we see the peak in adhesion at 45% of the flexible PEG monomer. Improving bond strengths does not appear to be as simple as just matching the modulus of the adhesive and the substrate. Ductility and strength of the adhesive material must now be considered.

2.3. Mechanical Properties of Biomimetic Terpolymers and Substrates

When examining the force versus extension curves from lap shear testing of the adhesive terpolymers, a dramatic effect of PEG became evident (**Figure 3**A). These curves are the raw data from adhesion measurement experiments in which a bonded pair of substrates was pulled until failure (Figure S2, Supporting Information). Adhesion values reported here use the highest force observed prior to failure. The sharp curves seen for 0%, 11%, 23%, and 34% PEG are indicative of brittle fracture. At loadings of 45% PEG and above, the force versus extension curves became more rounded. The high PEG polymers appeared to be softening. By incorporating PEG, a brittle to ductile transition may have occurred.

For examining potential changes to mechanical properties, the adhesive polymers were cast into thin films. Dynamic mechanical analysis in the controlled force mode was used to obtain stress versus strain data (Figure 3B). The polymers containing 0% and 23% PEG proved to be incredibly fragile when in a film of ≈0.3 mm thickness. If bent at all, the sample would fail catastrophically into numerous pieces. We were only able to obtain estimates of mechanical properties. With more PEG included, the films became increasingly durable, flexible, and workable. The samples containing the most PEG were malleable enough to be easily folded in half. The elastic moduli of these terpolymers ranged from ≈0.0002 GPa at 72% PEG to ≈2 GPa at 0% PEG (**Table 2**). For comparison, stiff commercial adhesives including epoxies have elastic moduli in the range of ≈3–5 GPa. Flexible adhesives such as poly(urethanes) are lower at ≈0.1 GPa.[40]

When transitioning from the 23% PEG to the 34% PEG polymer, a shift from elastic to plastic deformation was observed. The stress versus strain curve for the terpolymers

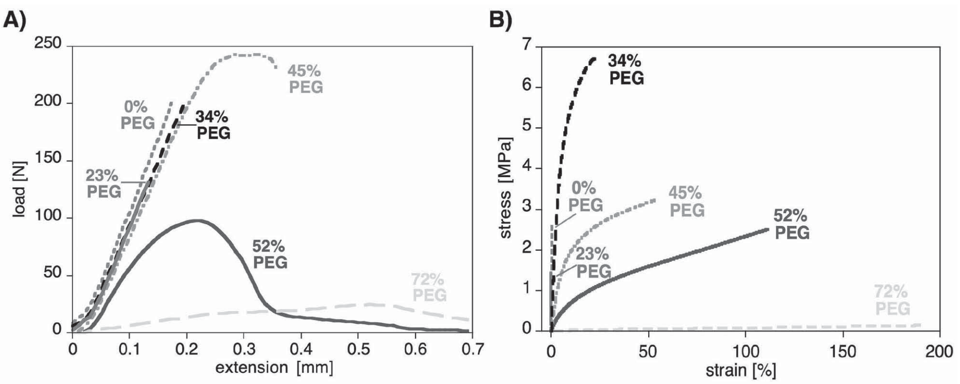


Figure 3. A) Force versus extension curves from lap shear adhesion testing of terpolymers containing ≈33 mol% dopamine methacrylamide and varying amounts of poly(ethylene glycol) methyl ether methacrylate on aluminum. B) Adhesive terpolymers were cast into thin films and tested in tension to obtain stress versus strain curves.

Table 2. Mechanical properties for a family of poly{[dopamine methacrylamide]-*co*-[methyl methacrylate]-*co*-[poly(ethylene glycol) methyl ether methacrylate]} terpolymers.

dopamine methacrylamide [mol%]	methyl methacrylate [mol%]	poly(ethylene glycol) [mol%]	elastic modulus [GPa]	yield strength [MPa]	ultimate tensile strength [MPa]	strain [%]
35	65	0	≈2	N/A[a)]	≈3	≈0.2
36	41	23	1.3 ± 0.5	N/A[a)]	2 ± 1	0.1 ± 0.1
34	32	34	0.15 ± 0.01	5 ± 1	7 ± 1	30 ± 10
29	27	45	0.042 ± 0.002	2.2 ± 0.4	4 ± 1	90 ± 30
33	16	52	0.012 ± 0.001	1.1 ± 0.1	2.2 ± 0.3	110 ± 20
28	0	72	0.00019 ± 0.00003	N/A[b)]	>0.1[b)]	>190[b)]

[a)] Specimens did not yield; [b)] Specimens did not fail prior to reaching the extension limit of the instrument.

containing 34% PEG was no longer linear, displaying a yield point, the stress at which the material began to deform plastically. With this shift came a rise in ductility, which could be quantified by the strain at break. With increasing amounts of PEG, the strain at break rose from ≈0.2% for the 0% PEG polymer to over 190% for the 72% PEG polymer. The 72% PEG specimens never actually failed, reaching the extension limit of the instrument at 190%. Although the terpolymer containing 34% PEG displayed the highest mechanical strength (≈7 MPa) and intermediate ductility (≈27%), this polymer was not the one exhibiting the highest adhesion. The peak in adhesion on aluminum was obtained at 45% PEG. Perhaps it is this balance between strength (≈4 MPa) and high ductility (≈88%) that combines to provide the highest adhesion.

Adhesion tests on substrates of varying stiffness were then conducted to determine if increases in bonding strengths could be observed when the moduli of both the glue and substrate were chosen to be similar. Poly(urethane) substrates were purchased in a wide range of durometer hardnesses (**Figure** 4A). The most flexible substrate, poly(urethane) of 40 Shore A hardness, felt similar to a flexible rubber. The stiffest substrate, 75D Shore D poly(urethane), was comparable to a construction hard hat. With a hardness between these two other substrates, 80 Shore A poly(urethane) was slightly malleable, similar to that of a shoe heel. Other common plastic substrates tested were PMMA and poly(vinyl chloride) (PVC). Mechanical properties of each material were determined by fabricating dumbbell-shaped specimens and testing in tension following the ASTM D638 standard method[41] (**Table 3**). The elastic moduli of these plastic substrates varied from ≈0.001 to ≈1 GPa. Contact angle measurements showed that the surface energies for the substrates were generally similar (Table 3).

2.4. Adhesion Studies: Butt Tensile

When bonding together the softer poly(urethane) substrates in lap shear configurations, the joints flexed and bent during

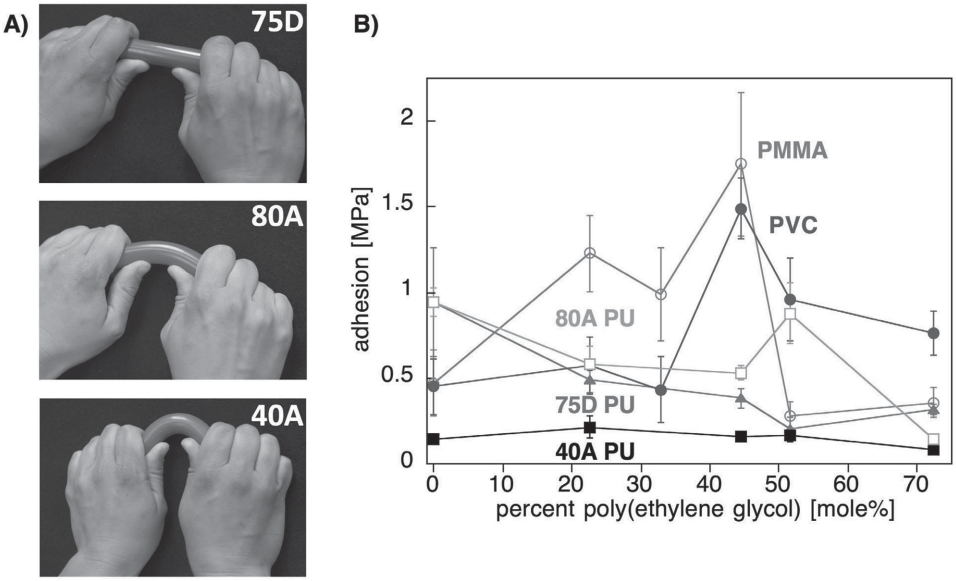


Figure 4. A) The flexibility of poly(urethane) (PU) substrates displayed. B) Butt tensile bonding of different substrates with varying stiffness. The adhesives used were terpolymers containing ≈33 mol% dopamine methacrylamide and varying percentages of methyl methacrylate versus poly(ethylene glycol) methyl ether methacrylate.

Table 3. Water contact angles and mechanical properties of aluminum and plastic substrates.

	water contact angle [°]	elastic modulus [GPa]	yield strength [MPa]	ultimate tensile strength [MPa]	strain [%]
aluminum[57]	90 ± 2	69	276	310	17
poly(methyl methacrylate)	79 ± 3	0.89 ± 0.04	82 ± 2	87 ± 1	12 ± 1
poly(vinyl chloride)	83 ± 3	0.8 ± 0.1	50 ± 1	40 ± 4	140 ± 60
75D poly(urethane)	81 ± 4	0.5 ± 0.1	N/A[a)]	27 ± 5	340 ± 70
80A poly(urethane)	85 ± 5	0.016 ± 0.001	N/A[a)]	>6 ± 1	>430 ± 80
40A poly(urethane)	86 ± 7	0.00115 ± 0.00002	N/A[a)]	1.6 ± 0.1	240 ± 20

[a)] Specimens did not yield.

adhesion testing (Figure S3, Supporting Information). Due to additional stresses on the joints from this bending, results were not considered reliable. Subsequently, we explored another simple adhesion configuration with butt tensile joints.[10] The arrangement and testing of rod-shaped butt-joined specimen can be seen in Figure S4 (Supporting Information). For comparison to the lap shear results, testing of all terpolymers was repeated in the butt tensile configuration on aluminum (Figure 2). These data are overlaid with the analogous lap shear experiments described earlier (Figure 2). A roughly similar relation of adhesion versus PEG content was observed with both butt tensile and lap shear joints. Changes in adhesion relative to PEG content were more subtle, however. This observation of a flatter trend in butt tensile versus lap shear may be a result of glues being more ductile in shear than in tension.[40] If a flaw (e.g., void due to evaporation of solvent) exists in a butt tensile joint, once a crack is triggered, the specimen will fail quickly due to this high stress concentration. In lap shear, if cracking at a void occurs, the remaining adhesive area is still available to deform, by withstanding higher strains.[40] A consequence here is that butt tensile bonding may not have as much to gain from the added PEG ductility as a lap shear joint.

With a bonding testing method in hand, the entire family of moduli-tuned adhesives was tested on the five plastic substrates of varying stiffness (Table 3). Substrates with the highest elastic modulus at ≈1 GPa were PMMA and PVC. For both PMMA and PVC substrates, adhesion peaked at 45% PEG, reaching ≈2 MPa (Figure 4B). Adhesion for this 45% PEG terpolymer on these two plastic substrates was slightly higher than that for aluminum in butt tensile (≈1.3 MPa) (Figure 2). The modulus of the 45% PEG terpolymer at ≈0.04 GPa (Table 2) is more similar to the moduli of these plastics (≈1 GPa) than to that of aluminum at ≈69 GPa. Still, the adhesive is ≈25 times less stiff than PMMA and PVC. The rise in adhesion at a point of 45% PEG content was likely a result of the adhesive having ductility from the PEG, being able to deform plastically. This ductility and plasticity allows mechanical stresses to be redistributed throughout the material while testing occurred.

The most flexible substrate, 40A poly(urethane) with an elastic modulus of only ≈0.001 GPa (Table 3), displayed the lowest adhesion at ≈0.2 MPa for all terpolymers (Figure 4B). Due to the flexibility of this substrate, both the adhesive and substrate were being stressed during testing. The lack of stiffness prohibits a strong adhesive bond. Generally speaking, substrates of low strength and high flexibility are difficult to bond well, regardless of the adhesive used.

The stiffest poly(urethane) substrate, 75D, had a modulus of ≈0.5 GPa (Table 3). On 75D poly(urethane), adhesion was highest at 0% PEG and gradually decreased with increasing amounts of this monomer added to the polymer (Figure 4). Tensile tests revealed that this substrate could be extended to high strains (≈339%) prior to failure (Table 3). Due to this high substrate extensibility, having PEG in the adhesive to promote ductility was not necessary to achieve stronger bonds. All the needed flexibility was already in the substrate. Additional ductility from PEG only served to weaken the system.

The 80A poly(urethane) substrate had an elastic modulus (≈0.02 GPa) higher than 40A poly(urethane) (≈0.001 GPa) and lower than 75D poly(urethane) (≈0.45 GPa) (Table 3). A slight rise in adhesion was seen at 52% PEG. At this 52% PEG content, the adhesive modulus (≈0.01 GPa) (Table 2) was a close match to that of the substrate. For this substrate, the strain at break was so high (>430%) that additional ductility from the adhesive polymer was not required in order to achieve maximum bond strength. Designing the adhesive such that the modulus is similar to that of the substrate modulus may be more important here.

For higher modulus substrates (≥1 GPa) such as aluminum, PMMA, and PVC, the point of maximum bonding can be found where the adhesive provides ductility, but can also maintain strength (Table 2). Thus for the bonding of metals and commodity plastics, matching the adhesive and substrate moduli is not necessarily the most critical factor. Ductility and the resulting decrease in modulus can yield the highest bond strengths (Figure 2). Too much ductility will weaken the adhesive and bond strengths may suffer. When the modulus of the substrate is above that of flexible rubber (≈0.001 GPa) or below that of common plastics (≈1 GPa), ductility is often built into the substrate (Table 3). Adding ductility to the adhesive will not benefit the joint performance (Figure 4). For these softer substrates, the adhesive may work best when the modulus is comparable to that of the substrate.

2.5. On the Origins of Poly(ethylene glycol) Influencing Adhesion

Poly(ethylene glycol) is one of the most widely used polymers within the biomedical industry and also the focus of countless academic studies.[42,43] Amongst the greatest aspects of this polymer is biocompatibility.[44] In a sense, this lack of toxicity has origins in a lack of adhesion.[45] Although the exact reasons behind the biocompatibility of PEG are still debated, the most accepted idea is that water attaches to the polymer's oxygens via hydrogen bonds.[46] The resulting hydrated structure, in essence, looks just like water. Macromolecules and cells do not "see" the polymer, do not adhere, and no biological response such as immunogenicity takes places.[46]

Data presented here in this paper show that the antiadhesive effects of PEG can be more complex. High PEG content within the polymer increased ductility, weakened the material strength, and could decrease adhesion. However, moderate levels of PEG actually increased adhesion. When considering the antiadhesive or antifouling effects of PEG, we should likely keep in mind which mechanisms are most relevant to the situation at hand.

3. Conclusion

Prior studies examining adhesive modulus or ductility are few, with the available data being derived from, effectively, mixing fillers into commercial adhesives.[8,9] Here we varied the composition of a terpolymer, without adding external fillers, flexibilizers, or cross-linkers. This approach also avoided phase separations, such as those observed with rubber-toughened epoxies.[47] Tuning the amount of methyl methacrylate and PEG in the polymer provided adhesives with moduli ranging from ≈0.0002 to 2 GPa, strengths from ≈0.1 to 3 MPa, and strains from ≈0.2% to 200%. By synthesizing these terpolymers, there was more control over the structure, allowing a wider range of mechanical properties when compared to prior studies.[8,9] This type of a systematic study allowed us to identify the point at which strength and ductility were complementary, leading to a toughened adhesive.

These data also shed light on some general design principles for making glues. Addition of poly(ethylene glycol) into the polymer chains allowed identification of the point at which both strength and ductility were balanced. Where adhesion peaked was also quite dependent upon the nature of the substrate being bonded. Although matching the moduli of adhesives to substrates should be considered, tuning the adhesive ductility is at least of equivalent importance. Further insights were provided on the antiadhesive or antifouling aspect of PEG. Increased ductility and decreased material strength with PEG can influence adhesion significantly, but by a mechanism quite different than that found for materials placed in biological or aqueous contexts. These data are presented in hopes of contributing design considerations for bonding in the automotive, aerospace, and biomedical sectors.

4. Experimental Section

General Procedures: A Varian Inova-300 MHz spectrometer was used to record proton nuclear magnetic resonance (^{1}H NMR) spectra (Figure S1, Supporting Information). In order to integrate the peaks accurately, a relaxation delay of 30 s between scans was implemented. Monomer ratios in the final polymers were determined by integration of the aromatic region (δ: 6.2–6.7 ppm) to give dopamine methacrylamide content, the OCH_2 peak at 3.8–4.2 ppm for poly(ethylene glycol) methyl ether methacrylate content, and the backbone region (δ: 0–2.3 ppm) for methyl methacrylate content. Molecular weights were found by gel permeation chromatography (GPC) using a Polymer Laboratories PL-GPC20 with eluent tetrahydrofuran (THF). Water contact angles for all substrates were determined using a Ramé-Hart Advanced Goniometer/Tensiometer Model 500. Thermal transitions were observed with a Perkin Elmer Jade Differential Scanning Calorimeter (DSC) from −40 °C to 140 °C at 5 °C min^{-1}. Methyl methacrylate and poly(ethylene glycol) methyl ether methacrylate (M_n ≈300 g mol^{-1}) monomers were purchased from Sigma Aldrich and purified using an alumina column. This M_n translates to an oligo(ethylene glycol) chain length of ≈4.3 ethylene glycol repeats. Synthesis of the dopamine methacrylamide monomer followed a published procedure and characterization employed ^{1}H NMR spectroscopy.[35] All polymers were prepared by free radical polymerization under an inert argon atmosphere using typical Schlenk techniques. The radical initiator, azobisisobutyronitrile (AIBN), was recrystallized from methanol and dried in vacuo prior to use. Dimethylformamide (DMF) solvent was kept over sieves and degassed with bubbling argon for at least 15 min prior to starting a reaction. To synthesize a family of terpolymers with target monomer compositions, the ratio of methyl methacrylate to poly(ethylene glycol) methyl ether methacrylate was altered in the feed (Table S1, Supporting Information). The content of dopamine methacrylamide in the polymer was always targeted to be 33 mol%. Combining a radical initiator such as AIBN with a radical inhibitor such as a catechol compound may appear to be counterintuitive. Several research groups have been producing acrylate polymers, often containing dopamine methacrylamide, using the general synthetic methods described below.[35, 48-51] Recently a study was published showing that this class of polymer can contain varied degrees of cross-linking at the end of the synthesis.[52] From this report[52] and our target of ≈33% dopamine methacrylamide, we may surmise that the polymers described below contain roughly one cross-link for every third polymer. In other words, the degree of cross-linking in the materials synthesized for this current study is quite low. Prior to adhesion studies, the majority of isolated polymer chains are free of any cross-links.

Synthesis of Poly{[dopamine methacrylamide]-co-[methyl methacrylate]-co-[poly(ethylene glycol) methyl ether methacrylate]}: Dopamine methacrylamide (1.5 g, 6.7 mmol), methyl methacrylate (0.68 mL, 6.4 mmol), poly(ethylene glycol) methyl ether methacrylate (1.9 mL, 6.5 mmol), and AIBN (31.6 mg, 0.192 mmol) were dissolved into dimethylformamide (14 mL) in a flame-dried Schlenk flask. After stirring for 30 min under argon and at room temperature, the flask was placed into an 80 °C oil bath for 2 d. The reaction mixture became a viscous solution. The flask was removed from the oil bath and 1 mL of methanol was added to quench the reaction. To the cooled reaction was added dichloromethane (≈10 mL) for dilution. The solution was then poured into excess ether (≈200 mL) to precipitate a white polymer. The product was reprecipitated two additional times in dichloromethane/ether. Sonication along with minimal methanol was often necessary to solubilize the polymer. The product was dried in vacuo for two nights yielding 3.3 g (81%) of pure polymer. The ^{1}H NMR spectrum in d^6-DMSO is shown in Figure S1 (Supporting Information).

Synthesis of Poly{[dopamine methacrylamide]-co-[poly(ethylene glycol) methyl ether methacrylate]}: Dopamine methacrylamide (0.89 g, 4.1 mmol), poly(ethylene glycol) methyl ether methacrylate (2.2 mL, 7.5 mmol), and AIBN (18.7 mg, 0.14 mmol) were dissolved into dimethylformamide (9 mL) in a flame-dried Schlenk flask. After stirring for 30 min under argon and at room temperature, the flask was placed in a 65 °C oil bath for 5.5 h. At this point, the reaction mixture was starting to gel. The flask was removed from the oil bath and 1 mL of methanol was added to quench the reaction. The reaction mixture was poured into excess ether (150 mL) to precipitate a white polymer. The product was reprecipitated two additional times in dichloromethane/ether and then dried in vacuo for two nights.

Synthesis of Poly[(dopamine methacrylamide)-co-(methyl methacrylate)]: Dopamine methacrylamide (1.1 g, 5.1 mmol), methyl methacrylate

(1.0 mL, 9.5 mmol), and AIBN (23.6 mg, 0.14 mmol) were dissolved into dimethylformamide (7 mL) in a flame-dried Schlenk flask. After stirring for 30 min under argon at room temperature, the flask was placed in a 70 °C oil bath for 17 h. The reaction mixture became a viscous solution. Upon removal from the oil bath, 1 mL of methanol was added. To the cooled reaction was added ≈5 mL of dichloromethane for dilution. This solution was poured into excess ether (≈200 mL) to precipitate a brownish-white polymer. The product was reprecipitated two additional times in dichloromethane/ether and then dried in vacuo for two nights.

Synthesis of Poly(methyl methacrylate): Methyl methacrylate (2.45 mL, 22.9 mmol) and AIBN (37 mg, 0.23 mmol) were added to anhydrous toluene (15 mL) in a flame-dried Schlenk flask. After stirring for 30 min at room temperature under argon, the flask was placed into a 75 °C oil bath overnight. The flask was removed from the oil bath and 1 mL of methanol was added. This reaction mixture was poured into excess hexanes (150 mL) to precipitate a white polymer. The product was reprecipitated two additional times in dichloromethane/hexanes and then dried in vacuo for two nights.

Mechanical Properties: Stress versus strain curves were obtained for the DOPA-containing terpolymers using dynamic mechanical analysis (TA Instruments Q800) in tension with controlled force (0.10 N min^{-1}). A preload force of 0.001 N was applied. Thin film samples were prepared by solvent casting. Typically, 0.05 g of polymer was dissolved at 0.15 g mL^{-1} in 10% volume trichloroethylene in methanol. Using a micropipette, the polymer solution (50 µL) was added into a custom-fashioned polydimethylsiloxane mold every 30 min until the entire sample was formed. Samples were cured at room temperature for ≈6 h, then at 37 °C for 48 h. Typical samples were 12.0 mm long, 3.0 mm wide, and 0.3 mm thick. To clamp into the instrument with consistent forces, a torque wrench was used. When samples had a PEG content greater than 23%, a torque of 2 in-lb was applied. For lower percent PEG samples, films could only be secured at fingertip tightness without breaking. At least three samples were tested for each trial. For the 0% PEG polymer, only one trial is reported due to how fragile the thin films were. Testing of at least ten samples was attempted, but could not be secured into the grips without cracking. Due to the flexibility and extensibility of 72% PEG, these samples did not fail before reaching the extension limit of the instrument. Tensile properties of the substrates were determined by the ASTM D638 standard method.[41] Specimens were fabricated into Type IV dumbbell shapes using a CNC mill for 75D polyurethane, poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC). A water jet cutter was used for the 40A and 80A polyurethane substrates. Specimens were tested on an MTS Insight Electromechanical Testing System using a 2000 N load cell. Poly(urethane) specimens were tested at 50 mm min^{-1}. The PMMA and PVC substrates were tested at 5 mm min^{-1}. It should be noted that 80A poly(urethane) slipped out of the grips at high extensions for all samples due to decreasing cross-sectional area as testing. For both adhesive films and substrates, the elastic moduli were determined from the initial slope of the linear portion of the stress–strain curve. For 75D poly(urethane) specimens the initial slope was not linear, thus the secant modulus is reported. The yield strength was defined by the 0.2% offset strain. Ultimate tensile strength was the load at fracture divided by the area. Strain was the percent elongation at break. Averages and errors at ±1 standard deviation are reported.

Adhesion Study onAluminum Substrates: For lap shear tests, adherends of 8.89 cm × 1.27 cm × 0.318 cm were precision cut using a water jet system from a sheet of aluminum 6061-T6 purchased at Farmer's Copper. For butt tensile tests, aluminum 6061-T6 rod stock with a diameter of 1.59 cm was cut and faced to a length of 7.68 cm using a CNC mill. Holes with a diameter of 0.633 cm were drilled 0.80 cm from the top using a drill press. The adherends were cleaned according to the ASTM D2651 standard method, followed by washes in boiling, deionized water and methanol.[53]

Adhesion Study on Plastic Substrates: For lap shear and butt tensile tests, toluene diisocyanate based-poly(urethane) bar stock (1.27 cm × 1.27 cm × 61.0 cm) and rod stock (1.59 cm × 122 cm) with durometer hardnesses of 40 Shore A, 80 Shore A, and 75 Shore D were purchased from Universal Urethane Products. Using a mold, specimens were cut with a Walnut Hollow Professional Hot Knife to a length of 8.89 cm for lap shear and 7.68 cm for butt tensile. Additionally for butt tensile tests, cast acrylic (i.e., PMMA) and polyvinyl chloride (Type II) rod stock with a diameter of 1.59 cm were purchased from McMaster Carr. Specimens were cut with a band saw to 8.0 cm and then a CNC lathe was used to face the ends giving a length of 7.68 cm. Using a drill press, holes with a diameter of 0.633 cm were drilled 0.80 cm from the top for 75D poly(urethane), cast acrylic, and polyvinyl chloride substrates. To clean prior to testing, soap and water were used, followed by ethanol and hexane washes. The specimens were heated at 70 °C to dry for 2 h. For adhesion tests, the polymers were dissolved at 0.15 g polymer mL^{-1} methanol, often using a sonicator. At high methyl methacrylate percentages (≈41–65 mol%), the solvent used was 8% volume trichloroethylene in methanol due to solubility issues. Polymer solutions (45 µL) were deposited onto the adherends and then overlapped (1.2 × 1.2 cm) to form single lap-joint configurations. The use of a homebuilt jig ensured consistency of the overlap area and alignment of the joints. Two Teflon blocks on either side of the joint were pushed together to precisely align the bonded substrates. For butt tensile specimens, after applying the polymer solutions (45 µL), 60 µm soda lime borosilicate glass beads from McMaster Carr were added before overlapping in order to control the thickness. A separate jig was used to ensure proper alignment of the butt tensile substrates once overlapped. Specimens were allowed to cure for 1 h at room temperature followed by 22 h at 70 °C and then 1 h at room temperature before testing. No cross-linker was added to the polymer, allowing the adhesive to cure into a transparent film with a slight brown tint. Single lap joint specimens were tested following a modified version of the ASTM D1002 standard (Figure S2, Supporting Information).[54,55] Butt tensile specimens were measured by the ASTM D2095 standard method.[56] A modified version of ASTM D2095 was followed when testing the 40A and 80A poly(urethane) substrates. Vacuum hose clamps were used to secure these substrates in place (Figure S4, Supporting Information). All trials were tested on an Instron 5544 Materials Testing System with a 2000 N load cell. A crosshead speed of 2 mm min^{-1} was used. For each study, a data set of at least five samples was collected. Averages and errors at 95% confidence intervals are reported. In all cases, tested bonds showed evidence of cohesive failure, with roughly even amounts of polymer left on each substrate after bond breakage.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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