ADVANCED FUNCTIONAL MATERIALS
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Enhancing the Adhesion of a Biomimetic Polymer Yields Performance Rivaling Commercial Glues

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Marine mussels clinging to rocks inspire the development of novel materials. Characterization of mussel adhesive plaques describes a matrix of proteins containing 3,4-dihydroxyphenylalanine (DOPA), which provides cross-linking chemistry that allows mussels to attach firmly. Several synthetic polymer systems have been developed based on this DOPA chemistry. High strength bonding has been achieved with poly[(3,4-dihydroxystyrene)-*co*-styrene], a simplified mimic of mussel proteins in which 3,4-dihydroxystyrene provides the cross-linking and adhesion of DOPA. The poly(styrene) host polymer stands in for a protein backbone. Prior efforts showed that a monomer ratio of 1:2 3,4-dihydroxystyrene:styrene within the statistical copolymer poly[(3,4-dihydroxystyrene)-*co*-styrene] yields the highest adhesion. To enhance adhesive performance of this biomimetic polymer, a systematic study is carried out in which a range of cross-linking agents, cure times, cure temperatures, polymer concentrations, and fillers are examined. Lap shear adhesion testing revealed substantial increases in bond strength from each study. Consensus conditions are then determined and bonding performance is assessed on several substrates. Adhesion of this system turns out to be one of the strongest of all biomimetic polymers. These studies show that DOPA chemistry may be able to stand alongside of cyanoacrylate (e.g., Super Glue) and epoxy when it comes to high strength bonding.

1. Introduction

Inspiration from nature has brought about a myriad of material designs and concepts. Marine mussels, for instance, possess an impressive ability to bind to surfaces. The adhesive plaques of these organisms are built from proteins that contain 3,4-dihydroxyphenylalanine (DOPA), an amino acid with a pendant catechol functionality.[1] Cross-linking of such proteins enables shellfish attachment to both inorganic and organic surfaces, even when wet.[1a-c,2] Applying what we are learning from this intriguing animal to allow the development of new adhesive polymers is yielding compelling bonding properties. Development of new engineered adhesives should allow for lighter weight automobiles and aircraft from reduced use of metal joinery. Bonding composite substrates and biomedical efforts will also benefit from the availability of new adhesive materials.

Harvesting mussel glue directly from the animals is not practical, owing to the minimal quantity available as well as protein insolubility resulting from cross-linking reactions. Furthermore, the mussel's glue has not evolved specifically for our purposes (e.g., metal-to-metal bonding) and thus requires tailoring. These limitations necessitate turning to synthetic systems. In the last few years there has been an exciting expansion in the number of mussel mimicking adhesive polymers.[3] Amongst the most popular approaches to using mussel chemistry are constructing polypeptides,[4] coacervate "suspensions",[5] and synthetic polymers.[3] Both homopolymers and copolymers have been made to incorporate some form of the amino acid moiety that provides stickiness to mussel plaques, whether it is DOPA, dopamine, or a pendant catechol.[3] Poly(dopamine)[6] and poly(vinylcatechol)[7] homopolymers have been reported. Most often there is at least one other monomer contained within the backbone. Copolymerization with acrylate derivatives,[8] poly(ethylene glycol) (PEG),[9] and styrene[10] are common. Other segments that have been investigated include those with electrostatic charge,[11] chitosan,[12] and urethane.[13] These non-catechol monomers can be incorporated to provide specific functionalities, tailor the general materials properties, or to "dilute" the cross-linking chemistry and prevent intractability. Use of these polymers is becoming more widespread and has expanded to include formation of hydrogels,[14] antifouling coatings,[15] self-healing materials,[16] modified nanoparticles,[17] and biosensors.[18]

Bulk, macroscopic adhesion requires both adhesive bonding to surfaces and cohesive bonding throughout the rest of the material. Some of the reported mussel mimicking polymers have been examined with regard to variation of adhesive versus cohesive bonding in attempts to provide glues with substantial bulk strength.[4c,19] Different polymer compositions (e.g., catechol content, backbone type, molecular weight, etc.) and

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DOI: 10.1002/adfm.201303536

testing conditions (e.g., tensile vs. shear, substrates, loading rate, varied cure time, etc.) make it difficult to draw direct comparisons between reported systems. Generally speaking, strengths measured in shear are lower than those in tensile, roughly by half.[20] Nonetheless, we will try to provide an overall idea of where the field stands and collect our data using the most general conditions possible. An overview of bonding performance for mussel mimicking polymers is provided for context.

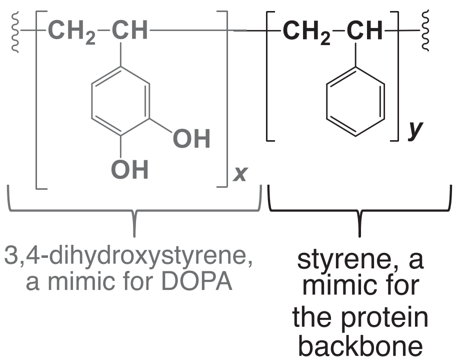
Testing in wet conditions often leads to lower adhesion, but is necessary when aspiring to biomedical relevance. The shear strength of poly(ethylene glycol)-based hydrogels containing DOPA can be ~0.03 MPa when bonding wet pig skin.[21] Adhesive proteins extracted from mussels have yielded strengths up to ~1 MPa for gluing pig skin in end-to-end tensile joints.[22] When applied to strips of a collagen membrane and overlapped in shear, mussel protein extracts have shown adhesion strengths of ~0.2 MPa, alone, and ~0.3 MPa with the addition of metal ions such as V^{5+} after only 1 h of cure time.[23] Chitosan and dopamine copolymers tested on glass slides gave shear strengths over ~0.4 MPa in both air and underwater.[12] The shear bonding of coacervates based on the sandcastle worm's adhesive reached ~1 MPa on aluminum when submerged underwater.[5b]

Bond strengths of dry substrates are almost always higher than the wet counterpart. A DOPA-containing recombinant fusion protein tested in shear on aluminum adhered at ~0.9 MPa, alone and ~1.1 MPa with the addition of sodium periodate for an oxidant.[4g] Recent work has shown increases in shear strength of this hybrid protein up to ~2.5 MPa with periodate.[24] Photopolymerization of ethylene glycol acrylate methacrylate-dopamine with a poly(vinyl alcohol) derivative for a cross-linker has given adhesion strengths approaching ~0.4 MPa on glass.[19b] A three-armed poly(ethylene glycol) backbone with dopamine end groups achieved shear strengths of ~2 MPa on glass slides when the cure time was 48 h.[25] Polypeptides containing 19 mole% DOPA and 81 mole% lysine bond well in shear with multiple plastics (<1 MPa), glass (~2.5 MPa), steel (~3 MPa), and aluminum (~4 MPa).[4c] An increase to ~6 MPa was seen on aluminum with the addition of a peroxide cross-linker.[4b] A similar polypeptide yielded a shear strength of ~5.5 MPa on steel with a ferric citrate curing agent.[4f] Using this cross-linker, shear strengths of ~0.3 MPa on bone and ~0.2 MPa on skin were also obtained.[4f] The shear bonding of dopamine-containing poly(urethane) on iron reached ~5 MPa.[13a] Polymer mimics containing only styrene and 3,4-dihydroxystyrene, when cross-linked with tetrabutylammonium periodate, achieved a shear strength of ~7 MPa on aluminum.[10a] Adaptions of this system to incorporate monomers with pendant oligo(ethylene glycol)[9c] or an electrostatic charge[11] resulted in bonding of ~2 MPa and ~3 MPa, respectively.[9c,11] The shear strength of a copolymer containing 3,4-dihydroxycinnamic acid and 4-hydroxycinnamic acid was tested on steel (~16 MPa), glass (~26 MPa), and carbon (~30 MPa).[26] When titanium rods were coated with poly(dopamine methacrylamide-*co*-methyl methacrylate) and then a poly(methyl methacrylate) bone cement was added, a tensile strength of ~16 MPa was found.[8b]

Figure 1. A pot full of mussels being held up by aluminum substrates bonded together in shear with poly[(3,4-dihydroxystyrene)-*co*-styrene].

We can designate high strength adhesion to be ~1 MPa and above. Higher bonding, still, is often desired for many applications. Although designing adhesives with mussel chemistry is progressing rapidly and showing great promise, few systems can bond in the vicinity of ~10 MPa. A systematic study of several factors influencing adhesion such as cross-linker choice, addition of fillers, and varied cure conditions should provide enhanced bonding. The copolymer poly[(3,4-dihydroxystyrene)-*co*-styrene] is one of the strongest bonding mussel mimetic polymers to date and well suited to being the subject of such an examination (**Figure 1**).

In order to gain insight on the potential of a polymeric system to bond strongly, it is necessary to examine the most significant parameters critical to affording adhesion. For poly[(3,4-dihydroxystyrene)-*co*-styrene], the styrene monomer offers several benefits including being low cost, providing no interfering adhesion, and being structurally as similar as possible to 3,4-dihydroxystyrene (**Scheme 1**). Studies performed previously by our laboratory provided useful data on the effect of polymer catechol content upon adhesion, with ~33 mole% 3,4-dihydroxystyrene and ~67 mole% styrene being optimal.[10a] Recent efforts have also provided data showing that this polymer adheres most strongly with a number average molecular weight (M_n) ≈ 84 000 g mol^{-1} and weight average



Scheme 1. Poly[(3,4-dihydroxystyrene)-*co*-styrene], a simplified polymer mimicking the adhesive proteins of marine mussels.

molecular weight (M_w) ≈ 105 000 g mol^{-1} when alone and M_n ≈ 37 000–50 000 g mol^{-1} and M_w ≈ 50 000–65 000 g mol^{-1} when cross-linked with tetrabutylammonium periodate.[27] With this information in hand, we can now examine conditions independent of the polymer, itself, in order to find the parameters bringing about maximum adhesion. Using a systematic structure-property approach, we studied both the polymer alone and the polymer after cross-linking. Conditions that were manipulated included a range of polymer concentrations, different oxidative cross-linkers, varied cure time, altered cure temperature, and the addition of fillers. Each of these studies was carried out independently of the others, often starting with conditions from prior experiments.[10a,10b,27] At the end, the best adhesion from each of the separate studies was combined to provide consensus conditions. This analysis has yielded an adhesive material with quite high strength bonding performance, comparable to the best commercial glues.

2. Results and Discussion

All individual condition tests leading up to the final consensus study included controls that have been examined previously.[10a,10b] Aluminum adherends provided the default substrate. Conditions that yielded appreciable strength in the past provided a logical starting point.[10a] Specifically, the polymer concentration was maintained at 0.3 g/mL 1:1 acetone:dichloromethane unless otherwise noted. Excluding the time and temperature studies presented below, samples were cured for 1 hour at room temperature, 22 h at 55 °C, and then followed with 1 hour at room temperature for cooling.[10a] Although the order of studies was not necessarily important given that all conditions were varied independently of one another, cross-linking agents were explored first, followed by cure time, cure temperature, polymer concentration, filler addition, and then ending with the consensus conditions. In general, each individual study was completed with the same batch of polymer. For each synthesis, a catechol percentage of ~33 mole% was targeted.

2.1. Cross-Linkers

The adhesive produced by mussels contains high concentrations of metals (Fe, Zn, Cu, Mn) relative to seawater.[1c,28] Cross-linking mechanisms used by these organisms may include metal coordination, redox chemistry, enzymatic reactions, and hydrogen bonding.[1,2,28a,29] Our laboratory has examined the effect of several cross-linking agents upon the curing of extracted mussel adhesive protein.[28,30] Information from these studies can now be applied to the poly[(3,4-dihydroxystyrene)-*co*-styrene] system.[10b]

Nine cross-linking agents were explored, including both metallic and nonmetallic oxidants. The oxidizing metal ions were tetrabutylammonium permanganate ($[(C_4H_9)_4N]Mn^{VII}O_4$), tetrabutylammonium dichromate ($[(C_4H_9)_4N]_2Cr^{VI}{}_2O_7]$), iron(III) acetonylacetonate ($Fe^{III}(acac)_3$), iron(III) nitrate ($Fe^{III}(NO_3)_3$), and potassium ferrate ($K_2Fe^{VI}O_4$). The nonmetallic oxidants tested were tetrabutylammonium periodate ($[(C_4H_9)_4N]IO_4$), di-*tert*-butyl peroxide ((t-$C_4H_9O)_2$ or (t-BuO$)_2$), cumene hydroperoxide ($C_6H_5C(CH_3)_2OOH$ or cumeneOOH), and 2-butanone peroxide (($H_3CCH_2COCH_2O)_2$ or 2-butanoneOOH). Previously we saw changes to cross-linking brought about by altering the percentage of 3,4-dihydroxystyrene in the polymer and keeping the tetrabutylammonium periodate cross-linker constant with regard to periodate:catechol ratio.[10a] Here we are keeping the 3,4-dihydroxystyrene content and cross-linker:catechol ratio constant and only changing the type of cross-linker.

The 1 to 3 ratio of cross-linker to 3,4-dihydroxystyrene was chosen to mimic the iron to DOPA ratio of $Fe(DOPA)_3$ proposed to be contained with mussel adhesive.[1b,29] Upon addition of cross-linkers to the polymer solutions color changes were observed, making it apparent that oxidation was occurring. Most cross-linkers caused an immediate change to a darker color. The peroxides took an extended time (>20 seconds) to turn such colors. Although not noticeable prior to overlapping the substrates for bonding, visual observation after testing sometimes revealed that a polymer was over or under cross-linked (Figure S1). Over cross-linked polymers appeared to be in dark black sheets, often exhibiting adhesive failure (i.e., polymer debonded from a substrate). Those polymers that were under cross-linked often behaved similarly to the polymer alone samples, showing a lack of color and typically displaying cohesive failure (i.e, even amount of polymer on each substrate after testing). In order to obtain the appropriate balance between surface adhesive and bulk cohesive forces, the ratio of cross-linker:3,4-dihydroxystyrene needed to be altered for cumene hydroperoxide (1:1) and iron(III) acetonylacetonate (1:100) according to visual estimates and adhesion testing (data not shown). Due to the insoluble nature of the polymer after cross-linking, quantitative evaluation of the cross-linking density could not be assessed when attempting extractions, ^1H NMR spectroscopy, or mass spectrometry. The 1:3 ratio was maintained with the other reagents at this stage.

Of the nine cross-linking agents tried, there was quite a large span in adhesion, ranging from under 1 MPa to over 5 MPa. **Figure 2**A shows that tetrabutylammonium periodate provided the highest adhesion with the lowest error. All three peroxides and potassium ferrate also showed improvement compared to the polymer alone. The addition of tetrabutylammonium dichromate, tetrabutylammonium permanganate, iron acetonylacetonate, and iron nitrate created strengths below that of polymer alone. It appears that with the highly oxidative

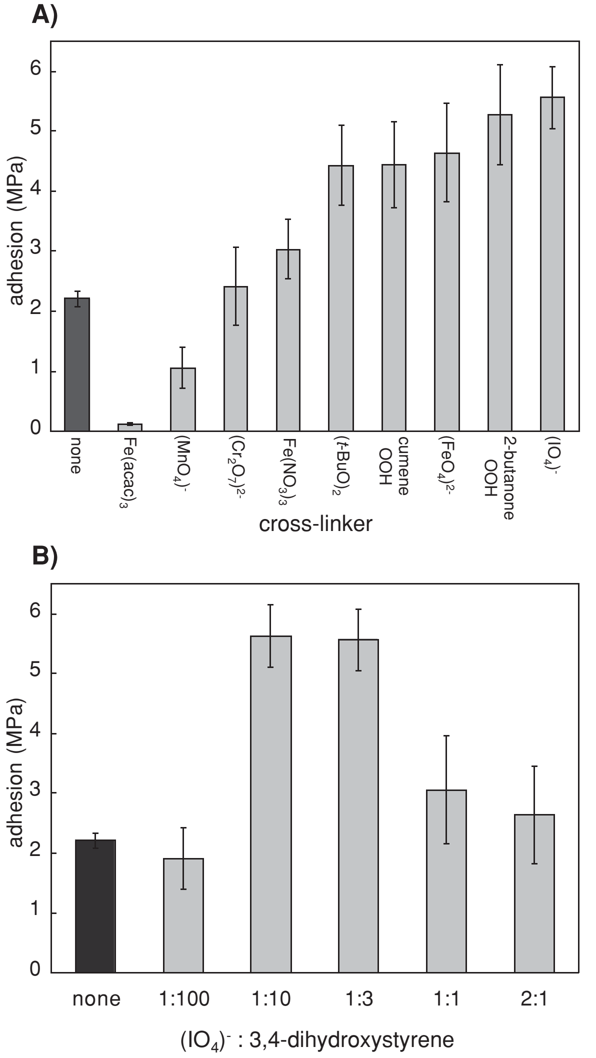


Figure 2. A) The effect of several cross-linking agents upon the lap shear adhesion of poly[(3,4-dihydroxystyrene)-*co*-styrene] on aluminum. B) The effect of different ratios of tetrabutylammonium periodate ([N(C$_4$H$_9$)$_4$](IO$_4$)) to 3,4-dihydroxystyrene upon lap shear adhesion on aluminum.

cross-linkers an increase in adhesion can be obtained. Changes in oxidation potential and the presence or absence of metal ions for chelation influence the extent and type of cross-linking chemistry that will result.[28,30] Perhaps more closely related to this current study is the fact that each reagent will cross-link the polymer to a differing degree. In terms of the optimal balance of cohesion:adhesion for the highest adhesive bonding, the optimal ratio of catechol:cross-linker will change with each reagent. Due to the demonstrated high adhesion and also the common use for cross-linking DOPA,[9a,31] tetrabutylammonium periodate was carried forth to subsequent experiments.

Next, the ratio of tetrabutylammonium periodate to 3,4-dihydroxystyrene was altered. Figure 2B shows that adhesion was often higher than the polymer alone. Both 1:10 and 1:3 tetrabutylammonium periodate:3,4-dihydroxystyrene yielded capable bonding. In order to provide some consistency with prior studies, the 1:3 ratio was used thereafter.

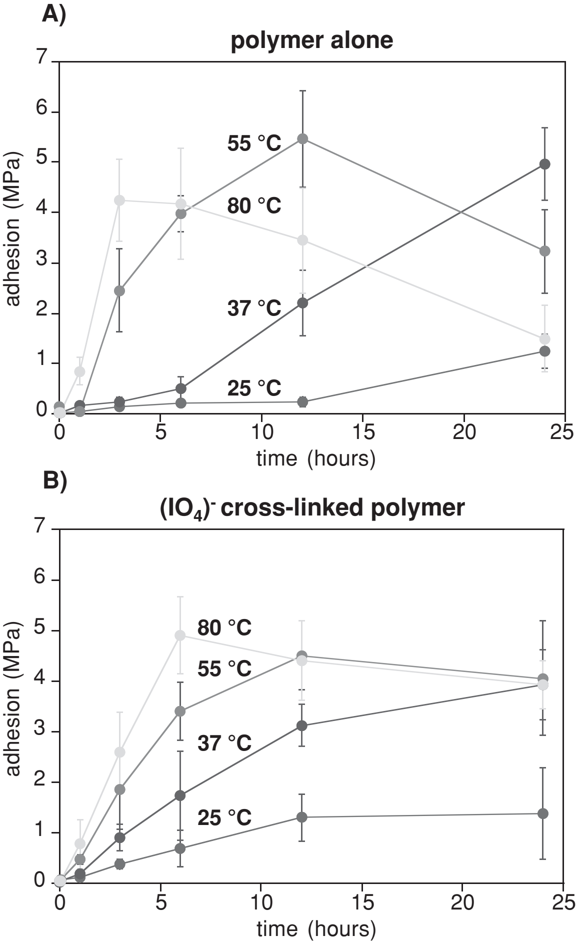


Figure 3. The effect of cure time and temperature upon lap shear adhesion of A) poly[(3,4-dihydroxystyrene)-*co*-styrene] alone and B) poly[(3,4-dihydroxystyrene)-*co*-styrene] cross-linked with [N(C$_4$H$_9$)$_4$](IO$_4$) on aluminum substrates.

2.2. Cure Time and Temperature

Short (1 minute, 5 minute, 1 hour) and long (3 hours, 6 hours, 12 hours, 24 hours) cure times were investigated, each at four different temperatures, including room (25 °C), body (37 °C), what was used previously (55 °C),[10a,10b,27] and a higher temperature (80 °C). For these studies there was no cure period at room temperature; samples were immediately placed in the oven after overlapping (~20 seconds) and once the cure time was completed, samples were tested directly (~60 seconds) after removal from the oven. For both the polymer alone and the cross-linked systems there was an evident cure time and temperature combination that yielded a considerable increase in strength. Plots for the polymer alone and when cross-linked are both provided in **Figure 3**. Most likely, optimal adhesion cannot be obtained at shorter times due to solvent persisting (boiling point of dichloromethane = 40 °C, acetone = 56 °C). Bulk strength was less than 1 MPa for all of the 1 minute, 5 minutes, and 1 hour time points. Possibly acting like a plasticizer, this remaining solvent might cause the polymer chains to be mobile, allowing them to slip past one another easily.[32]

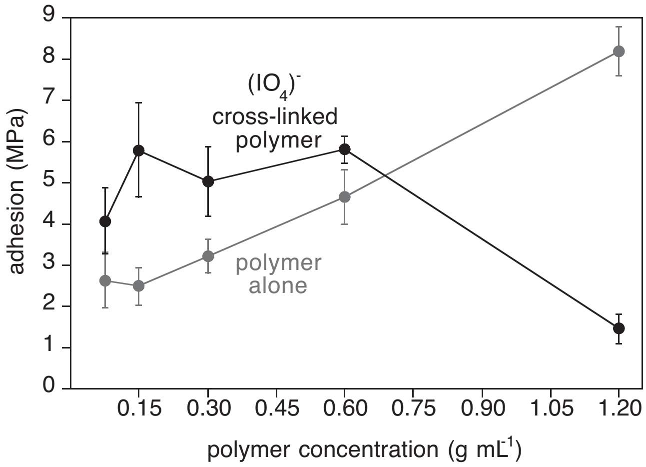


Figure 4. The effect of polymer solution concentration upon lap shear adhesion of aluminum substrates. Poly[(3,4-dihydroxystyrene)-*co*-styrene] alone is depicted in red and this same polymer cross-linked with $[N(C_4H_9)_4](IO_4)$ is shown in black.

After being pulled apart, the samples were often wet (1 minute) or tacky (1 hour).

Appreciable strength was obtained with elevated temperatures, extended times, or both. For poly[(3,4-dihydroxystyrene)-*co*-styrene] cross-linked with tetrabutylammonium periodate, there is a trend of decreased cure time with increasing temperature. As the boiling point of the solvent system is approached, solvent is removed, causing a decrease in ductility and, consequently, a rise in bond strength.[32] Unlike the shorter time points, an extended cure resulted in a sudden, sharp fracture, indicative of brittle failure (Figure S2). Observation of the cross-linked polymer post curing revealed a dark brown coating that could only be removed with excess scraping, followed by base and acid baths. Figure 3 shows that the optimal cure conditions are 6 hours at 80 °C when tetrabutylammonium periodate is present, giving adhesion of ~5 MPa.

Without the addition of a cross-linker, we observed the highest adhesion at intermediate temperatures, perhaps allowing for a balance between strength and ductility.[32] At 55 °C and 37 °C, longer cure times (12 hours and 24 hours, respectively) brought about an increase in adhesion. Further increasing the temperature to 80 °C resulted in an adhesion decrease, beyond a 3 hour cure. The glass transition temperature (T_g) for this polymer containing ~30 mole% 3,4-dihydroxystyrene is 89 °C. At 80 °C, approaching the T_g may mean that the polymer cannot sustain high loads due to chain mobility, resulting in a significant loss of adhesion.[33] When observing the samples post testing, a conspicuous color change in the polymer was not noticed, leading us to believe that oxidation is not occurring with the polymer alone. Unlike the cross-linked samples, after fracture, flakes of polymer could be easily brushed off or removed completely by soaking in acetone. Cohesive failure was typical for the polymer alone trials. Also noticed were small voids in the cured glue possibly due to trapped air bubbles. Such discontinuities may contribute to the initiation of catastrophic crack propagation, thereby weakening the material.[34]

2.3. Polymer Concentration

Controlling viscosity is important for achieving appreciable bond strength. The viscosity of our polymer solutions varied from a water like-consistency at 0.075 g mL^{-1} to a paste-like consistency at 1.2 g mL^{-1}. The maximum solubility of 1.2 g mL^{-1} could only be achieved when the solvent was changed to acetonitrile.

Figure 4 shows adhesion as a function of initial solution concentration. Bonding of poly[(3,4-dihydroxystyrene)-*co*-styrene], alone, maximized at a concentration of 1.2 g mL^{-1}. At this highest concentration, the overlap area between substrates contains more polymer than experiments with lower concentration, given that the volume of applied polymer solution was held constant. Cross-linking poly[(3,4-dihydroxystyrene)-*co*-styrene] changed the dependence of adhesion upon concentration. Maximum bonding was obtained with less viscous solutions (0.15–0.6 g mL^{-1}) than the polymer alone (1.2 g mL^{-1}), seen in Figure 4. After adhesion testing, we found that some areas of the sample appeared to be over cross-linked whereas others were under cross-linked, noted by darker coloring when the polymer became overly cross-linked. Perhaps these solutions were too viscous to allow sufficient mixing of the tetrabutylammonium periodate and polymer, despite efforts to ensure proper reactivity.

2.4. Fillers

Composites are becoming more prominent in the polymer field.[35] With these systems, mechanical performance benefits can be gained by combining a polymeric matrix (i.e., low density) with a reinforcing material (i.e., high strength or stiffness). Fillers can also decrease costs significantly.[36] With filled polymer systems, matrix-filler interactions (i.e., interfacial adhesion), particle characteristics (i.e., size, shape, surface chemistry), and weight fractions all need to be considered.[37] Although fillers can enhance the performance of a glue, on balance, addition of fillers could also become detrimental. For example, an inorganic particle within a polymer matrix might inhibit crack growth or it might just as easily concentrate stress.

Three of the most common fillers in adhesive and sealants systems are calcium carbonate, glass fibers, and cellulose fibers, hence the examination here.[36] Increases in adhesion strength have been seen with the addition of both micrometer and nanometer sized $CaCO_3$ particles therefore both sizes were studied.[38] Adhesion gains have also been seen with systems that incorporate short fibers of submillimeter length, consequently this size was chosen for both cellulose and glass.[35b,39] All fillers were dispersed randomly into the polymer solutions by vortexing.

In order to get the most effective transfer of strength from a filler to the polymer matrix we needed to determine the appropriate weight fraction of filler versus polymer. Composites typically have from 10–50% (w/v) filler added.[36,40] For the 70 nm and 3.5 µm $CaCO_3$ particles, we investigated a range of 10–50% (w/w). The ranges were limited to 2.5–20% (w/w) for glass fibers and 2.5–30% (w/w) for cellulose fibers due to an inability to completely disperse the fillers uniformly at higher loadings.

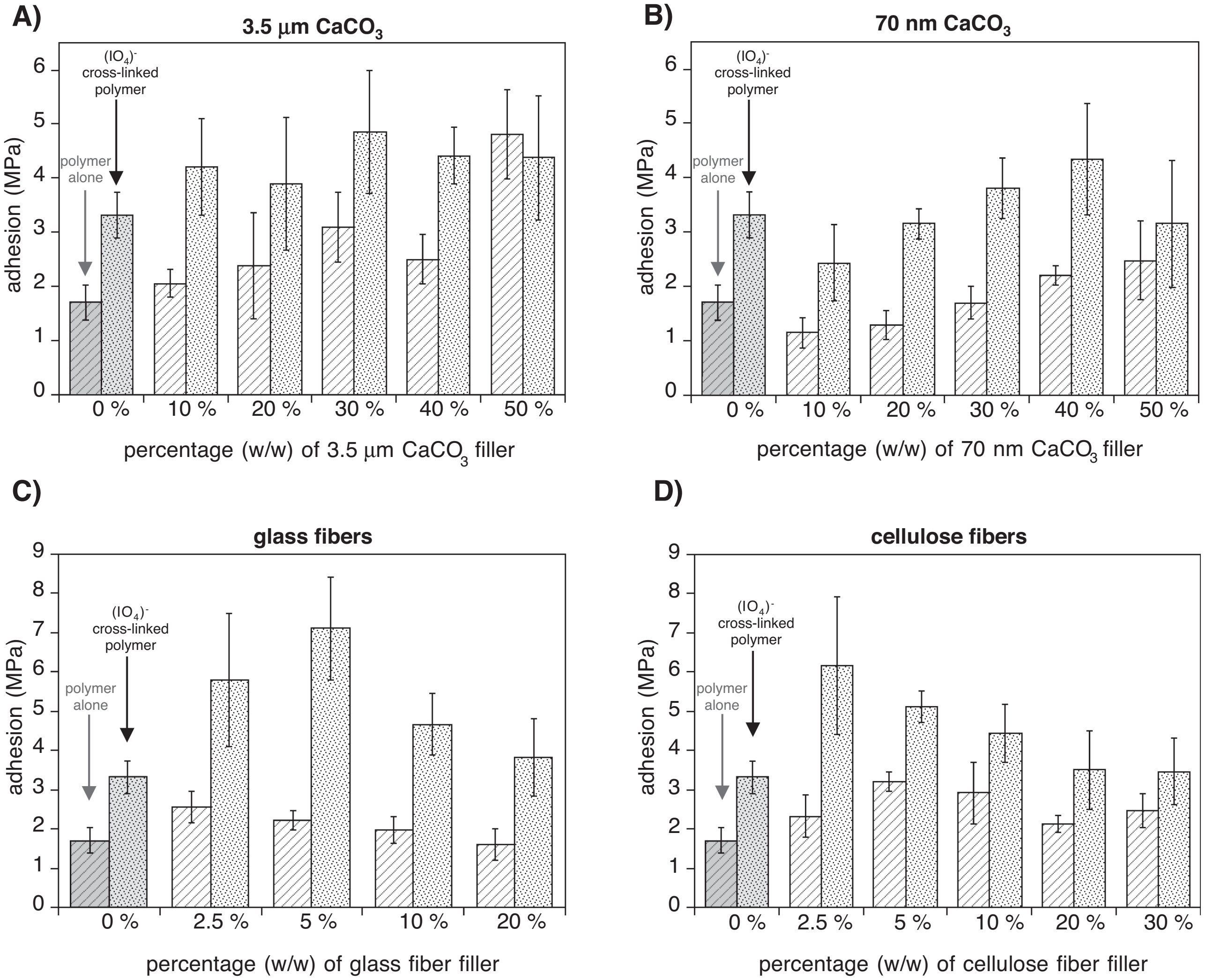


Figure 5. The effect upon adhesion of added A) 3.5 µm $CaCO_3$, B) 70 nm $CaCO_3$, C) glass fibers, and D) cellulose fibers for poly[(3,4-dihydroxystyrene)-*co*-styrene] both alone (red) and cross-linked with $[N(C_4H_9)_4](IO_4)$ (black).

Figure 5 shows the influence upon adhesion of different fillers at varied loadings for poly[(3,4-dihydroxystyrene)-*co*-styrene]. Data from both the polymer alone (red) and the cross-linked polymer (black) are presented in the panel. The poly[(3,4-dihydroxystyrene)-*co*-styrene], alone, benefited most from addition of the 3.5 µm $CaCO_3$ filler (Figure 5A). Adhesion more than doubled from ~1.7 MPa (unfilled) to ~4.8 MPa (50% w/w). Higher particle loadings can enhance viscosity.[38a] Our concentration study (Figure 4) showed that increases in viscosity may give rise to increases in adhesion. Beyond viscosity effects, the incorporation of $CaCO_3$ has been shown to decrease the surface tension of an adhesive, bringing about improved wetting of the substrate.[38a] In general, increased adhesion strengths can be obtained with smaller particles due to higher surface area. We did not observe such an effect here with nanometer versus micrometer sized $CaCO_3$ particles (Figure 5A,B).[35a] Although surface modifications can improve adhesion and reduce agglomeration between inorganic fillers, no major effect was seen here. Perhaps the stearic acid coating on the 70 nm $CaCO_3$ filler interfered with catechol binding to the particles.[41]

When cross-linked, the polymer gained the most strength from glass and cellulose fibers. Figure 5 shows a substantial increase from ~3.3 MPa for unfilled, cross-linked polymer up to ~7.1 MPa with glass fibers at 5% (w/w) and ~6.2 MPa with cellulose fibers at 2.5% (w/w). Glass fiber has a higher tensile strength compared to cellulose, possibly explaining the difference in adhesion noted here.[42] At lower weight fractions there could be improved interfacial contact between the filler and the polymer matrix.[35a] Cellulose is also known to aggregate easily due to being hydrophilic, perhaps explaining why this filler exhibits higher adhesion at lower weight fractions.[43]

2.5. Consensus Conditions

After the individual condition studies were completed, we combined each of the optimized parameters both for the polymer

Table 1. Adhesion performance, in MPa, on several substrates for commercial glues and poly[(3,4-dihydroxystyrene)-*co*-styrene].

	consensus conditions for polymer alone	adjusted conditions for maximum adhesion
catechol percentage	~33 mole%	~29 mole%
M_n	~84 000 g mol^{-1}	~61 000 g mol^{-1}
M_w	~105 000 g mol^{-1}	~92 000 g mol^{-1}
cure time	12 hours	24 hours
cure temperature	55 °C	55 °C
polymer concentration	1.2 g mL^{-1}	1.2 g mL^{-1}
filler	50% (w/w) 3.5 µm $CaCO_3$	10% (w/w) 3.5 µm $CaCO_3$
solvent	acetone/dichloromethane or acetonitrile	acetonitrile

alone and when cross-linked. Due to the complexity of incorporating so many tests into one set of conditions, minor adjustments were necessary, provided in **Table 1**. In the end, a cross-linker was not included when achieving the highest strength from poly[(3,4-dihydroxystyrene)-*co*-styrene]. For poly[(3,4-dihydroxystyrene)-*co*-styrene], alone, the concentration study (Figure 4) showed clearly that a polymer concentration of 1.2 g mL^{-1} in acetonitrile worked best. With the acetonitrile needed to achieve this high concentration and the relatively high solvent boiling point (81 °C), an extended cure time was necessary. A heating cycle of 30 minutes at room temperature followed by 24 hours at 55 °C and then 30 minutes at room temperature prior to testing provided bonding at ~8.2 MPa. This higher polymer concentration also affected the filler loading. When the polymer was dissolved at 0.3 g mL^{-1}, a much higher content of $CaCO_3$ gave drastically improved adhesion strengths (Figure 5). At 1.2 g mL^{-1}, this same loading of $CaCO_3$ made the polymer solution too viscous and did not adequately cover the bonding area. Although previous studies have shown maximum adhesion at higher molecular weights ($M_n \approx 83\ 000$ g mol^{-1}, $M_w \approx 105\ 000$ g mol^{-1}),[27] this result changed with increased polymer concentration and the addition of $CaCO_3$ filler. Overall, the best bonding was achieved with an uncross-linked polymer ($M_n \approx 60\ 000$ g mol^{-1}, $M_w \approx 90\ 000$ g mol^{-1}) at 1.2 g mL^{-1} and loaded with 10% (w/w) of 3.5 µm sized calcium carbonate (Table 1). After applying the adjusted polymer formulation to aluminum adherends, the samples were cured at room temperature for 30 minutes, followed by 24 hours at 55 °C, and then 30 minutes at room temperature (Figure S3). A very high strength of ~11 MPa was achieved. Force-versus-extension curves showing such adhesive bonding are provided in Figure S4. Applying these consensus parameters more than tripled the adhesion that had been seen previously for this polymer without a cross-linker.[10a]

2.6. Different Substrates and Comparisons to Commercial Glues

Table 2. Comparison of consensus conditions determined from individual studies and the final conditions after adjustments to provide maximum bonding for poly[(3,4-dihydroxystyrene)-*co*-styrene].

	aluminum	sanded steel	red oak	Teflon (PTFE)
poly(vinyl acetate) (Elmer's Glue All)	3.8 ± 0.6	7 ± 1	11 ± 2	0.48 ± 0.07
ethylcyanoacrylate (Loctite Super Glue)	5.0 ± 0.7	7 ± 1	9 ± 2	0.7 ± 0.2
epoxy (Loctite Quick-Set)	18 ± 2	18 ± 2	15 ± 2	1.0 ± 0.1
biomimetic polymer	11.0 ± 0.5	10 ± 1	6.0 ± 0.5	0.23 ± 0.08

With the adjusted and optimized conditions of Table 1, bonding performance of poly[(3,4-dihydroxystyrene)-*co*-styrene] was evaluated on a small collection of typical substrates. Surface energies ranged from low (PTFE) to high (metals). These results will help assess the practicality of using this biomimetic polymer for future bonding needs. Commercial glues were also tested on these same substrates under identical cure and quantity conditions, thereby providing benchmarks of performance. **Table 2** shows that the biomimetic adhesive bonds the strongest to high energy surfaces. We are excited to report that, when compared to commercial adhesives on aluminum, the biomimetic polymer achieved higher performance than Loctite Super Glue and Elmer's Glue All. Unlike these well known products, poly[(3,4-dihydroxystyrene)-*co*-styrene] has not yet benefitted from decades of performance optimization. Classically, epoxies are considered to be the strongest class of adhesives.[44] On steel, bonding of poly[(3,4-dihydroxystyrene)-*co*-styrene] is significant but not as high as with epoxy. With red oak, adhesion is appreciable. We did find that the high polymer concentration and solution viscosity appear to keep the adhesive from penetrating into the wood pores and bonding more strongly. In the case of each commercial glue, the wood broke apart to some degree when tested. Previously, our polymer used with different conditions such as a lower polymer concentration provided bonding of oak at ~10 MPa, to the point of substrate failure.[10a] Teflon-to-Teflon (i.e., PTFE-to-PTFE) adhesion was weakest for all the glues.

3. Conclusion

By taking a systematic approach to adhesive design, we identified cross-linkers, cure times, cure temperatures, concentrations, and fillers to bring about the maximum performance of a biomimetic polymer system. Identifying such parameters yielded adhesion strengths up to ~11 MPa for poly[(3,4-dihydroxystyrene)-*co*-styrene]. This bonding performance is some of the highest seen for any biomimetic polymer and is also able to rival that of established commercial products. For decades, high strength adhesive bonding has been limited to only a few classes of polymer chemistries. Data presented here show that biomimetic design principles may be able to provide the next generation of high performance adhesive materials.

4. Experimental Section

Materials: Synthesis of tetrabutylammonium periodate followed a published procedure. Characterization was accomplished with ultraviolet-visible absorption spectroscopy, ^{1}H NMR spectroscopy and melting point determinations.[45] Similarly, tetrabutylammonium permanganate was made according to a literature method and confirmed by ultraviolet-visible absorption spectroscopy.[46]

All initial adhesion testing was carried out on aluminum substrates. Adherends (8.89 cm × 1.27 cm × 0.318 cm) were cut from a sheet of aluminum 6061-T6 purchased at Farmer's Copper. Adherends were cleaned following the ASTM D2651–01 standard method.[47] Red oak was purchased at a local hardware store, cut to the appropriate size (8.89 cm × 1.27 cm × 1.27 cm), and used without any surface modification. Roughness of the wood felt similar to oak sanded with 220 grit paper. Steel adherends (8.89 cm × 1.27 cm × 0.318 cm) were sanded with 50 grit sandpaper, washed with soapy water, and rinsed with acetone prior to testing. Poly(tetrafluoroethylene) (PTFE) adherends were purchased from Ridout Plastics (San Diego, CA), cut (8.89 cm × 1.27 cm × 1.27 cm), cleaned with soap and water, soaked in an ethanol bath, rinsed with deionized water, and dried overnight in air.

Two types of calcium carbonate ($CaCO_3$) filler were donated by Specialty Minerals, Inc., a fine ground limestone (VICRON 15–15) with an average particle size of 3.5 µm and a precipitated calcium carbonate surface treated with stearic acid (ULTRA-PFLEX) that had an average particle size of 70 nm. Cellulose fibers with a length of 40 µm (Arbocel BE600–30PU) were donated by J. Rettenmaier USA LP. Milled glass fibers (Part # 29) of 0.16 cm length were purchased from Fibre Glast Developments Corporation. All fillers were added to the polymer by weight before dissolving in solvent. The filler was randomly dispersed in the polymer solution by vortexing.

Polymer Synthesis: A detailed procedure for the synthesis of poly[(3,4-dihydroxystyrene)-*co*-styrene] was described with prior work.[10b] In short, *n*-BuLi was used to initiate the anionic copolymerization of purified styrene and 3,4-dimethoxystyrene. Deprotection of the methoxy groups used BBr_3. The monomer composition of poly[(3,4-dimethoxystyrene)-*co*-styrene] was determined with ^{1}H NMR spectra recorded on a Varian Inova-300 MHz spectrometer. Molecular weights were found by gel permeation chromatography (GPC) using a Polymer Laboratories PL-GPC20 system. A family of polymers was synthesized with catechol percentages all close to the optimal (27–34 mole%) and a tight range of molecular weights ($M_n \approx$ 34 800–75 000 g mol^{-1}, $M_w \approx$ 48 400–96 000 g mol^{-1}) with low polydispersities (PDIs) (1.2–1.5). Most separate studies described below were carried out with a single batch of polymer. For the cross-linker studies, three batches of polymer were required (30% catechol, $M_n \approx$ 40 100 g mol^{-1}, $M_w \approx$ 49 800 g mol^{-1}, PDI = 1.24, 25% catechol, $M_n \approx$ 72 500 g mol^{-1}, $M_w \approx$ 96 800 g mol^{-1}, PDI = 1.32, 30% catechol, $M_n \approx$ 75 000 g mol^{-1}, $M_w \approx$ 84 700 g mol^{-1}, PDI = 1.13). For the following studies, cure time and temperature (30% catechol, $M_n \approx$ 67 600 g mol^{-1}, $M_w \approx$ 85 800 g mol^{-1}, PDI = 1.27), concentration (30% catechol, $M_n \approx$ 75 00 g mol^{-1}, $M_w \approx$ 84 700 g mol^{-1}, PDI = 1.13), fillers (34% catechol, $M_n \approx$ 34 800 g mol^{-1}, $M_w \approx$ 48 400 g mol^{-1}, PDI = 1.39), cross-linked consensus (27% catechol, $M_n \approx$ 37 200 g mol^{-1}, $M_w \approx$ 54 400 g mol^{-1}, PDI = 1.46), and polymer alone consensus (29% catechol, $M_n \approx$ 60 900 g mol^{-1}, $M_w \approx$ 91 900 g mol^{-1}, PDI = 1.51) individual batches were used.

Adhesion Testing: Lap shear testing is one of the most common ways to evaluate adhesion and, consequently, was used here.[36,44] Most often a polymer solution of 0.30 g poly[(3,4-dihydroxystyrene)-*co*-styrene] dissolved in 1.0 mL 1:1 acetone:dichloromethane was employed. The polymer solution (45 µL) was spread onto the adherends using a syringe and then overlapped (1.2 × 1.2 cm) in a single lap-shear configuration. At higher polymer concentrations (1.2 g mL^{-1}), acetonitrile was required for the solvent, along with sonication, to achieve the desired solubility.

Unless noted otherwise, tetrabutylammonium periodate ($[N(C_4H_9)_4](IO_4)$) was the cross-linker of choice. Typically, 0.34 g of ($[N(C_4H_9)_4](IO_4)$) was dissolved into 1.0 mL of 1:1 acetone:dichloromethane. During the polymer concentration studies, the cross-linker concentration reflected that of the polymer solution, always maintaining a 1:3 ratio of cross-linker:3,4-dihydroxystyrene. The cross-linker solution (15 µL) was deposited directly onto the polymer solution on one adherend before overlapping the substrates during lap shear bonding. The other cross-linkers were also dissolved in 1:1 acetone:dichloromethane with the exception of iron nitrate (in acetone), tetrabutylammonium permanganate (in dichloromethane), and potassium ferrate (in methanol). Once overlapped, samples were cured for 1 hour at room temperature, then 22 hours at 55 °C, and lastly cooled for 1 hour at room temperature.

Bulk adhesion was tested in shear with single lap joint aluminum specimens following a modified version of the ASTM D1002 standard.[48] Most trials were tested using an Instron 5544 Materials Testing System with a 2000 N load cell. The commercial adhesives as well as the consensus polymer on red oak and sanded steel were examined on an MTS Insight Electromechanical Testing System with a 10 000 N load cell. A crosshead speed of 2 mm min^{-1} was employed in all cases. For each study, a data set of at least five trials was collected. The consensus and commercial adhesive studies in Table 1 had ten replicates each. Averages and errors at 95% confidence intervals are reported.

Supporting Information

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

Acknowledgements

This work was supported by the Office of Naval Research. We thank Specialty Minerals and J. Rettenmaier USA LP for donating the fillers. Valerie Wiesner, Rodney Trice, and Jeffrey Youngblood aided these studies by providing access to their materials testing system. Allison Mattes helped with polymer synthesis.

Received: October 15, 2013
Revised: December 7, 2013

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