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Journal:	*Soft Matter*
Manuscript ID	SM-ART-10-2020-001944.R1
Article Type:	Paper
Date Submitted by the Author:	03-Dec-2020
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Soft Matter

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Changing Polymer Catechol Content to Generate Adhesives for High versus Low Energy Surfaces†

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Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

Adhesive bonding is commonly used to replace mechanical fasteners in many applications. However, the surface chemistry of different substrates varies, making adhesion to a variety of materials difficult. Many biological adhesives are adept at sticking to multiple surfaces with a range of surface chemistries. Marine mussels utilize a catechol moiety within their adhesive proteins to bring about surface binding as well as cohesive cross-linking. Mimicking this functionality in synthetic polymers has yielded high strength adhesives that can attach to both high and low surface energy materials, although not equally well. Here, the amount of catechol within a copolymer system was varied for potential tailoring to specific surfaces. Structure-function studies revealed differing trends of optimal catechol content for high energy aluminum versus low energy polytetrafluoroethylene (Teflon™) surfaces. Adhesion strengths were optimized with ∼10 mol% catechol for aluminum and ∼41 mol% for Teflon™. Varying the catechol incorporation also resulted in changes to wettability, failure modes, and mechanics on these substrates. When considering performance of the entire bulk material, the different surfaces required an altered adhesive-cohesive balance. Tailoring the composition of polymeric adhesives for different surfaces may aid future manufacturing in cases where joining a variety of materials is required.

1 Introduction

Adhesives are essential to our everyday lives, with new glues sought continually for advancing future technologies. From commercial industries spanning automotive, aerospace, packaging, and construction, to consumer goods like shoes and electronics all are dependent upon increasingly higher performance adhesives.[1–3] Different materials are required for a variety of substrates. For example, bonding metals will usually be accomplished with glues unique from those joining woods or plastics. Some substrates also tend to be easier to bond than others. High surface energy materials, including ceramics and metals, are usually less challenging when it comes to achieving high bond strengths. These surface energies can fall into a range of ∼300 to ∼1,400 mJ/m^2.[3] By contrast, low surface energy plastics including polyethylene, polypropylene, and polytetrafluoroethylene are classically quite difficult to bond. Plastic surface energies can be between ∼20 to ∼50 mJ/m^2.[1,4] Technically speaking, nearly any adhesive can bond almost all substrates. However, obtaining functional bond strengths is a more difficult matter.

There are few adhesives that are equally adept at attaching plastics and metals. Harsh surface treatments are required for many applications when bonding high energy metals to low energy polymer composites, such as the joints in airplanes, cars, or ships.[1–3,5–7] We are interested in developing the highest performance adhesives possible that are tailored specifically for high versus low energy substrates. Biomimetics is a tool that we can use to add adhesion into a base polymer system with desirable mechanical properties. Mimicking biological materials has yielded many new adhesives derived from several synthetic polymer hosts including poly(meth)acrylates,[8–13] polyethylene glycol (PEG),[14–16] polypropylene oxide and polyethylene oxide (PPO-PEO),[17,18] poly(acrylic acid),[19–21] polystyrene,[22,23] polysaccharides,[24,25] or proteins.[26,27]

In a prior study, we altered the mechanical properties of a polymer by changing the modulus in order to incorporate ductility for distributing mechanical stresses throughout joints and contributing to increased performance.[8] This biomimetic system used catechols pendant from a polymethacrylate chain to mimic the amino acid 3,4-dihydroxyphenylalanine (DOPA) found throughout mussel adhesive proteins. The polymethacrylates contained three monomers, shown in Fig. 1. Dopamine methacrylamide (DMA) provided adhesion via catechol chemistry and was held at ∼33 mol% of the total polymer. The modulus was then tuned by altering the ratio of stiff methyl methacrylate (MMA) to the soft-

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† Electronic Supplementary Information (ESI) available: Further discussion of polymer synthesis, characterization data for polymers, statistical analysis, solvent effects on adhesion, analysis of mechanical properties, and failure modes. See DOI: 00.0000/00000000.

ening oligo(ethylene glycol) (OEG) monomers. Overall bonding was appreciable on substrates including aluminum, polymethyl methacrylate, polyvinyl chloride, and polyurethane rubbers of various hardnesses (Shore 40A, 80A, 75D). With aluminum substrates the best adhesive performance was found with a moderate polymer elastic modulus (~0.04 GPa).[8] When the polymer was either stiffer (~0.1, ~1, or ~2 GPa) or more ductile (~0.01 or ~0.0002 GPa) adhesion decreased.[8]

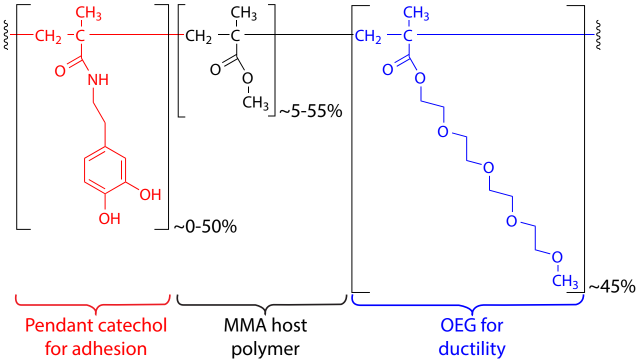

Fig. 1 Poly(catechol-MMA-OEG) terpolymer used for structure-function studies on high energy aluminum and low energy Teflon. The OEG monomer content (blue) was held constant while the adhesive monomer (red) varied in loadings.

Among other things, bulk bonding requires a balance between surface adhesion and cohesion within the entire material.[2,28,29] Varying catechol content in a polymer can allow us to adjust adhesion versus cohesion. Catechol binds to surfaces via hydrogen bonding, chelation of metals, organic radicals, and several additional types of non-covalent interactions.[26,28,30–36] Cohesion is achieved through oxidation and subsequent generation of covalent cross-links in the bulk material,[23,28,37–40] chain entanglements,[23,28,41] as well as several potential non-covalent bonds.[35,36] The substrate can also be varied to determine how surface energies affect the adhesive-cohesive balance. It is possible that bonding to the substrate will be weak regardless of polymer composition, and any attempt to increase surface attachment will merely disrupt the adhesive-cohesive balance to result in decreased performance. With the case at hand, too many catechols could yield a bulk material that is overly cross-linked and of undesirably high cohesion.

Thus, predicting polymer design for a given class of substrates is far from straight forward. There have been relatively few studies in which an effort was made to design adhesive polymers specifically for high performance with low surface energy substrates. Poly(acrylate/epoxy),[42] poly(acrylate/siloxane),[43] and poly(acrylate/urethane)[44,45] have been examined for joining plastics. Polymer compositions were changed in these studies in order to identify where performance was greatest using several low surface energy substrates. Catechol-bonding polymers have been used to form joints between low energy substrates. A polyhydroxyurethane with an optimal incorporation of 3.9% catechol was investigated on a range of surfaces from aluminum to polyethylene.[46] At this time, the high expense of catechol-based starting materials has kept such systems out of the marketplace. If unique performance and differentiation from available systems can be obtained, commercial viability of biomimetic adhesives could arrive. There has not yet been a major effort to design a polymer system specifically for bonding low versus high energy surfaces. How might the polymer differ when considering the best composition in light of the substrate?

Structure-function studies are one of the best ways to assess the relationships between polymer composition and performance with substrates of different surface energies. Mechanical testing of adhesives alone provides limited insights on chemical mechanisms of adhesion. Likewise, chemical changes to molecules can only teach us a subset of needed insights. However, a coupling of mechanical measurements with systematic changes to macromolecules can be one of the most powerful ways to learn about adhesive design. In work described below, we varied the catechol content of a polymer system and examined the effects on bulk adhesion with high surface energy aluminum versus low surface energy polytetrafluoroethylene (PTFE, Teflon™) substrates. In the end, the optimal catechol content differed for the high compared to low energy surfaces. These data can now inform efforts to design adhesives that function well when working with different substrate types.

2 Experimental

2.1 Polymer Synthesis and Characterization

Dopamine methacrylamide (DMA) monomer was synthesized following literature methods[8,13,47] and characterized using ^{1}H NMR spectroscopy. Methyl methacrylate (MMA), poly(ethylene glycol) methyl ether methacrylate (OEG), and DMA monomers were polymerized with recrystallized 2,2-Azobis(2-methylpropionitrile) (AIBN) in *N,N*-dimethylformamide (DMF) to yield a random terpolymer, poly{[dopamine methacrylamide]-*co*-[methyl methacrylate]-*co*-[poly(ethylene glycol) methyl ether methacrylate]}, based on prior methods.[8] The polymers were characterized by ^{1}H NMR spectroscopy to confirm incorporation of monomers, and gel permeation chromatography (GPC) was used to determine molecular weights.

2.1.1 Synthesis of Dopamine Methacrylamide.

To synthesize the DMA monomer, sodium tetraborate decahydrate (20 g) and sodium bicarbonate (8 g) were added to a 1 L Schlenk flask with 100 mL of deionized water. After the slurry was degassed with argon for 30 minutes, dopamine HCl (10 g) was added to the flask. Methacrylic anhydride (9.4 mL) was dissolved in 50 mL of tetrahydrofuran (THF), and the solution was slowly added to the slurry. The pH was adjusted to ~8 with the addition 1 M sodium hydroxide, and the slurry stirred under argon overnight. The white solid was filtered off with vacuum filtration and washed with ethyl acetate. The pH of the filtrate was decreased to 2 using 6 M hydrochloric acid. A separatory funnel was used for extraction with ethyl acetate, yielding a slightly tan solution. The ethyl acetate was dried with magnesium sulfate and filtered into a round-bottom flask. The solution was concentrated to about 50 mL via rotary evaporation, and excess hexane was added to the flask to precipitate out a tan powder. The flask was chilled to 4 °C for 3 hours to allow the DMA to precipitate fully. The supernatant was decanted and the solid was dissolved in 45 °C acetone. Hexane was added again to reprecipitate the solid. The liquid was decanted and solvent was removed by placement under vacuum overnight. The successful synthesis was confirmed by ^{1}H NMR spectroscopy.

2.1.2 Synthesis of Poly(catechol-MMA-OEG).

The MMA and OEG monomers were purchased and purified with alumina columns prior to polymerization. For a typical polymer synthesis, 1.5 g of DMA (6.8 mmol), 0.68 mL of MMA (6.4 mmol), and 1.9 mL of OEG (6.7 mmol) were combined with 32.8 mg AIBN as the initiator and dissolved in 12 mL DMF. The tan colored solution was stirred under argon for 30 minutes before being heated to 70 °C in an oil bath for 2 days. The reaction was quenched by addition of 1 mL of methanol (MeOH). The viscous solution was diluted with dichloromethane (DCM) and then precipitated with cold diethyl ether. Solvent was decanted from the resulting white solid, which was then dried under vacuum before redissolving in DCM and MeOH solvents. The terpolymer was dissolved and precipitated a total of three times to remove unreacted monomer and dried under vacuum. Monomer incorporation and purity of the polymer were determined by ^{1}H NMR spectroscopy by integrating the relative ratio of monomers. Yield of poly{[dopamine methacrylamide]-*co*-[methyl methacrylate]-*co*-[poly(ethylene glycol) methyl ether methacrylate]} was 3.2 g, 15 mmol, 77%. ^{1}H NMR (d-DMSO): δ 0-2.3 ppm (broad, polymer backbone), 3.2 ppm (broad, $-OCH_3$ from poly(ethylene glycol) methyl ether methacrylate, 3.4-3.7 (broad, $-OCH_2CH_2$ from poly(ethylene glycol) methyl ether methacrylate and $-OCH_3$ from methyl methacrylate), 3.8-4.2 ppm ($-OCH_2$ from poly(ethylene glycol) methyl ether methacrylate), 6.2-6.7 ppm (broad, aromatic), 8.5-8.8 ppm (broad, hydroxyl).

2.2 Lap Shear Adhesion Studies

Substrates were prepared following previous methods to test adhesion strengths for each of the polymers on aluminum and commercial polytetrafluoroethylene (PTFE, Teflon™).[22,48,49] Teflon™ is the trademarked name of polytetrafluoroethylene from Chemours. Aluminum was purchased from Farmer's Copper (Texas City, TX) as a 6061-T6 alloy in 3 mm thick sheets. These aluminum sheets were cut with a waterjet to 1.2 cm wide × 8.9 cm long adherends and cleaned using an adaptation of an ASTM standard method (ASTM D2651-01) prior to testing.[50] Teflon sheets were 1.25 cm thick and purchased from ePlastics (Ridout Plastics, San Diego, CA). Teflon substrates were also cut to dimensions of 1.2 cm × 8.9 cm, cleaned with soap and water, and soaked in ethanol before use. The Teflon had a thickness of 1.25 cm so that the material was stiff and did not introduce flexibility, or additional mechanical stresses, to the bonded joints. Polyvinyl chloride (PVC) sheets (0.32 cm thick) were also purchased from ePlastics (San Diego, CA), machined to 1.2 cm x 8.9 cm, and were used for adhesion testing without prior surface modification. Each of the adherends had a hole drilled 2 cm from the end to insert rods through for pulling the bonded joint apart to failure at a rate of 2 mm/min with an Instron 5544 materials testing system equipped with a 2 kN load cell.

To test adhesion, polymers were dissolved in 1:1 DCM:MeOH at 0.1 g/mL. For each joint, 45 μL of the solution was divided and distributed across the overlap area of 1.2 cm × 1.2 cm on both substrates before joining together the two surfaces in a lap shear configuration. This procedure helped to prevent any excess polymer solution leaking down the sides or beyond the ends of adherends, thereby avoiding misleadingly higher adhesion values. The resulting bond line thickness using 45 μL of 0.1 g/mL polymer solution was approximately 0.6 mm for the cured bonded joints. The glued adherends were cured at room temperature for 1 hour, heated at 70 °C for 22 hours, and cooled to room temperature for an hour prior to testing. Bonding strengths reported were calculated from the maximum force at failure (N) divided by the overlap area (m^2) to yield adhesion in MPa. Each data point was an average of at least $n = 10$ samples. Error bars are 90% confidence intervals.

2.2.1 Statistical Analysis.

Adhesion data are represented by the mean ± 90% confidence intervals. For statistics, data were assessed with one-way analysis of variance (ANOVA) followed by Tukey's Honest Significant Difference post hoc test. Normal probability plots were evaluated to verify model assumptions. Statistical analyses were performed using Minitab 16 (State College, PA). A p-value ≤ 0.1 was considered significant.

2.3 Mechanical Properties

Force-versus-extension curves obtained from lap shear adhesion tests were graphed using OriginPro or Kaleidagraph software. Full width at half maximum (FWHM) of the force-vs-extension curves were calculated using OriginPro 2019 (OriginLab Corporation, Northampton, MA). All test samples were analyzed and averaged with error reported as one standard deviation.

2.3.1 Shear Modulus.

Shear modulus (G) of the polymer adhesive samples were calculated from lap shear adhesion measurements following calculations outlined in ASTM D5656-10 standard.[51] Shear stress and shear strain were calculated from measured force vs extension curves for each lap shear measurement. The resulting shear stress-strain curves were used to determine shear modulus. Shear stress (τ) was calculated using the equation:

$$\tau = \frac{F}{A}$$

where the force (F) was the recorded load applied to the adhesive bond (in N) and A was the overlap area to which the force was applied. The overlap area of the bonded joint was measured in mm^2 to give the shear stress in N/mm^2, or MPa. The shear strain (γ) was calculated using the equation:

$$\gamma = \frac{\delta_{\mathrm{a}} - \delta_{\mathrm{m}}}{t}$$

where δ_a is the is the displacement, or the extension of the bonded joint, in mm. The bond line thickness (t) was also recorded in mm. The correction factor δ_m was modified from the ASTM D5656-10 methods because the outlined KGR-type extensometer was not used for these measurements. For calculations here, the correction factor δ_m accounted for excess displacement before force was applied to the bonded joint caused by the gap between the pin and the hole in the substrate after loading the sample for testing with the Instron.

Shear stress-strain curves were plotted after calculating τ and γ for each test sample. Shear modulus was calculated following the equation:

$$G = \frac{\tau}{\gamma}$$

or the slope of the shear stress-strain curve. The initial slope before plastic deformation was determined for each graph, and the average G was reported with error of one standard deviation. Shear modulus was analyzed only for lap shear adhesion tests performed on aluminum substrates because this method is only valid for cohesive failure modes.

2.4 Contact angles

Contact angles were measured using a smartphone contact angle measurement application (CircuDyn). Photographs for contact angles were taken with a smartphone equipped with a 15x macro lens attachment. Aluminum or Teflon substrates were placed in a saturated chamber with dichloromethane and methanol to reduce evaporation of the solvent from the adhesive solution. Polymers were dissolved in 1:1 DCM:MeOH at 0.1 g/mL, and 10 μL of a polymer solution was deposited onto the substrate surface immediately before photographing the droplet. An average of at least $n = 10$ measurements was analyzed for the polymers on each substrate. Errors reported are one standard deviation.

2.5 Surface roughness

Average roughness (Ra) values were measured using a Mahr Federal 2191800 Pocket Surf Portable Roughness Gauge calibrated with a Mahr Federal PMD-90101 Surface Roughness Standard (3.02 ± 0.05 μm). Each Ra was measured with a travel length of 5 mm and evaluation of 4 mm. A total of nine measurements were taken over three substrates for each surface. Errors reported are one standard deviation.

3 Results and Discussion

3.1 Polymer Synthesis, Design, and Characterization

The random terpolymer system, poly{[dopamine methacrylamide]-*co*-[methyl methacrylate]-*co*-[poly(ethylene glycol) methyl ether methacrylate]}, poly(catechol-MMA-OEG) (Fig. 1), has a poly(methyl methacrylate) (pMMA) backbone incorporating dopamine methacrylamide (DMA) for catechol adhesive functionality with an oligoethylene glycol (OEG) group to lower the material modulus. Owing to prior studies identifying 45 mol% OEG for maximum bond strengths,[8] this monomer content was held constant. A series of eight polymers were synthesized, each with roughly 45 mol% OEG (Table S1). The catechol content varied from 0-50 mol%, and the remainder was filled with MMA. Molecular weights of polymer chains can affect adhesion.[23] Consequently, monomer concentrations were adjusted for each feed ratio to keep molecular weights amongst the different polymers as similar as was practical. Molecular weights and molecular weight distributions (Đ) were determined using a Polymer Laboratories PL-GPC20 system for gel permeation chromatography (GPC) with a tetrahydrofuran (THF) eluent and polystyrene standards (Agilent Technologies) for calibration. Final polymer compositions were provided by ^{1}H NMR spectroscopy. The family of synthesized polymers had a weight-average molecular weight (M_w) range between 13,000 - 59,000 g/mol (Table S1). Lower molecular weights were observed with more catechol present, which is consistent with other catechol-containing methacrylate polymers.[52] Consequently, the feed monomer concentrations for low DMA percentage polymerizations were lowered to decrease the resulting molecular weights.

Prior work with another catechol-containing polymer system has shown that molecular weights can influence adhesive performance.[23] For a styrene-based biomimetic polymer, adhesion only began to increase when molecular weights reached over ~40,000 g/mol and appeared to continue an upward trend exceeding 100,000 g/mol.[23] The range of 13,000 - 59,000 g/mol found amongst this family of poly(catechol-MMA-OEG) polymers described here was as tight as could be achieved practically and may not have a major impact upon adhesion. Between this variability plus composition and molecular weight targets, it took over 90 syntheses to achieve a series of eight polymer samples similar enough to use for the following structure-function studies (Table S1). Further details on synthetic methods are included in the Supporting Information.

3.2 Adhesion Studies

In order to determine how polymer design might be changed for high versus low energy surfaces, two extreme cases were chosen: aluminum for a high energy substrate and polytetrafluoroethylene (PTFE), or Teflon™, for a low energy case. A lap shear configuration was chosen because, in our experience, this bond type is the most practical and closest to an ideal when comparing adhesion of many samples. Adhesion tests were performed by applying solutions of polymers across both substrates before joining in the lap shear configuration. The specimens were cured for 1 hour at room temperature, heated to 70 °C for 22 hours, and cooled to room temperature for an hour prior to testing. Ambient pressure was used to minimize forcing excess adhesive out the sides of the overlap area. The hour before heating ensured that the specimens could be handled for transporting to the oven, and heating to 70 °C aided solvent evaporation for full curing of the adhesive.

The choice of solvent came from seeking one system to dissolve all derivatives of poly(catechol-MMA-OEG). The 1:1 dicholoromethane:methanol (DCM:MeOH) combination proved to be quite useful in these studies. Dichloromethane (BP = 40 °C) and methanol (BP = 65 °C) form an azeotrope at 93:7, a different ratio than what was used here. Monitoring the evapora-

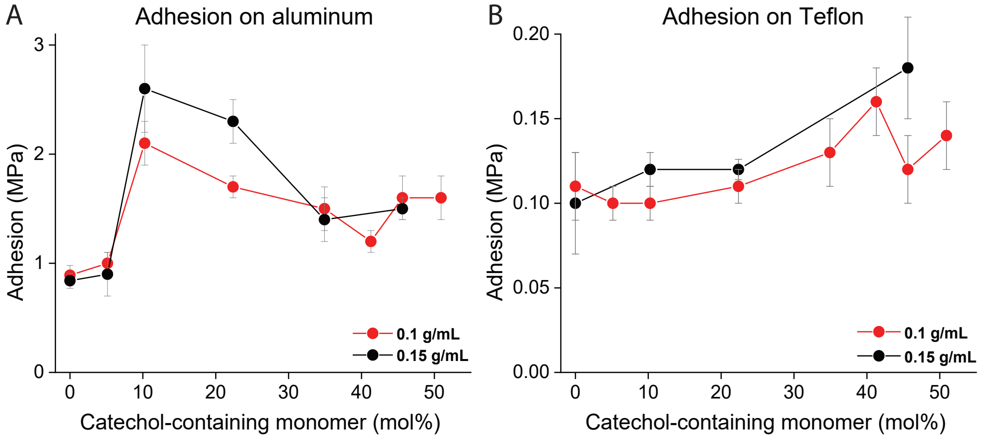

Fig. 2 Adhesion for several variants of poly(catechol-MMA-OEG) on A) high energy aluminum substrates and B) low energy Teflon substrates.

tion for 1:1 DCM:MeOH (100 μL, room temperature) showed a time (∼120 min) right in between those of the individual components (DCM ≈ 45 min, MeOH ≈ 195 min). Polymer solutions were observed when in use. In no case was any phase separation or turbidity seen when handling solutions of polymers in 1:1 DCM:MeOH.

The 45 mol% OEG and 55 mol% MMA polymer with no catechol provided a control. Lap shear adhesion with this control polymer was quite low with both aluminum (0.89 MPa) and Teflon (0.11 MPa) substrates. Acrylic resins having low strengths are used in bonding plastics or for pressure-sensitive adhesives.[53] Thus, some initial adhesion from these copolymer controls was not surprising. Catechol increased bonding on aluminum, as shown in Fig. 2A, but only up to a point. Performance dropped beyond ∼10 mol% catechol but still remained higher than the control polymer without catechol.

By contrast, a prior study found that ∼33 mol% of catechol-containing monomer brought about the strongest bonds with aluminum substrates when working with a styrene-based biomimetic polymer.[48] Here with poly(catechol-MMA-OEG), there is a clear optimum at lower catechol content with aluminum substrates. The styrene-based polymer was less polar than poly(catechol-MMA-OEG) and likely relied more upon catechol for cohesion. Polarity of the methacrylate host may provide more cohesive chain-chain interactions, thereby requiring less catechol to generate cohesive forces.

When switching over to Teflon substrates, a different story emerged. The adhesion-versus-catechol content plot in Fig. 2B provides indications of an upward slope. Statistical analysis of data at the solution concentration of 0.1 g/mL (red) indicated that several points had similar strengths. Fig. S1B shows that the lowest and highest bonding strengths were statistically different. Testing with a higher polymer concentration of 0.15 g/mL (Fig. 2B, black) yielded a more pronounced increase in adhesion strengths with greater catechol content in the polymer.

Higher concentration enhanced adhesion strengths with both aluminum and Teflon. For aluminum substrates, increased concentration of the polymer improved bonding from ∼2.1 to ∼2.6 MPa (Fig. 2A). However, polymer solubility at 0.15 g/mL was difficult, and only a limited number of these tests could be performed. Additionally, different solvents can also influence bonding strengths. Fig. S2 shows that using only DCM increased adhesion to ∼3.7 MPa on aluminum, but not all polymers were easily soluble in this one solvent. Altering the incorporation of three different monomers resulted in varying solubilities among the family of polymers. Thus, one solvent system (1:1 DCM:MeOH) and concentration (0.1 g/mL) were chosen to ensure consistency and enable direct comparisons. The lower 0.1 g/mL concentration was used for all remaining studies.

The structure-function data in Fig. 2 indicate that the composition of glues for maximum bonding on low energy surfaces may be different than with high energy materials. Given the general non-stick nature of Teflon, bonding strengths are much lower compared to aluminum. Poly(catechol-MMA-OEG) also had lower adhesion than prior reports of epoxy (0.7 MPa), cyanoacrylate (1.5 MPa), and a styrene-based biomimetic polymer (0.7 MPa) with Teflon.[48] Although we might be able to extract even stronger bonding from higher catechol-content polymers on Teflon, the OEG monomer was being held at 45 mol%. Prior results found this percentage to be best in terms of modulus for overall adhesion,[8] thereby providing a maximum of ∼50 mol% catechol available here. Decreasing OEG content in favor of more catechol would change polymer modulus[8] and render direct comparisons difficult.

Further insights on bonding to low energy surfaces was explored with polyvinylchloride (PVC) substrates. With one of the highest surface energies amongst common plastics at 40 mJ/m^2, PVC provides something of a contrast to lower surface energy Teflon at ∼20 mJ/m^2.[4] Fig. S3 shows the structure-function data for each polymer when used to join PVC substrates. Bond strengths were significantly higher than those seen with Teflon and lower than what was noted with the aluminum data. A pronounced decrease in adhesion with increasing catechol content could be seen. This trend may contrast from the one observed with Teflon. However, there are differences between PVC and Teflon that should be kept in mind. Commercial PVC contains plasticizers that can influence interactions at surfaces as well as leach from the bulk. Furthermore, Teflon tends to be chemically inert, whereas solvents interact more readily with PVC and other plastics.

In order to examine potential effects from the solvent system used to dissolve the poly-(catechol-MMA-OEG) variants, a solvent welding control with 1:1 DCM:MeOH and PVC substrates (and no polymer) was carried out. No measurable bonding was observed. With 100% DCM, two pieces of PVC could be joined (2.3 ± 0.3 MPa). With the 1:1 DCM:MeOH solvent not appearing to influence PVC attachment under these conditions, all measured adhesion can be attributed to poly(catechol-MMA-OEG). The downward trend of decreasing adhesion with increasing catechol may indicate that, in this PVC case, increased cross-linking biases the system toward cohesion at the expense of surface adhesion.

3.3 Mechanical Properties

Fig. 3 shows typical force-versus-extension curves when examining adhesion of both aluminum and Teflon. Correlating quantitative comparisons of the full width at half maximum (FWHM) of force-versus-extension curves in Table S2 and Fig. S4 show the same trend. Note how the curves became sharper with higher catechol content and aluminum substrates (Fig. 3A). This observation indicated that more catechol made the polymers increasingly brittle. Other systems have also reported similar changes from ductile to more brittle with increased catechol.[46,52] Most likely, higher catechol content contributes to covalent cross-links, thereby decreasing ductility. This effect was more prominent when the polymer catechol content increased. Interestingly, the analogous plots looked different with Teflon substrates. Most curves appeared, at first glance, to show brittle failure. However, going from low to high catechol content, the curves did narrow. Given that the substrate here was Teflon and most samples (0-35 mol%) failed adhesively, the maximum forces observed (e.g., ∼30 N) were lower than those seen with aluminum substrates (e.g., ∼250 N). Thus, the aluminum data (Fig. 3A) with more cohesive failure may be more representative of the bulk mechanical properties of these polymers.

Methacrylate polymers with pendant catechols have been shown to be cross-linked even without the addition of external oxidizing agents.[52] With higher catechol content, cross-linking increased to the point that the homopolymer poly(dopamine methacrylamide) was nearly insoluble. The data seen in Fig. 3 indicate that here, too, higher catechol contents bring about increased cross-linking of the polymers. However, all polymers used were soluble in 1:1 DCM:MeOH at 0.1 g/mL. Thus, we may surmise that, prior to curing of the adhesive formulations, cross-linking is present to varying extents, but never to an extreme degree such that insolubility was reached. After measuring bond strengths, we attempted to dissolve the polymers for further characterization. However, conditions were not found in which the cured materials could be solubilized.

The limited quantities of available polymer did not permit making specimens for direct mechanical property analysis. However, further insights on the implications of changing catechol content in polymers could be extracted from the force-versus-extension data by conversion to shear stress-strain plots. These conversions were suitable for the aluminum bonding data sets given that at least partial cohesive failure was observed with each polymer. Thus the mechanical data are a reflection of the bulk polymer properties. By contrast, the Teflon samples were left out of this analysis, given that the noted adhesive failure indicated that force-extension data did not provide as much information on the bulk polymer mechanics. Briefly, shear stress was obtained by dividing measured force by the substrate overlap area. Shear strain came from division of displacement distance by bond line thickness. Fig. S5 shows the resulting shear stress-strain curves for all polymers when bonding aluminum. Note that the lowest catechol content polymers, at 0% and 5%, displayed shallow, gradual curves differing from the more steep increases seen with greater catechol loadings.

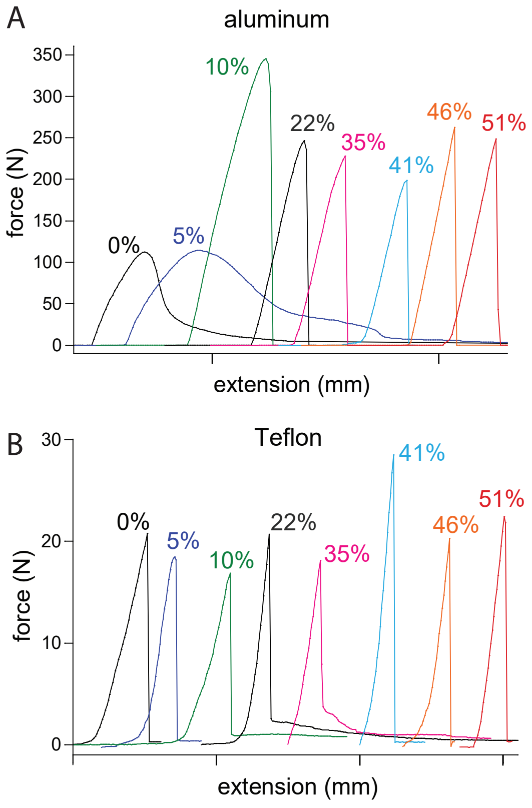

Fig. 3 Force-versus-extension curves representative of several polymers on A) aluminum and B) Teflon. Each curve was offset on the x-axis for clarity. Note that the two plots are shown with different y-axis scales.

Shear modulus (G) values could be obtained from these plots by determining slopes prior to where plastic deformation occurred. The plot of Fig. S6 provides these shear moduli. The 0% catechol control polymer had the lowest modulus at 35 MPa, followed by the 5% catechol polymer at 290 MPa. Interestingly, moduli values for all remaining poly(catechol-MMA-OEG) derivatives were close to ∼500 MPa. These data indicate that cross-linking from catechols increases polymer modulus, but only up until about ∼10%. Further catechol and cross-linking appear to have little added impact on polymer modulus. This observation may help to explain why the adhesion-versus-catechol content plot for aluminum substrates in Fig. 2A maximizes at ∼10%.

Analogous conclusions cannot be drawn with Teflon given that adhesive failure was often observed and the bulk adhesive mechanics were less at play.

3.4 Surface Wetting

Even before strengths of adhesion were measured, a noticeable difference in solution wetting of each substrate was observed when working with this family of polymers. Formulations of poly(catechol-MMA-OEG) in dichloromethane/methanol solvent behaved noticeably different on each substrate, seen in Fig. 4. Wetting and spreading of solutions onto high energy aluminum was relatively easy for all polymers. Contact angles of the solutions varied from $31° \pm 6°$ at 10 mol% catechol to $50° \pm 7°$ for 51 mol% catechol. By contrast, the Teflon surface was wetted more easily when the polymer contained higher catechol content. Contact angles of the polymer solutions on Teflon shifted from $40° \pm 2°$ at 10 mol% catechol to $32° \pm 2°$ for 51 mol% catechol. Fig. 4 shows the different behavior of low versus high catechol polymers. Most typically, low surface energy substrates like Teflon resist wetting, giving rise to higher contact angles. With Teflon, higher catechol polymer contents yielded easy spreading.

This interesting observation indicated that catechol groups are particularly good at wetting a Teflon surface. Given the hydrophilic nature of phenolic $-$OH's in catechol and the hydrophobicity of Teflon, such a result was somewhat unexpected. Thus, it appears that catechol groups have an ability to generate hydrophobic contacts when atop hydrophobic surfaces. These results are consistent with prior reports in which peptide mimics of mussel adhesives showed differences in side chain orientations on high surface energy glass compared to low surface energy polyethylene.[54] The π-system of catechol can lay flat atop a hydrophobic surface.[54] Catechol can be viewed to be a Janus-faced molecule with the phenyl ring creating a hydrophobic region and the $-$OH's being hydrophilic. Metallic substrates may see the two $-$OH's chelate surface ions such as Al^{3+} for aluminum substrates and Fe^{3+} with steel. Iron binding to DOPA-containing adhesive proteins has been shown to be a key aspect of mussels generating their adhesive.[55] Which side of the catechol is more pronounced for surface bonding will likely depend upon the substrate. Such flexibility may, at least in part, explain the ability of biological and biomimetic catechol systems to wet and bind to nearly every type of surface.

Surface roughness and adhesive formulation viscosity can also play roles in surface wetting. Measured average roughness (Ra) values were found to be 4.9 ± 0.4 μm for aluminum and 1.1 ± 0.2 μm for Teflon. Although there is a modest difference in roughness here, surface energy can play a more substantial role in bonding and wettability.[4] Additionally, the low polymer concentration of 0.1 g/mL was chosen to dissolve each polymer well and keep a consistent viscosity. Higher adhesion was achievable with select polymers at higher concentrations (Fig. 2), but the solubility of each variant differed along with viscosity when changing concentrations. The same 0.1 g/mL concentration used for all other studies ensured that viscosities also remained close to one another.

3.5 Failure Modes

Fig. 5 and S7 show images of substrates pulled apart after bond strength testing. Cohesive failure occurs when a polymer is spread evenly across both substrates. Alternatively, adhesive failure is noted when patches of a substrate are absent of any glue. In the case of aluminum here, all polymer solutions spread evenly to bond to the entire overlap area. Adhesion strengths were highest for low catechol content polymers and mostly cohesive failure was observed. Interestingly, as bulk cohesion increased with more catechol in the polymer, the failure modes changed to adhesive. Conversely, some cohesive failure ensued on Teflon with higher catechol content, likely derived from better wetting and adhesion to the surface (cf., Fig. 4). In the case of the 51 mol% catechol polymer, adhesive was observed on each Teflon substrate after being pulled apart. Some areas showed thicker regions of glue whereas others maintained only a thin layer of polymer on each surface. The left substrate in Figure 5 shows regions both with and without persisting polymer. Several of the left substrate regions with polymer correspond to areas of the right substrate that are also covered with the adhesive. Thus, cohesive failure was introduced somewhat to this low energy substrate. Lower catechol polymers with decreased bond strengths and less wetting of this low energy surface correlated to more adhesive failure.

Higher adhesion strengths for both aluminum and Teflon corresponded to more cohesive failure. Greater ability to wet the surfaces also seemed to match higher performance. However, it was the lower catechol content polymer that brought about more cohesive failure, wetting, and overall bonding with aluminum. On Teflon, more solution wetting, cohesive failure, and higher bond strengths all came from polymers having more catechol.

Results with the Teflon substrates were interesting. Teflon is a classically challenging material for bonding, with simple adhesive failure at low strengths predominating. The cohesive failure noted here with high catechol content polymers and Teflon indicated that we shifted the weakest part of the joint from common detachment at this surface to failure within the bulk polymeric glue. It was also the high catechol polymer solutions that showed more extensive surface wetting and the greatest bond strengths. The greatest overall bonding with low energy substrates appears to come from maximized surface interactions. These results also help to support the indications seen in Fig. 2 and 5 that higher catechol content is best with Teflon and contrast to the aluminum case.

4 Conclusions

Data presented here provide one of the first systematic studies aimed at designing biomimetic adhesives specifically for high versus low energy surfaces. Catechol groups were the essential adhesive functionality used to provide both surface adhesion and bulk cohesion. The optimal polymer catechol content appeared to be different for each substrate. A lower loading of the catechol-containing monomer yielded maximized adhesion between strips of aluminum. When the substrates were Teflon, trending was less clear but may have optimized with more catechol in the polymer than the aluminum case. That said, maximum adhesion of Teflon substrates (0.18 MPa) was still well below that of aluminum (2.6

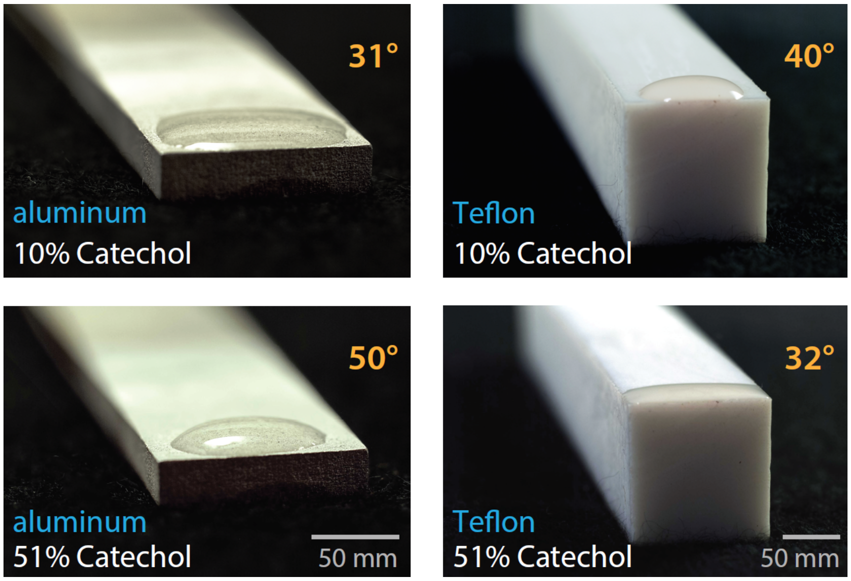

Fig. 4 Wetting of aluminum (left) and Teflon (right) substrates by polymers in DCM/MeOH solutions with varying catechol content.

MPa). Factors that contributed to altered performance included balancing adhesive versus cohesive bonding, evidenced by differing failure modes as well as peak performance.

Amongst the interesting results found here was that, when bonding aluminum substrates, catechol content optimized at ∼10%. Prior work with a catechol-containing copolymer and aluminum substrates had maximized adhesion with significantly more catechol, at ∼33%.[48] These data indicate that design of the entire copolymer is relevant. A non-polar polystyrene host may have little inherent cohesion, thereby requiring more catechol to provide all of the cohesive and surface adhesive forces of a glue. The more polar polymethacrylate host used in this current study is likely to bring more cohesion even without catechols. Indeed, the no catechol control polymer displayed significant adhesion on aluminum at almost 1 MPa. Nonetheless, addition of catechol did increase copolymer adhesion by more than a factor of two. When catechol was placed into polylactic acid (PLA), more than a five-fold increase was seen versus pure PLA.[56] In the polystyrene case, catechol within the copolymer raised bonding more than 10-fold.[48]

These data may provide some degree of predictive ability when designing new biomimetic copolymer systems. If the bonding target is a plastic of low surface energy, maximizing the catechol content may be best. Conversely, less catechol within a copolymer could be called for when joining higher surface energy metals. Note, however, that our ability to predict relations between copolymer composition and mechanical performance is still fairly rudimentary.[57] Bulk cohesive versus surface adhesive forces can be observed experimentally only to some degree and remain a challenge in predictive calculations.[57] Data presented here may help bring us closer to having an ability to tailor polymers for specific bonding situations. Biomimetic adhesives can be designed to maximize performance when having specific substrates in mind.

Author Contributions

AAP carried out all laboratory work. AAP and JJW wrote the paper together.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We appreciate helpful discussions with Dr. Michael North and Dr. Michael Mazzotta. Ms. Carly Battistoni helped with statistical analysis. Mr. Jordan Neeb helped with profilometry measurements. Aaron Harkleroad and the Purdue Chemistry Maintenance Shop helped with cutting of substrates. This work was supported by the Office of Naval Research (Grants N000141310327, N000141612709, and N000141912342).

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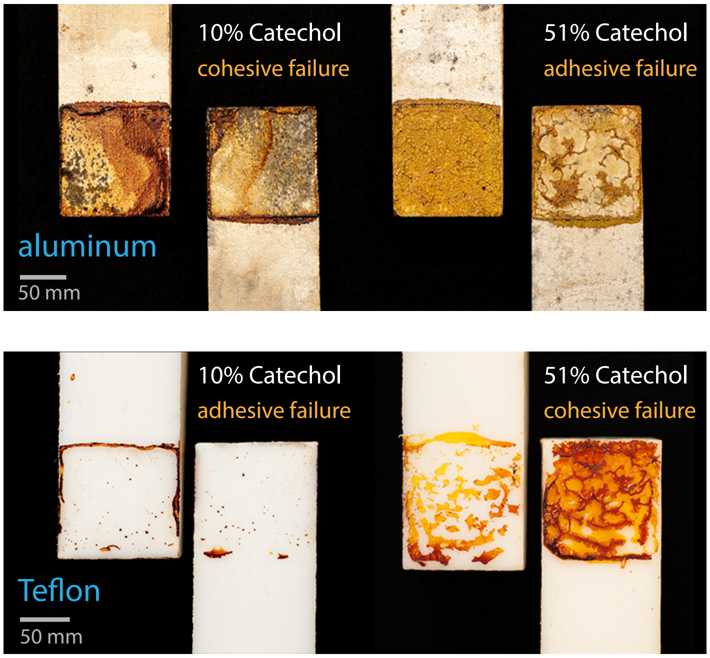

Fig. 5 Variations in failure modes with poly(catechol-MMA-OEG) on aluminum (top) and Teflon (bottom). Higher bonding strengths occurred with more cohesive failure, which could be seen with 10 mol% catechol on aluminum and 51 mol% catechol on Teflon. Note that samples shown here were stained with iodine to aid visualizing the polymers. The same samples prior to staining can be seen in Fig. S7.

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TOC Graphic

Changing catechol content in a biomimetic polymer alters affinity for high versus low surface energy substrates.