

ARTICLE

Biopolymers as sustainable metal bio-adhesives

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Abstract

We describe the use of biopolymers, such as sodium alginate, as an sustainable adhesive binder for several metals and high-density polyethylene. A standard pull test and peel test was performed with disks, made of different material and size. Adhesive failure was investigated by varying the amount of applied alginate solution, drying time, drying temperature, effect of surface area, and the nature of the adherend. Alginate adhesion was remarkably strong, relatively general, and sensitive to the presence of water. A brief comparison with other biopolymers is also provided.

KEYWORDS

adhesives, hydrophilic polymers, polysaccharides

1 | INTRODUCTION

During the last decade, great emphasis has been placed on the need to improve the sustainability of industrial chemical products and processes. Bio-based materials are increasingly attractive because of their enhanced environmental footprint.¹ This is as true for adhesives as for any other class of materials.² Adhesives usually contain a polymer that either covalently links to the material or uses extensive physiochemical attraction forces to enable a connection. Often the adhesive is applied in solution and the adhesive joint is formed during or after solvent evaporation.

A good example is provided by epoxy-diamine materials that are used in a wide variety of applications including in metal adhesives and paints.^{3–5} Liquid

monomers, or unreacted epoxide groups in the polymers, can react with metallic surface oxide/hydroxide groups to form chemical bonds between the polymer and the surface during curing, thus enhancing adhesion. Roughening of the metal surface, such as by etching, anodization, plasma treatment, or acid treatment, enhances the production of a metal oxide layer and thereby covalent and noncovalent interactions with the adhesive polymer. This was nicely illustrated by Yoshida and Ishida in their exploration of the cure behavior on copper, steel, and aluminum surfaces of commercially available Epon 828 epoxy resin, consisting of a typical diglycidal ether from epichlorohydrin and bisphenol A.^{6–8} Polyurethanes constitute another important class of metal adhesives.^{9,10}

In both cases, a switch from organic solvents to water-soluble or high solid adhesives would avoid

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harmful evaporation during production as well as maintain lifetime and minimize disposal costs and environmental problems. Natural products are a versatile source of water-soluble materials that can function as adhesives. Well-known representatives include dextrin, gelatin, casein, and starches.¹¹ For example, Imam et al. formulated a replacement for phenol-formaldehyde resin using starch, polyvinyl alcohol, and hexamethoxymethylmelamine with citric acid as catalyst.¹² The advantages of this system included its formaldehyde-free nature, low cost, and lack of environmental footprint, since starch could be obtained in large amounts from commodity crops. Other examples of water-soluble bio-based adhesive materials include the scleroprotein collagen, which is collected from animal tissue and has been used for thousands of years.¹³

We focus here on alginates as inexpensive, biodegradable, and biocompatible anionic polysaccharides with low toxicity. Alginate is widely used as a food additive, and has also been employed in such varied materials applications as binders for composite wood- and cotton fiber-based building insulation materials,¹⁴ additives to improve the adhesive strength of polyamide adhesive (FixTM),¹⁵ and in hydrogel adhesives for cell encapsulation.^{16,17}

Inspired by these reports but noticing a lack of testing of simple alginate, we explored sodium alginate as an adhesive binder for several metals and high-density polyethylene (HDPE). Simple pull and peel tests (Figure 1) were performed with different disks using different variables, such as amount of applied alginate solution, drying

time, drying temperature, surface area, and the material being adhered.

2 | EXPERIMENTAL

2.1 | Materials

Alginates having low molecular weight (viscosity: 4–12 cps, 1% in H₂O at 25 °C) and high molecular weight (viscosity: 1000–1500 cps, 1% in H₂O at 25 °C) were obtained from Sigma–Aldrich and Alfa Aesar, respectively. Methyl cellulose (MeCel, viscosity: 400 cps), gelatin (from porcine skin, gel strength 300, type A) were obtained from Sigma–Aldrich. Dextran 40 (MW-40,000) was obtained from TCI. Sodium hyaluronate (Hyal) gifted by Novozymes Biopharma, Denmark. The commercial metal glue used for comparison (brand name UHU-Metal) was obtained from UHU GmbH & Co, Bühl, Germany. Copper, brass, aluminum, titanium, steel, cast iron, and HDPE test samples were prepared by the workshop of Universität Regensburg, Germany. Each material was obtained in the form of 4 cm diameter rods and were cut into 1.5 cm equal pieces, drilled to make a hole in the middle, and equipped with a hook for pull test measurements.

2.2 | Surface and sample preparation

Each metal surface was cleaned by brief sanding with aluminum oxide sanding paper (120 followed by 180 grit) to remove surface contaminants, followed by exposure to concentrated H₂SO₄ for 1 min and then rinsing with water, ethanol, and acetone. Alginate solutions in distilled water were freshly prepared before use. Previous experiments showed very similar results with phosphate-buffered saline buffer. The surfaces were glued by applying different concentrations of alginate solution to one of the two adherends, which was then immediately placed in contact with the other adherend, and the materials were then allowed to dry for the prescribed period of time. Failure load testing was performed in two modes (pull test and 90° peel test, Figure 1) by hanging weights from the hook for 1.5 min, increasing by increments of 2.5 kg from 1 to 28.5 kg.

3 | RESULTS AND DISCUSSION

A standard pull test was repeated multiple times with brass disks using different amounts of applied alginate solution (Table S1, Figure 2). When the amounts of adhesive were insufficient to cover all the metal surface (25, 50, and

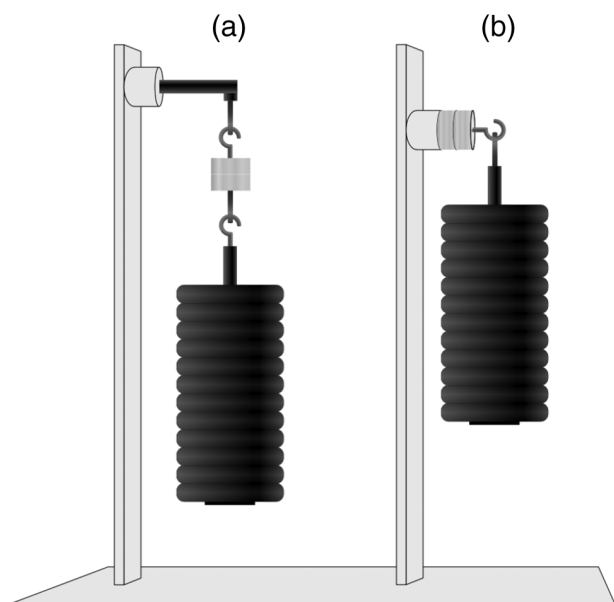


FIGURE 1 Illustration of adhesive strength measurements by (a) pull test and (b) peel test

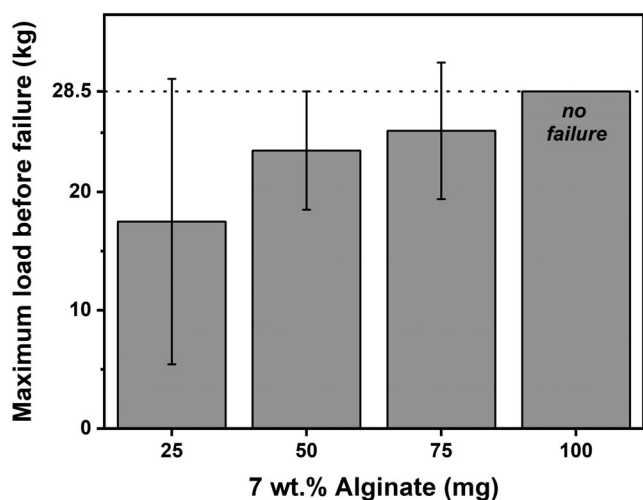


FIGURE 2 Effect of amount of alginate on adhesive failure

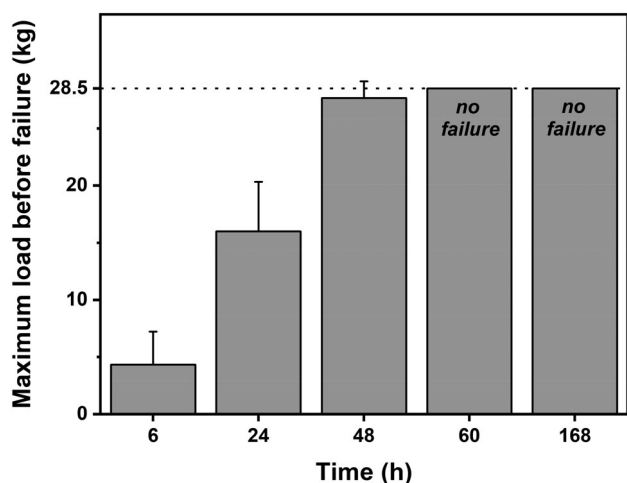


FIGURE 3 Effect of drying time on adhesive failure (pull test, 4 cm diameter brass plates)

75 mg), the amount of weight tolerated before failure varied widely. In contrast, use of 100 mg of alginate solution (7.0 mg + 93 mg water), sufficient to completely cover the adherent metal surfaces, provided for consistently strong bonding. The drying time of this alginate adhesive after surface contact proved to be an important factor: poor results were observed when the brass plates were tested at 6 or 24 h after application of the adhesive (Table S2, Figure 3). However, after 48 h, all the test samples were properly dried, and all exceeded the maximum load that could be measured with our apparatus. The drying time could be shortened by curing adhered disks in an oven at 60°C for 12 h, giving the same maximum load-bearing performance. Alginate adhesion of brass disks retained full strength after standing for at least 2 weeks under ambient conditions, or at 90°C for 3 days. However, the adhered blocks were released by delamination of the adhesive after 20 min soaking in water.

The use of low- versus high-molecular weight alginate at 2 wt% (the maximum concentration for high molecular-weight alginate in water) did not seem to make much difference in adhesive performance, but more studies are necessary to definitively explore this variable. All other experiments described here were performed with low molecular-weight alginate.

As expected, the contact surface area was found to have a large impact on adhesion strength as measured by the peel test, which is more sensitive to failure by crack propagation.¹⁸ We tested seven materials (six metals and HDPE, Figure 4, Tables S3 and S4) and found alginate to provide excellent resistance against the pull test for all of them over the larger surface area (4 cm diameter), and for all but polyethylene with the smaller surface contact (2 cm diameter). The peel test revealed significant differences: aluminum, brass, and copper provided strong

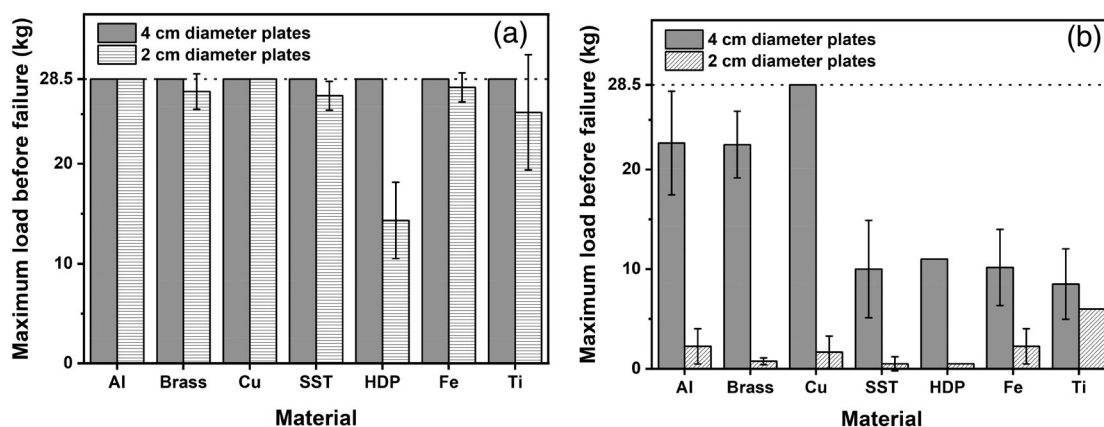


FIGURE 4 Adhesion of different metals and surface areas. (a) Pull test. (b) Peel test. HDPE, high-density polyethylene; SST, stainless-steel

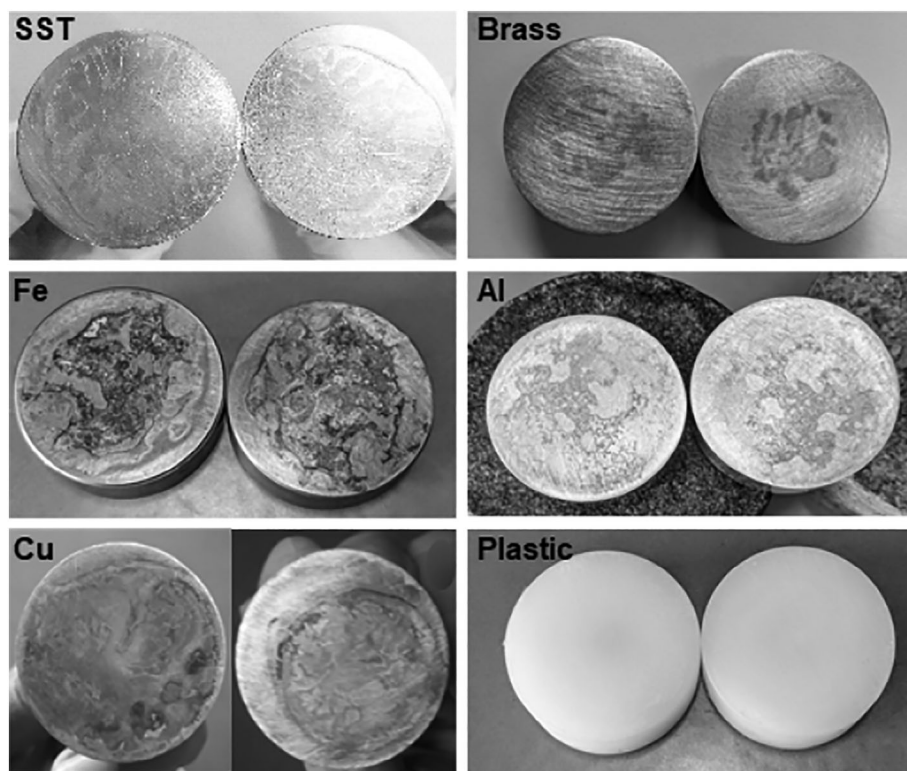


FIGURE 5 Different material surfaces (4 cm diameter) after pull test failure

adhesion with the larger disks, but no material performed well when subjected to peel testing with smaller disks (Table S5 and Table S6). In all cases, pretreatment by light sanding and strong acid was necessary for effective adhesion (Figure S1).

Additionally, we have investigated other biopolymers on adhesive failure (Figure S2) and found that alginate, Hyal, and gelatin provide excellent resistance against the pull test, whereas dextran and methyl cellulose showed comparatively lower adhesive strength. For comparative purposes, we also used commercially available UHU-metal glue, which showed the same maximum load-bearing performance.

Examination of disk surfaces after adhesion and pull test separation revealed patterns of adhesive failure (characterized by separation of the adhesive from the disc surface), rather than cohesive failure (Figure 5). Fourier Transform Infrared (FTIR) spectroscopy of adhesive material removed after this failure (Figure 6) showed only small variations in the position of the characteristic carboxylate asymmetric stretching band at approximately 1596 cm^{-1} , suggesting no significant difference from the expected metal (sodium or other) carboxylate moiety.¹⁹ Unfortunately, FTIR cannot provide meaningful information on the failure mechanism. While it is likely to involve intermolecular interactions involving the carboxylate residues, only a tiny proportion of the total number of carboxylate groups would be affected during adhesive

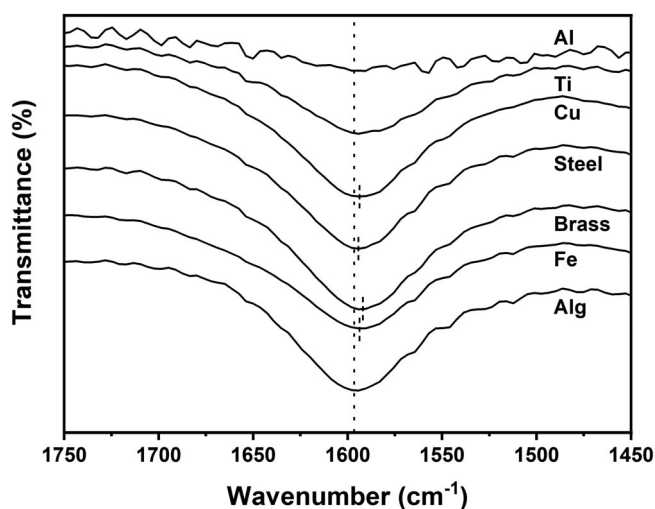


FIGURE 6 FTIR spectra of pure sodium alginate (alg) and scratched alginate sample from the different metal plates after failure

failure. Furthermore, a primary determinant of the observed peak position is the counterion, and in our case (unlike examples of cation exchange¹⁹) the cation remains sodium throughout. Nevertheless, some plausible failure modes may include, at least, (a) rupture of intermolecular interactions, such as between surface metal-hydroxyls and adhesive carboxylate groups; and (b) plasticization of the adhesive layer under stress,

presumably with the assistance of water vapor adsorbed from the air.

4 | CONCLUSION

These data show that simple solutions of sodium alginate serve as effective adhesives for a variety of metal surfaces, and are somewhat less powerful but still substantial adhesives for polyethylene. To our knowledge, this is the first description of such a phenomenon, although it is not surprising given the fact that alginate contains many functional groups able to interact noncovalently with oxidized or acid-etched surfaces. Adhesion requires drying, either slowly at room temperature or faster at elevated temperatures, and the adhesive interaction can be disrupted by treatment with water. Alginates warrant further study as potential inexpensive and strong metal adhesives when extended curing times can be tolerated.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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SUPPORTING INFORMATION

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