

Preparation of Chitosan-Based Adhesives and Assessment of Their Mechanical Properties

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ABSTRACT: The aim of this study is to develop chitosan-based adhesives and to characterize their shear strength. The desirable features of such adhesives are biodegradability, biocompatibility, non-toxicity, and anti-microbial properties. Various eco-friendly polyanionic polysaccharides, acids, and plasticizers, in single or multiple formulations, were associated with chitosan. The resulting cross-linked polymers were glued on some chemically treated aluminum adherends. The shear strength of these formulations was measured with the “double lap-joint” bonding method, as it features a low-peeling effect. The shear strength of 40.8 MPa obtained for formulations containing chitosan and glycerol plasticizer was the most significant finding in this study. This value is equivalent to that obtained with a synthetic adhesive used in industry. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Most industrial adhesives such as polyvinyl acetate, epoxy adhesives, phenol/formaldehyde, urea/formaldehyde, and polyurethane, depend on nonrenewable, shrinking petrochemical resources. Moreover, numerous adhesives are prepared with chemicals that leave toxic residues such as formaldehyde and volatile organic compounds (VOCs), which are injurious to health and the environment.¹ Reducing the use of these toxic materials has now become a major issue, as illustrated by the recent pollution prevention program of the United States Environmental Protection Agency, which aims to curb the use of these types of materials. Likewise, the synthetic adhesives industry is encouraging proper environmental and health safety for their products. Hazardous ingredients, VOC emissions, and difficulties in recycling adhesives derived from petrochemical feedstocks are prompting the development of environment-friendly biological adhesives. Finally, rising-oil prices are also stimulating commercial interest in biological alternatives for synthetic adhesives.

Natural adhesives, also called “bioadhesives”, are often polymers obtained from bioresources such as plants (gluten, starch and other polysaccharides, or natural resins), animals (casein, chitin, chitosan, or gelatin) or non-living mineral sources. These adhe-

sives are not derived from petrochemical products, thus securing economic manufacturing processes and reducing environmental shock after use.² Some polysaccharides and proteins have been used in adhesion for many decades, in particular, for book binding and wood joining. For example, starch is widely used as an adhesive for bonding paper products. Concerning proteins, De Keyser and Dessel³ patented a gelatin that was widely explored as an adhesive. It was also reported as a potential adhesive for plywood.⁴ Proteins have also been mixed with polysaccharides to obtain synergistic properties for adhesion. In this method, chitosan/gelatin blends were prepared using chitosan hydrogel mixed with gelatin. The progressive addition of gelatin decreases the crystallinity of chitosan and its tensile strength.⁵ It was also found that the interactions between the two polymers in solution were closely related to the mechanical properties of the biomaterial formed.⁶ All these bioadhesives have been traditionally used for many years, but have been gradually superseded by synthetic alternatives, due to their poor performance, especially, in terms of water-resistance properties and limited strength.⁷ Hence the development of efficient adhesives from bioresources is now a challenging field. The most attractive polysaccharide for this purpose appeared to be chitosan. This polymer of β -(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose is obtained

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by alkaline deacetylation of chitin, the main component of the exoskeleton of crustaceans.⁸ Its production is economical and environment-friendly.⁹ Chitosan itself is costly, at nearly 10 USD/kg, but it is currently used in aqueous solution at less than 10% (w/v), bringing the cost down to less than 1 USD/L of solution, which is acceptable. Chitosan is the only cationic polysaccharide due to its positive charges (NH_3^+) at acidic pH ($\text{pH} < 7$). These charges increase retention at the site of application.¹⁰ The main parameters influencing the desirable characteristics of chitosan are its molecular weight and degree of deacetylation. Its adhesive properties can, however, be weakened when both the degree of deacetylation and the molecular weight are low.^{11,12}

The adhesive properties of chitosan in a swollen state have been shown to persist better by repeated contacts of chitosan and substrate.¹³ This implies that in addition to the adhesion by hydration, other mechanisms such as hydrogen bonding and ionic interactions are also involved. An important mechanism of action was suggested to be ionic interactions between amino groups of chitosan and negatively charged adherends. The interactions are strong at acidic and slightly acidic pH levels for which the charge density of chitosan is high.⁹ An increase in the molecular weight of chitosan results in stronger adhesion.¹³ Umemura et al. (2010) studied the bonding properties of low-molecular-weight chitosans on wood.¹⁴ These properties were markedly improved by glucose addition, whereas a high-molecular-weight chitosan was shown to have a negative effect. The weight, color, free amino groups, insoluble fraction, and thermal properties of the adhesive film changed with varying glucose concentrations and chitosan molecular weight.

The aim of this study was to evaluate the potential of chitosan-based adhesives. For this purpose, solutions of chitosan alone and chitosan formulations including plasticizers and anionic compounds were tested as potential adhesives. The performance of these formulations was compared in terms of shear strength. Interactions between chitosan and aluminum adherends were also examined by microscopy.

MATERIALS AND METHODS

Specimen Preparation

The adherends used to prepare the specimens were made of 2014 aluminum alloy. They measured 150 mm × 20 mm × 2 mm. These dimensions were very similar to those used in other studies of adhesive characterization with double-lap tests.¹⁵ The adherends were first dipped for 10 s in 0.5 mol/L NaOH (Sigma Aldrich), then washed with detergent and dried. Five surface treatments were tested to evaluate their influence on the mechanical behaviors of the bonded joints: no treatment; deep scratching with a metal file; shallow scratching with sandpaper; pressing to obtain small oval-shaped grooves, and a 1 mol/L NaOH treatment (1 h) followed by washing with mild detergent and storage overnight in 2% (vol/vol) acetic acid (Sigma Aldrich). For each treatment, three specimens were prepared and tested.

Commercial chitosan powder with a degree of deacetylation greater than 75% (Sigma Aldrich—C3646 chitosan) (CS) was used for adhesive formulations. The dissolved chitosan solution

was left for 24 h at 50 °C to remove bubbles before application. Chitosan concentrations ranging between 4 and 9% (wt/vol) with 1% deviation were tested on NaOH-treated Al adherends. Chitosan at 4–5 and 6–8% was dissolved in adequate concentrations of acetic acid, 1 and 2 % (vol/vol), respectively. Some other formulations were also tested to obtain ionic, noncovalent, and covalent reticulations.

First, the shear strength of chitosan reticulated with anionic compounds was evaluated with alginate, carrageenan (Degussa, France) and sodium citrate (Sigma Aldrich). The crosslinking of the two polyanionic polysaccharides (PP) and chitosan (CS4% + AcOH1%) was performed at different concentration ratios: CS4%:PP3%, CS4%:PP4%, and CS4%:PP5% (wt/vol). Likewise, 3–7 mmol/L citrates with 2 mmol/L deviations were blended with 6% (wt/vol) chitosan, and shear strength analysis was performed.

In a second formulation, glycerol was tested as a plasticizer.¹⁶ A 6% (wt/vol) solution of chitosan was supplemented with 0.5–1.5% (vol/vol) glycerol (Sigma Aldrich) concentrations with 0.5% deviation. A 7% (wt/vol) solution of chitosan with 1% (vol/vol) glycerol was also tested to measure shear strength. This specimen was then prepared for microscopy and mapping after failure.

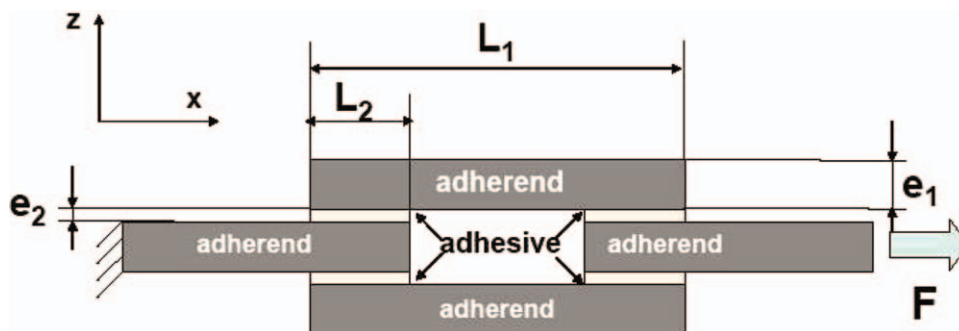
In a third set of experiments, chitosan (4% solution) was covalently reticulated with 0.010–0.016% (wt/vol) glutaraldehyde (glut).¹⁷

Finally, multivalent formulations with citrate 4–6 mmol/L and glycerol 0.5–1.5% were tested together on 5% chitosan.

Aluminum adherends were used to manufacture double-lap specimens (Scheme 1). For each bonded joint, the lap region had an area of $50 \times 20 = 1000 \text{ mm}^2$. The overall length L_1 was 350 mm. Thick teflon molds were used for specimen preparation to obtain parallel adherends and thereby regular adhesive thicknesses (Scheme 2). The first step was to apply a thin layer of adhesive on the two ends of an adherend (a), which was then laid on two other adherends (b) and (c) so that an overlap of 5 cm was obtained at the ends of adherends (b) and (c) (Scheme 2a). This first portion of the specimen was dried for 6 h at 40°C. The second step of the procedure was to bond a fourth adherend (d) symmetrically (Scheme 2b) and to dry the resulting specimen for 48 h at 40°C. The authors assumed that chitosan chemical composition and structure are highly stable for temperatures in the range 20–100°C.¹⁸ The thickness of the adhesive layer was measured before the test using a caliper square with a precision of 0.02 mm.

Shear Tests

The specimens were placed in the grips of a universal Zwick Roell testing machine. The crosshead speed was 5 $\mu\text{m/s}$ until failure. Testxpert V11.02 software was used to drive the jacks of the machine, to collect the force vs. time data and to deduce the shear strength. Standard tests such as the ASTM D 5573-99 standard generally provide the apparent-shear strength by calculating the ratio $F/(2A)$, where F is the applied force (N) and A the lap area (m^2) defined in Scheme 1. However, it is well



Scheme 1. Schematic view of the double lap-bonded specimen (L_1 : length of adherend; L_2 : lap area of adherend; e_1 : adherend thickness; e_2 : adhesive thickness). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

known that the shear stress in the adhesive depends on the thickness of the adhesive because of the shear-stress peak occurring at the free ends.¹⁵ Hence this shear strength has a meaning only if all the tested specimens have the same adhesive thickness. However, it was not possible to obtain the same thickness for all types of adhesives because significant changes in the viscosity were observed from one formulation to another (from nearly liquid to hydrogels). It was decided to take this influence into account to compare consistent values of the shear strength for all adhesives. It is well known that the shear stress is not constant along a bonded joint. In particular, a shear-stress peak occurs near the free boundaries. It is clear that this peak directly governs adhesive failure. Therefore, this effect has to be taken into account for correct determination of the shear strength, as proposed for instance by Chataigner et al.¹⁵ The model proposed by Volkersen¹⁹ was used to account for this thickness variation in the strength calculation. With this model, the value of the shear-stress peak is given by the following equations:

$$\tau(0) = \frac{G_2 \sigma_0}{\sinh(\lambda L_2) e_2 \lambda E_1} (1 + \cosh(\lambda L_2)) \quad (1)$$

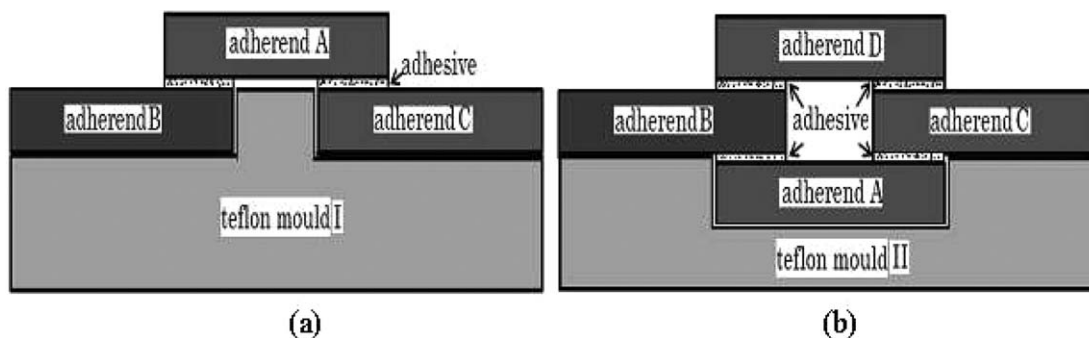
with

$$\lambda = \sqrt{\frac{2G_2}{e_2 e_1 E_1}} \quad (2)$$

where σ_0 is the axial stress, equal to the ratio of the applied force F (N) by the cross-section S (m²) of the adherend, e_2 (m) is the adhesive thickness. $e_1 = 0.002$ m is the thickness of the

adherends, $L_2 = 0.05$ m is the lap length, and E_1 is the Young's modulus of the aluminum adherends ($E_1 = 72$ GPa). G_2 is the shear modulus of the adhesive: it must therefore be known if the shear strength is determined with eq. (1). This model is sufficient for this first approach, although it does not, for example, taken into account some nonlinear phenomena.¹⁵

As the testing machine used was equipped with self-tightening grips, the specimens slightly slid within the grips during the tests. It was therefore not possible to deduce a reliable value for the shear modulus G_2 from the shear tests despite the near-linear responses obtained in all cases. It was therefore decided to deduce G_2 from the Young's modulus E_2 and the Poisson's ratio ν_2 of the adhesive. E_2 was measured with tensile tests performed on bulk specimens. However, ν_2 could not be measured during these tests. It was therefore decided to choose a value of 0.30 for ν_2 for all the formulations (a reasonable approximation for such polymers). Another problem was the fact the Young's modulus could potentially change with the formulation. To overcome this difficulty, a two-stage analysis was carried out. During the first stage, a common value for the shear modulus G_2 equal to 0.76 GPa was chosen for all the formulations (a typical value deduced from some preliminary tests). This enabled us to estimate the shear strength of all the formulations using eq. (1) and to compare the values obtained. The best formulations were detected at the end of the first stage. Bulk-tensile specimens were then prepared specifically during the second stage for all these "best" formulations to measure their value of E_2 , and then to deduce G_2 (ν_2 was still assumed to be equal to 0.30). These values of G_2 were finally used to calculate a more reliable value of the shear strength of each of these "best" formulations.



Scheme 2. Schematic view of specimen preparation stages using a set of teflon molds. (a) first stage, (b) second stage.

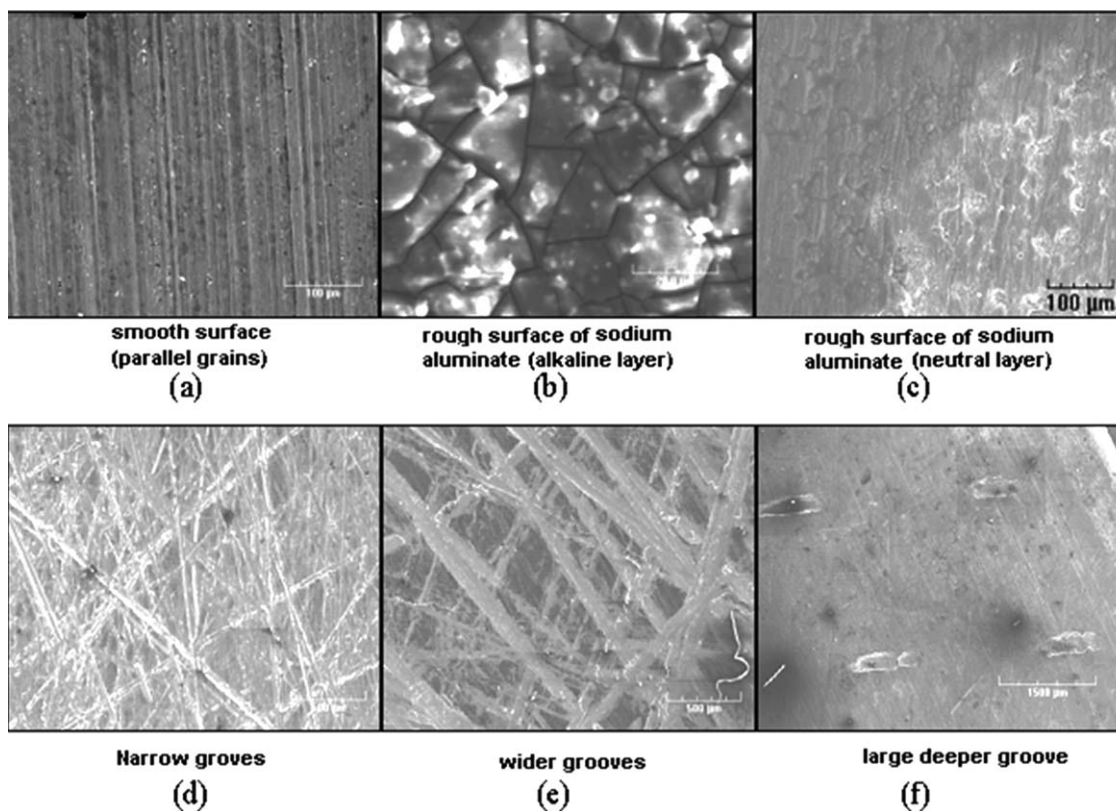


Figure 1. Adherend surface treatments: (a) untreated (X: 100 μm); (b) NaOH (X: 20 μm); (c) NaOH + Ac (X: 100 μm); (d) sandpaper (X: 500 μm); (e) metal filing (X: 500 μm); (f) mechanical pressing (X: 1500 μm).

It must be pointed out that the value of the shear-stress peak deduced from eq. (1) is correct in the case of straight edges only. The authors, therefore, took care to clean the edges of the specimens to avoid any spew fillet that would make the stress distribution different from that predicted by eq. (2). The authors also note that a cohesive failure was generally observed with all the different types of adhesives tested in this article. This lends credence to the results obtained, since cohesive failure is generally the preferred mode of failure.

Microscopy

A Jeol scanning electron microscope was used to record micrographs of adherends and failed specimens using a secondary electron detector. X-ray mapping was used to study the failure of the specimens. The gold metallization was performed for 2 min with a current of 40 mA. The working distance and acceleration potential were equal to 22 mm and 20 kV, respectively.

RESULTS AND DISCUSSION

Effect of Surface Treatment

The nature of the adherend surface obtained with the various processes was examined by SEM imaging to determine its influence in the bonding process [Figure 1(a–f)]. The values of the shear strength obtained from the five different treatments are given in Table I. Chemically treated adherends (NaOH + AcOH) clearly gave the maximum-shear strength, which was equal to 27.2 MPa. This result can be explained by the formation of sodium aluminate from the exothermic action

of sodium hydroxide on elemental aluminum.²⁰ The reaction is accompanied by the production of hydrogen gas.

Sodium aluminate provided a rough layer on each aluminum grain boundary of the adherend surface [Figure 1(a)], which supported better adsorption and linear holding of adhesive material all over the lap area. This layer did not appear on the untreated specimen [Figure 1(a)]. The adhesive mode of failure was often obtained with untreated, mechanically pressed, filed, and sandpaper-scratched surfaces, whereas chemically treated specimens exhibited a cohesive mode of failure, which was the more desirable mode. In Table I, the authors see that specimens prepared with sandpaper gave better results than untreated, mechanically pressed, or filed specimens. However, these results were greatly inferior to those obtained with the specimens treated chemically (NaOH and acetic acid). This last treatment was therefore selected for further experiments. The authors note that adherends treated only with NaOH showed some traces of salts and other undesirable particles over the sodium aluminate layer, although the surface was apparently rough [Figure 1(b)]. Hence, treatments with NaOH and acetic acid were tested on adherends that were morphologically better and free of unwanted particles [Figure 1(c)]. These adherend surfaces thus comparatively facilitated better adhesivity.

Formulations

The complete outcomes of the tests carried out with all the formulations are given in Table II. For each set of experiments, a control (CS4% + AcOH1%) was tested in the same conditions as those applied to the other formulations. First, the shear

Table I. Adherent Surface Treatment and Shear Strength (MPa) Obtained with CS6% + AcOH2% Higher Values are in Bold

Adherent surface treatment	Shear strength (MPa) \pm SD
Chemical	27.2 \pm 2.1
Sandpaper	08.8 \pm 2.4
Mechanical	05.7 \pm 1.68
Metal file	06.2 \pm 0.84
Untreated	06.9 \pm 1.21

strength was evaluated with ranging concentrations of chitosan in 1 or 2% acetic acid (vol/vol). In all the tested formulations, the maximum-shear strength obtained was 31.4 MPa with CS6%. Concentration of chitosan very much affects the shear strength.²¹ This effect is due to the increased entanglements among the macromolecular chains. Higher chitosan concentration was certainly inimical to good solubilization before the bonding process.

Another strategy to improve the bond strength is to mix the adhesive with other compounds, such as crosslinking agents or plasticizers. Some studies have revealed that polymers with increased charge density provide superior adhesive properties.²² It has also been reported in the published reports that polyanionic polymers are more effective bioadhesives than polycationic or nonionic ones.²³ Alginate and carrageenan were therefore tested at different concentration ratios with 4% (wt/vol) chitosan (4 : 3, 4 : 4, and 4 : 5). It was hypothesized that ionic interactions between these acidic polysaccharides and cationic chitosan could increase the shear strength. The pKa of alginate lies between 3.38 and 3.65, whereas the pKa of chitosan is \sim 6.3.^{24,25} It was therefore difficult to obtain total ionization and good solubility of alginate in the test conditions (pH 4.5). At this pH the CS4% + AcOH1% blend did not homogenize completely and did not lead to a better-shear strength (Table III). Another anionic polysaccharide was tested to counteract the gellifying properties of alginate at low pH. The anionic charges of carrageenan are due to sulfate substituents. A higher solubility than that of alginate exhibited at pH 4.5 was therefore expected. However, the chitosan–carrageenan mix exhibited a poor solubility due to rapid reticulation of chitosan and carrageenan. The authors note that this effect has already been exploited with success for the design of drug delivery matrices.²⁶ Table III shows the shear strengths obtained from crosslinked chitosan with ranging carrageenan and alginate concentrations. Both types of formulations exhibit a lower-shear strength when compared with the results obtained with 4% chitosan (wt/vol).

Sodium citrate was then tested to generate ionic interactions between chitosan and non-polymeric anionic compounds with anionic charges at a pH above 4.5. The pKa values for this triprotic weak acid were 3.13, 4.76, and 6.40. Addition of sodium citrate thus significantly reduced the chitosan solubility in water because of the pH increase (8). In this context, acetic acid was added to reach a pH close to 4.5 and to maintain the chitosan solubility. In the same method, the sodium citrate solution was adjusted to pH 5 before adding it to chitosan solution for better crosslinking.²⁷ Chitosan crosslinking with citrate up to 3–5 mmol/L slightly improved mechanical strength. The maximum shear strength (28.4 MPa) was obtained with 3

mmol/L citrate concentrations (Table II). Using high-citrate concentrations implied supplementary acetic acid additions (pH adjustment), favoring polysaccharide degradation and lower shear strengths. Further, high-citrate concentrations caused lower solubility of chitosan by gel development. This effect caused some difficulty in homogenous adhesive application on adherends, which could result in low failure force.

The hydrogen-bonded structure of chitosan changes when plasticizers such as glycerol are added. Hydroxyl groups of glycerol ($-\text{CH}_2\text{OH}$ and $-\text{CHOH}$) can generate hydrogen bonds with chitosan functional groups such as ($-\text{CH}_2\text{OH}$, $-\text{NH}_2$, $-\text{NH}_3^+-\text{OH}$, and $-\text{NHCOCH}_3$). It was found to be the best plasticizer, able to affect the mobility of acetamide group by formation of H bonds between adjacent chains.²⁸ As shown in Table II, the shear strength of CS4% + AcOH1% formulation (control) was equal to 25.7 MPa, whereas that of CS6% + AcOH2% + gly1% combination had a value of 39.8 MPa. The shear strength of CS7% + AcOH2% + gly1% was equal to 40.8 MPa, the best result obtained in this study. The authors note that the same formulation without glycerol (CS7% + AcOH2%) exhibited a shear strength of 19.2 MPa. To conclude, glycerol afforded further improvement in terms of shear strength.

To increase the strength of chitosan-based adhesives, covalent crosslinkages of chitosan chains were investigated after ionic

Table II. Shear Strength (MPa) Obtained with Blended Chitosan Using Anionic Acids and Plasticizers Higher Values Are in Bold

Formulation	Shear strength (MPa) \pm SD
CS4% + AcOH1%	28.7 \pm 1.1
CS5% + AcOH1%	29.4 \pm 1.5
CS6% + AcOH2%	31.4 \pm 1.2
CS7% + AcOH2%	19.2 \pm 1.4
CS8% + AcOH2%	13.9 \pm 1.8
Control	23.7 \pm 3.0
CS6% + 2%AcOH	25.7 \pm 2.8
CS6% + AcOH2% + cit3 mmol/L	28.4 \pm 2.1
CS6% + AcOH2% + cit5 mmol/L	25.8 \pm 2.7
CS6% + AcOH2% + cit7 mmol/L	19.5 \pm 3.2
Control	25.7 \pm 1.5
CS6% + AcOH2%	32.0 \pm 1.8
CS6% + AcOH2% + gly0.5%	37.0 \pm 1.8
CS6% + AcOH2% + gly 1.0%	39.8 \pm 2.2
CS6% + AcOH2% + gly 1.5%	29.0 \pm 3.2
CS7% + AcOH2%	19.2 \pm 2.2
CS7% + AcOH2% + gly1%	40.8 \pm 2.5
Control	28.7 \pm 1.2
CS4% + AcOH1% + glut0.010%	21.2 \pm 3.9
CS4% + AcOH1% + glut0.013%	18.9 \pm 2.5
CS4% + AcOH1% + glut0.016%	6.40 \pm 0.4

CS, chitosan; AcOH, acetic acid; gly, glycerol; cit, citrate; glut, glutaraldehyde; Control, CS4% + AcOH1%.

Table III. Shear Strength (MPa) Obtained with Crosslinked Chitosan (CS) Using Polyanionic Polysaccharides (PP)

CS (%) : PP (%)	Chitosan : alginate	Chitosan : carrageenan
	Shear strength (MPa) \pm SD	Shear strength (MPa) \pm SD
4:3	5.60 \pm 0.84	1.10 \pm 0.24
4:4	5.50 \pm 1.10	1.40 \pm 0.31
4:5	4.10 \pm 0.40	1.50 \pm 0.23
4:0	24.2 \pm 2.72	23.10 \pm 2.4

interactions and plasticizer action. The chitosan–glutaraldehyde gelation is due to covalent bonding between CHO groups of glutaraldehyde and NH₂ groups of chitosan.^{29,30} This crosslinkage takes place initially with a weak self-associated network of chitosan. It is gradually replaced by a permanent covalent network. The published reports does not reveal any adhesion studies on adherends of such crosslinked polymers. The present study demonstrates the effect of glutaraldehyde, which was

found to be trivial for the shear strength of a crosslinked chitosan–glutaraldehyde polymer (Table II). The maximum shear strength was equal to 21.2 MPa with a 0.010% (wt/vol) glutaraldehyde concentration.

Shear strengths obtained in this study using chitosan-based adhesives were compared with those obtained with the commercial epoxy adhesive E-504. The value obtained with E-504 was 39.1 Mpa, which is equivalent to that of the best chitosan-based adhesive in this work. However, specimens prepared with E-504 exhibited adhesive mode failures, whereas those observed with chitosan adhesives were cohesive.

Microscopic Analysis

Some SEM images of both adhesive (CS7% + AcOH2% + gly1%) and aluminum interface were taken for this set of experiments. Mapping was used to discriminate the precise surface of adhesive or adherend material; three tags were spotted over the images of the specimen during the X-ray microanalysis [Figure 2(a)]. The graphic depiction of tag 1 in Figure 2(c)

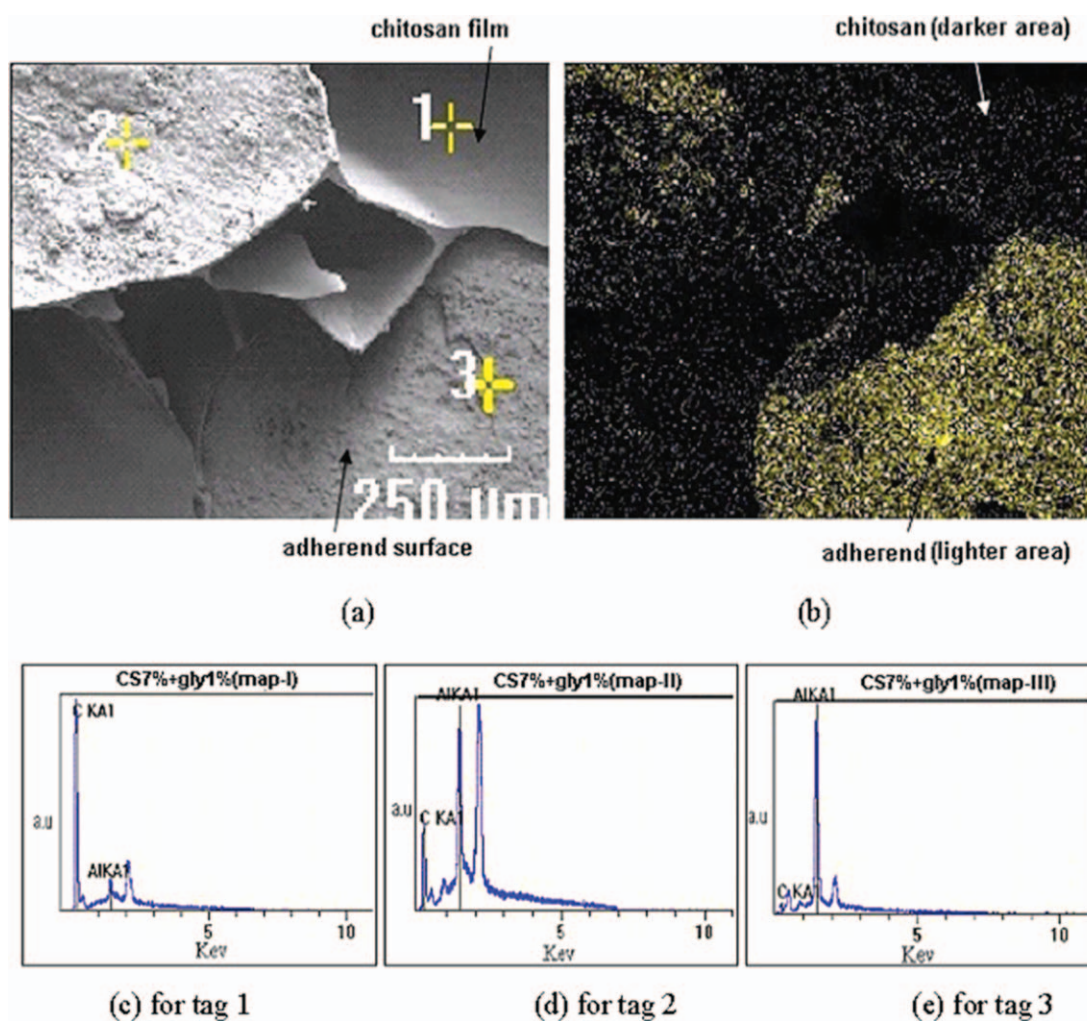


Figure 2. SEM image and elemental analysis of CS7% + gly1% crosslinked adhesive; (c) peaks of C atoms (adhesive); (d) peaks of Al and C atoms (adhesive–adherend interface); (e) peak of Al atoms (adherend). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

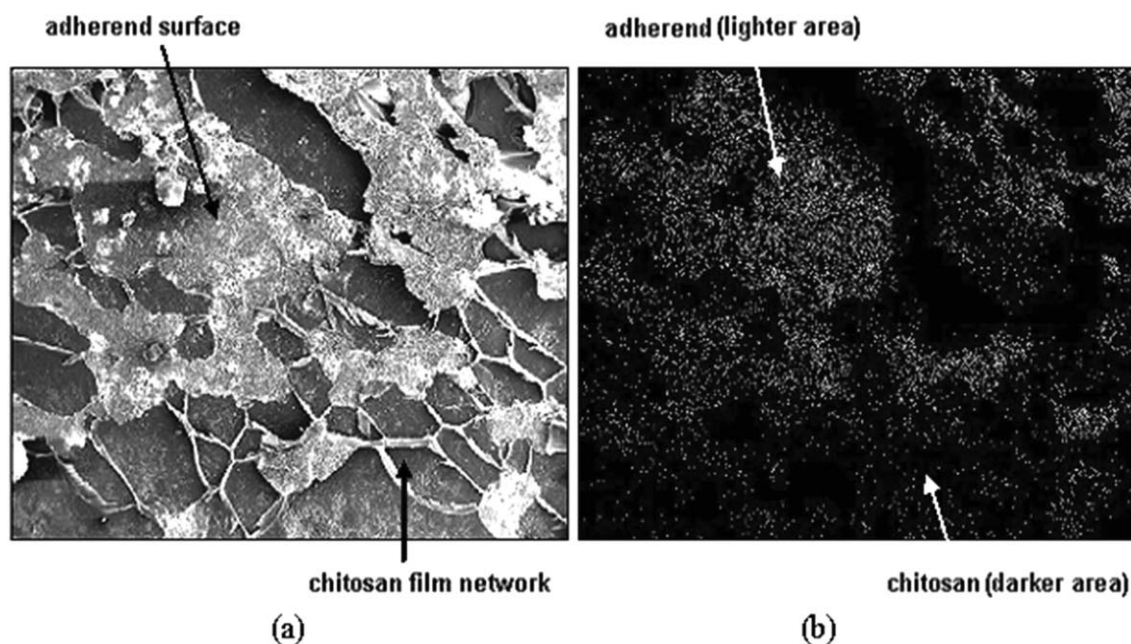


Figure 3. (a) Morphology of the failure surface of CS7% + gly1%; (b) mapping of CS7% + gly1%.

shows the peak of C atoms only (for the innermost chitosan layer), while tag 2 in Figure 2(d) explains the peak of both aluminum (traces of external adherend are clearly visible) and C atoms (cf. adhesive). Figure 2(e) of tag 3 shows aluminum atoms belonging to the internal adherend surface. Tag 2 exhibits the chitosan layer with some traces of aluminum particles. These may have been left during specimen failure. The morphology of the CS7% + Ac2% + gly1% surface of failure clearly shows a network-like structure because of glycerol presence. This may have caused the higher values for the shear strength. Figures 2(b) and 3(b) are mapping images, apparently showing a lighter region of aluminum surface and a darker region of chitosan film. This is consistent with the results shown in Figures 2(a) and 3(a).

Determination of Shear Modulus

As stated in “Shear Tests,” the shear modulus was measured only for the adhesives featuring the best shear strength. Results obtained with dried specimens are given in Table IV. Interestingly, the shear modulus was nearly the same for all the formulations (0.76 GPa on average). It corresponds to the common value used during the first stage of this procedure. This also lends credence to the results obtained with eq. (1), in which, the shear modulus was assumed for convenience to be the same for all the formulations.

Table IV. Shear Modulus of the Adhesive Specimens

Specimen	Shear's modulus (GPa) \pm SD
CS4% + AcOH1%	0.82 \pm 0.12
CS4% + AcOH1% + gly1%	0.68 \pm 0.08
CS6% + AcOH2% + gly1%	0.66 \pm 0.10
CS7% + AcOH2% + gly1%	0.77 \pm 0.12

CONCLUSION

In this study, NaOH-treated adherends exhibited the best adhesion performance among various surface treatments. The maximum shear strength obtained with formulations including only chitosan and acetic acid was 31.4 MPa with CS6%. A low citrate concentration (4 mmol/L) had a slight-positive effect on the chitosan-shear strength, but higher concentrations were shown to have a negative effect on adhesion abilities. A 1% (vol/vol) glycerol content exhibited the best plasticizing effect on 7% chitosan with 40.8 MPa. This is the most-interesting result in this study. Covalent bonding with glutaraldehyde showed a trivial effect on the shear strength of the resultant polymer.

The present study thus reveals the potential of chitosan bioadhesives for enhanced adhesion abilities on metal adherends with appropriate surface improvements. More studies are still needed to characterize these chitosan-based bioadhesives more precisely, in particular, using other adherends.

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