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Polyvinylamine Boronate Adhesion to Cellulose Hydrogel

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The adhesion of polyvinylamine to wet cellulose was significantly enhanced by the presence of pendant phenylboronic acid groups. It is proposed that adhesion results from boronate ester formation with cellulose at pH > 8. Experiments with phenol derivatized polyvinylamine gave low adhesion supporting the fact that the boronate moiety was responsible for strong adhesion to never-dried cellulose surfaces.

Introduction

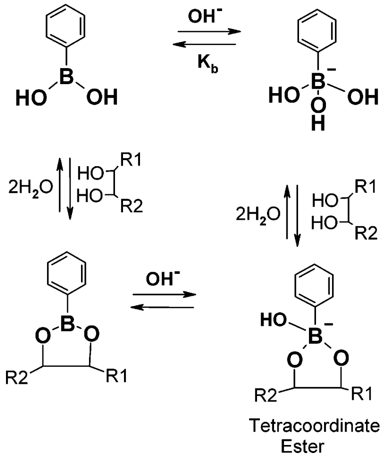
It is often difficult to form a strong adhesive joint with a wet surface, particularly when the substrate is a swollen hydrogel. Water has a high surface energy and thus effectively competes with substrate adhesive interactions. This communication describes a potential new adhesive for wet cellulose which may have other potential applications, including adhesion to wet biological tissue.

Wet cellulose is a particularly challenging substrate for adhesion because cellulose is very hydrophilic, it has little surface charge, and the hydroxyl groups are not very reactive. There exist commercial reactive polymers[1] (wet strength resins) which can form strong, water resistant adhesive bonds with cellulose provided that the joint is dried. This gives an opportunity for covalent bonds to form between the adhesive and cellulose. On the other hand, we are not aware of water-stable polymers which instantaneously form strong adhesive bonds with wet cellulose.

In this communication, we report adhesion results for wet regenerated cellulose films laminated with polyvinylamine derivatized with pendant phenylboronic acid. Our hypothesis was that the phenylboronic acid would spontaneously form covalent bonds to wet cellulose, giving strong adhesion in water. Phenylboronic acid is known to form esters with cis diols (Scheme 1),[2,3] and this interaction has been exploited for affinity chromatography[4−6] and glucose sensing.[7−9] It is generally accepted that charged boronate ($RBOH_3^-$ − top right in Scheme 1) is far more reactive than the uncharged phenylboronic groups ($RBOH_2$, top left in Scheme 1).[10,11] Therefore, pH values above 8.4, the pK_a of 4-carboxyphenylboronic acid,[12] promote ester formation. In addition, there is evidence that nearby amine groups lower the pK_a of phenylboronic acid.[13,14]

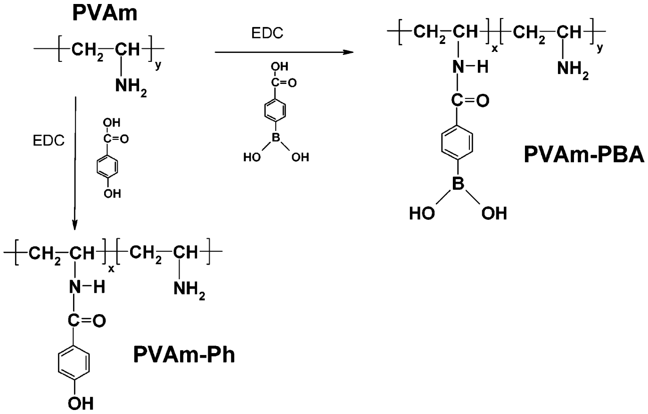
Although there is no doubt that phenylboronic acid covalently bonds to some carbohydrates, the bonds are weak, perhaps too weak for improving adhesion. For example, the equilibrium constant for phenyl boronic acid bonding to glucose at pH 9 is 26 L/mol as determined from competitive binding to a fluorescent probe. This binding constant corresponds to a free energy of −1.9 kcal/mol, which is less than a hydrogen bond.[15] Of course polymeric phenylboronates can have many simultaneous points of attachment, which leads to stable complexes with water soluble polyols.[16,17]

Scheme 1. Phenylboronic Acid Ester Formation[a]



[a] Adapted from Keita et al.[16]

Scheme 2



The goal of this work was to determine if phenylboronates could give significant practical adhesion to never-dried cellulose surfaces.

Experimental Section

Poly(*N*-vinylformamide) with a molecular weight of ca. 150 KDa was obtained from BASF Aktiengesellschaft, (Ludwigshafen, Germany) and was fully hydrolyzed to give the corresponding polyvinylamine (PVAm) homopolymer. The hydrolysis procedure has been described elsewhere,[18] and all polymer compositions were determined with proton NMR.

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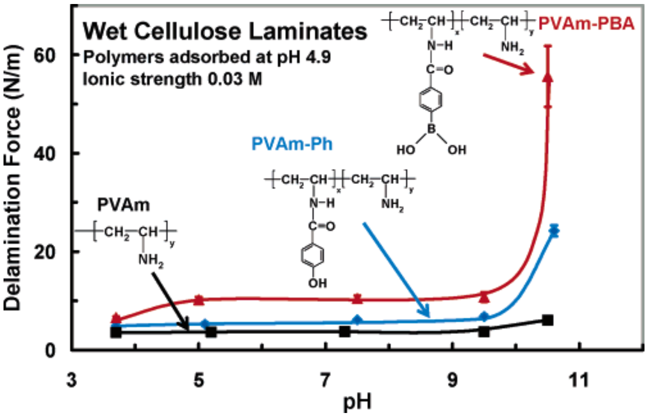

Figure 1. Forces required to delaminate wet cellulose films as functions of pH for three polyvinylamine derivatives. The phenylbornate groups gave the strongest adhesion to wet cellulose.

The PVAm was derivatized with 4-carboxyphenylboronic acid to give PVAm−PBA (Scheme 2) with 15 mol % pendant phenylboronic acid groups. All chemicals were purchased from Aldrich and were used without further purification. For the coupling reaction, 0.4 g of PVAm was dissolved in 10 mL of 0.1 M 2-morpholinoethanesulfonic acid (MES) buffer at pH 6.1, and 90 mL of 4.4 g/L 4-carboxyphenylboronic acid pH = 6.1 in the buffer and 7.5 g of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) were added, and the mixture was stirred for 120 min at 25 °C. The product was purified by dialysis against water for two weeks. Proton NMR determined that 15% of the amine groups were substituted. The corresponding phenolic polymer, PVAm−Ph (Scheme 2) was prepared the same way and the degree of substitution was 16%.

Regenerated cellulose dialysis tubing (Spectra/Por 4 product No: 132682 12kDa MWCO, Spectrum Laboratories, Inc.) was cut to the following dimensions: top membrane, 2 cm × 6 cm; and the bottom membrane, 3 cm × 6 cm. Samples were cut with the long axis in the roll direction, and only the interior surface of the tubing was used to study adhesion. Cellulose film strips were soaked in room temperature water for 24 h to remove any preservatives (glycerin). The cellulose films were then rinsed thoroughly and stored in water with a small amount of methanol (to prevent spoilage) at 4 °C.

In a typical experiment, two cellulose membranes were soaked in 0.01 wt % polymer dissolved in 0.03 M NaCl with pH adjusted to 4.9. The polymer saturated membranes were rinsed with pH 4.9 salt solution to remove unadsorbed polymer and then were soaked for 5 min in 0.03 M NaCl with the pH adjusted with HCl or NaOH to give the pH values shown in Figure 1. The films were then laminated by pressing between two blotter papers using a pressure of 1.73 MPa giving laminates with a water content of 46 ± 1.5 wt %. The delamination force was immediately measured by a 90° peeling at a peel rate of 20 mm/min. Details of the peeling apparatus and procedures have been described previously.[19,20]

Results and Discussion

Figure 1 shows the wet delamination peel force, divided by the sample width, as a function of pH for three polymers PVAm, PVAm−Ph, and PVAm−PBA. For all experiments, the polymers were adsorbed at pH 4.9 where the polymers bear a high positive charge density resulting in monolayer adsorption. The laminate joints thus contain the equivalent of two adsorbed monolayers of the polyvinylamines and derivatives.[21] We anticipate that the adsorbed polymer adopts a more expanded configuration when the pH is raised in response to the decreased charge density on polyvinylamine.

The phenylboronate modified PVAm−PBA gave the strongest laminates, particularly at pH above 9.5. This is the first polymer we have observed to give strong adhesion with never-dried cellulose laminates. By contrast, the unmodified PVAm gave very little adhesion for never-dried laminates over the pH range. Furthermore, the phenolic derivative, PVAm−Ph, gave only modest adhesion at high pH. In previous work, we showed that poly(tyrosine-*co*-lysine) polypeptides gave stronger wet adhesion to cellulose (dried and rewetted) than did polylysine homopolymer suggesting a contribution of aromatic rings to adhesion.[19]

Although it is too early to proclaim a mechanism for enhanced adhesion with phenylboronic groups, the results in Figure 1 are consistent with the tetravalent boronate ester formation with cellulose (see Scheme 1) contributing to the wet adhesion at high pH.

In conclusion, the presence of phenylboronate groups on polyvinylamine greatly enhances the adhesion of polyvinylamine to cellulose, suggesting a new family of carbohydrate-specific wet adhesives.

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