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Opportunities for Reversible Bonding at the Cellulose/Matrix Interface of Composites via Mussel-Inspired Interface Design [†]

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Abstract: With the increasing demand for recycling composite materials and re-use of fibers and matrices as new resources in the context of a circular economy, composite materials often pose problems as they form complex aggregates. The user properties of high strength and long lifetime require strong interfaces between a matrix and reinforcing fibers, while recycling would benefit from easy separation of the two phases. Therefore, the design of an interface with reversible bonding upon thermal or chemical activation may offer a good balance. In addition, the request for bio-based composites incorporating cellulose fibers should be combined with bio-inspired interface modification avoiding traditional chemical surface modification. An impressive example of reversible bonding in nature is observed in mussels and is regulated by the so-called mussel foot proteins. The latter includes dopamine as a main component that presents reversible bonding upon a change in pH. In the present work, cellulose fibers were modified with a dopamine (DA) or polydopamine (PDA) coating that was polymerized when in contact with the cellulose surface, thus providing good chemical compatibility and interaction with cellulose hydroxyl groups. The adhesive properties of the modified cellulose fibers were investigated via local adhesive measurements using atomic force microscopy and varied between strong adhesion (low pH) and weak adhesion (high pH). In parallel, the macroscale mechanical strength of the epoxy composites with modified fibers improved, while the interface adhesion of the modified fibers dropped after submersion in solutions with pH = 9.8. Based on these observations, a proof of concept for recycling of cellulose/epoxy composites and recovery of cellulose fibers is demonstrated after grinding and chemical treatment at a high pH.

Keywords: composite; interface; debonding; mussel-inspired

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1. Introduction

Composites offer excellent combinations of mechanical properties and lightweight through the crucial selection of their components, including a polymer matrix and reinforcing fibers. Their performance particularly relies on a strong interface between the fibers and matrix through maximizing the chemical interaction after surface modification [1], e.g., through silanization or alternative methods. Driven by the scarcity in resources, in parallel, a circular economy requires more proficient use of materials through the incorporation of renewables and recycling them into pure fractions. The end-of-life scenarios for cellulose-based composites are often complex as they contain multiple materials that are explicitly well integrated with each other to provide best performance, while incorporation of long cellulose fibers as a bio-based reinforcing phase provides strength and stiffness [2]. In a circular economy, however, it remains a crucial challenge how to disassemble and recycle high-performance cellulose-based composites [3].

The mechanisms for reversible bonding with a transition between strong and weak adhesion strength depending on external triggers are exploited in adhesives and bondable joints of fiber-reinforced plastics [4]: possible debonding technologies include thermally expanding microspheres, induction heating, foaming agents, or chemical degradation in combination with a variety of reversible chemistries. An impressive example of reversible bonding is observed in nature, regulated through mussel foot proteins (*Mefp*) [5], which are enriched in adhesive catechol groups of dopamine. Various synthetic polymers have been functionalized with a catechol, offering diverse adhesive, sealant, coating, or anchoring properties [6]. The reversible molecular interactions and binding mechanisms of *Mefp* were elucidated through force measurements and translated into the design of self-healing composites [7]. The general principles of mussel-inspired surface modification as a functionalization method for polymers were further exploited to introduce reinforcement, flame retardance [8], or conductivity [9]. Alternatively, modification of NiTi and Ti-V-Al wires with adhesive proteins yield better macroscale properties of composites through promotion of the interfacial adhesion [10]. The ecofriendly surface modification of bamboo fibers through self-assembly into a polydopamine layer showed better compatibility with the polybutylene succinate (PBS) matrix, opening a wide range of applications for natural fiber-reinforced composites [11]. Moreover, the good compatibility and interactions between polydopamine and polysaccharide materials [12], or the modification of cellulose with polydopamine in particular [13], have been extensively reviewed before. Therefore, new pathways should be explored for the design of functional materials and interfaces by combining these biomaterials. However, most attention at present is placed on interface compatibilization and bonding of matrices and fibers, while introducing debonding effects with dopamine has not yet been firmly investigated.

Below, a feasibility study is presented to illustrate the possibilities for reversible adhesive bonding between cellulose fibers and an epoxy resin matrix, which is promising in providing both high interface strength and debonding properties after dissolving the composite material at a suitable pH. The better recovery of modified cellulose fibers from the matrix may provide a novel method to enhance the recyclability of composite materials.

2. Materials and Methods

2.1. Cellulose Materials and Modification

The cellulose fibers originated from Kraft hardwood pulp with cellulose fibers having diameters of 20 to 25 µm. The pulp fibers were modified through deposition of a coating layer with dopamine (Cell-DA) or polydopamine (Cell-PDA), according to Figure 1. The dopamine hydrochloride powder was purchased from Merck and dissolved in water at a concentration of 1 mg/mL in the presence of a buffer solution at a neutral pH (Cell-DA) or an alkaline pH (Cell-PDA). A 2 wt.% suspension of the cellulose pulp was added into the solution and mixed overnight under continuous stirring on a magnetic plate at room temperature. The slurry was subsequently washed with water and filtered for recovery of the modified fibers, which were further dried in a hot-air oven at 60 °C for 30 min.

The samples of Cell-DA were obtained after mixing under neutral pH = 7.2 conditions while maintaining the non-polymerized dopamine structure. The latter allows the assembly of the hydroxyl groups towards the cellulose surface through hydrogen bonding and the accessibility of the primary amine groups (Figure 1a). The interaction mechanisms between dopamine and cellulose have been reviewed before [13] and include absorption and physical interaction through hydrogen bonding.

The assembled dopamine layer was converted into a polymerized coating on the cellulose surface of the Cell-PDA samples, introduced through oxidative self-polymerization of dopamine under known weak alkaline conditions at pH = 8.5 in 10 mM tris(hydroxymethyl)-aminomethane (TRIS) buffer. During the reaction, a polymerized layer formed, composed of individual PDA particles deposited onto the cellulose surface (Figure 1b). The success of the polymerization reaction was visually observed through the black color of the solution.

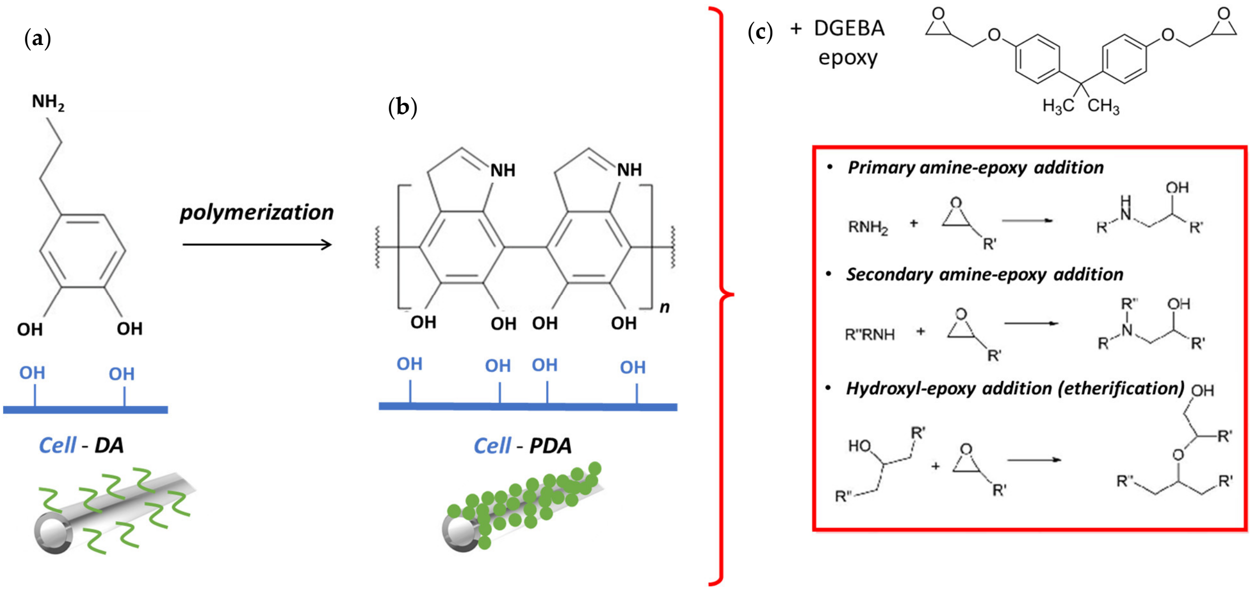

Figure 1. Cellulose fiber modification and formulation of composites with epoxy matrix: (**a**) physical layer deposit with dopamine layer (Cell-DA), (**b**) coating with polydopamine (Cell-PDA), and (**c**) mixing of modified cellulose fibers in epoxy matrix.

2.2. Composite Formulation

A composite was formulated by mixing 20 wt.% and 30 wt.% Cell, Cell-DA, or Cell-PDA fibers (*w*/*w*) in an epoxy matrix and casting the blend as a film. The sample codes are as follows: epoxy+Cell20, epoxy+Cell30, epoxy+Cell-DA20, epoxy+Cell-DA30, epoxy+Cell-PDA20, and epoxy+Cell-PDA30. The epoxy resin was formulated by mixing bisphenol A diglycidyl ether or DGEBA (EP101, Resion Resin Technology, Moordrecht, The Netherlands) with an amine hardener composed of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (30 to 50 wt.%) and m-phenylene bis(methylamine) (10 to 30 wt.% (EP113, Resion Resin Technology, Moordrecht, The Netherlands). The resin and hardener were mixed in a 1:1 stoichiometric ratio as calculated from the epoxy equivalent weight (EEW) = 200 g/eq and amine hydrogen equivalent weight (AHEW) = 100 g/eq, followed by the incorporation of the cellulose fibers during mixing for 5 min.

The composite formulations were cast as thin films (2 mm) in an aluminum dish and thermally cured overnight at 80 °C in a hot circulating air oven. During curing, the presence of primary amine, secondary amine, and hydroxyl groups aided in the crosslinking reaction of the epoxy resin (Figure 1c), with the highest reactivity recorded for primary amine addition.

2.3. Characterization Methods

The intrinsic adhesive properties of DA under different pH conditions towards a cellulose fiber were probed through AFM adhesion measurements using a chemically modified AFM tip (Si_3N_4). The tip was functionalized by grafting of DA and submersed in buffer solutions of pH = 4 and pH = 9.5. The tip was lowered at constant rate until it made contact under a maximum load of 30 nN with a native cellulose fiber that was fixated on a glass support. The force–displacement curve was recorded during approach and retraction of the cantilever, allowing the calculation of the adhesive force from the characteristic point of separation between the tip and the surface. The measurements were repeated 20 times in order to draw a histogram and determine the intrinsic adhesive forces.

The tensile strength of the cellulose/epoxy composites was determined based on standard mechanical testing of composite films (ASTM D3039). Microscopic images were taken using a TM3000 tabletop scanning electron microscope (Hitachi, Krefeld, Germany).

The fiber recovery was determined after mechanical grinding and dissolution of the epoxy films in an aqueous buffer solution at pH = 4 and pH = 9.5, followed by centrifugation and weight determination of the recovered fiber fraction after oven drying.

3. Results and Discussion

3.1. Reversible Adhesive Properties towards Cellulose Fibers

The fundamentals for reversible bonding at the fiber/matrix interface of composites rely on the intrinsic interactions between both components under different chemical environments. The interactions between the functionalized AFM tip and cellulose fibers were probed in aqueous buffer solutions at pH = 4 and pH = 9.5 to identify the effects of the functional groups in dopamine under hydrolyzed conditions (dopa) or oxidized conditions (dopa-quinone), according to the set-up in Figure 2a. Similar experiments for determination of single-molecule adhesion of mussel-inspired adhesives towards metal or TiO_2 surfaces had previously been conducted [14], indicating reversible bonding of dopamine depending on pH. Indeed, also for the adhesive contact with a cellulose fiber surface, two force ranges were detected with weak adhesion (300 ± 20 pN) at a high pH and strong adhesion (775 ± 40 pN) at a low pH (Figure 2b). Whereas metal complexation plays a role in the contact with inorganic substrates, the interactions through hydrogen bonding with cellulose fiber surfaces at neutral to low pH are efficiently demonstrated. The switch in adhesion of dopamine towards cellulose fibers at a high pH raises opportunities for reversible bonding [5].

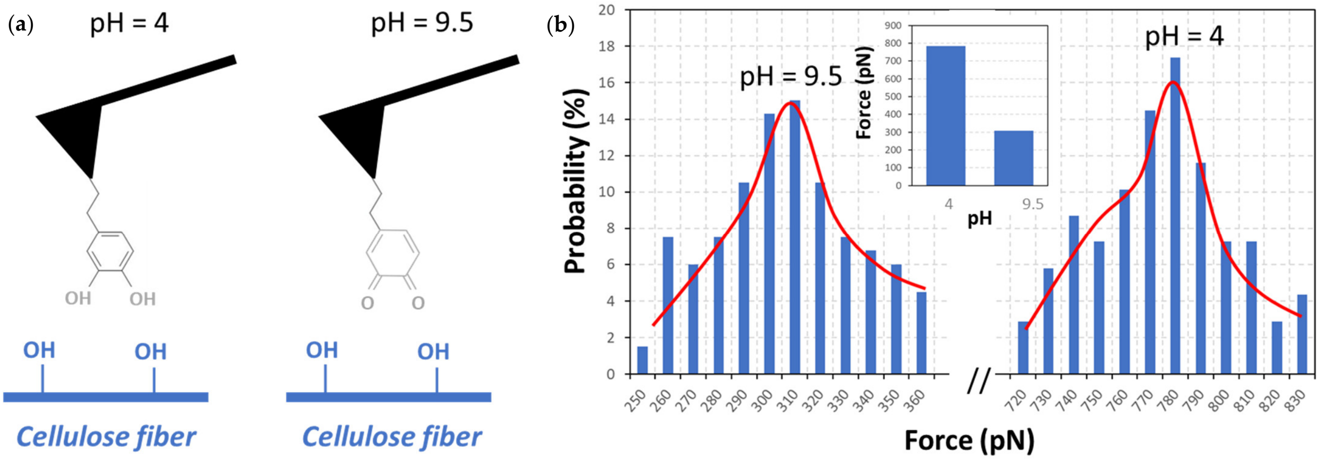

Figure 2. Adhesive measurements of DA molecules towards cellulose fibers under different pH conditions through approach and retraction experiment with modified AFM tip: (**a**) test set-up with positioning of modified AFM tip and native cellulose fiber, and (**b**) distribution of adhesive forces measured during retraction at pH = 4 and pH = 9.5.

3.2. Composite Properties

The effects of surface modification of cellulose fibers on the mechanical properties of the epoxy composites were evaluated by measuring the maximum tensile strength at break (Figure 3a) for different composite compositions. The interface modification clearly improved the strength properties of the composites relatively to unmodified fibers, with a higher mechanical strength for epoxy composites reinforced with Cell-DA fibers relatively to those reinforced with Cell-PDA fibers, which was confirmed for both fiber concentrations of 20 wt.% and 30 wt.%. The high strength of the epoxy+Cell-DA can be attributed either to the efficient hydrogen bonding at the interface or good accessibility of free primary amine that aids in crosslinking with the epoxy resin. The surface features of the modified fibers are visualized as thread-like deposits for Cell-DA (Figure 3b), or as arranged particles for Cell-PDA (Figure 3c), in parallel with known morphologies for polydopamine coatings [12].

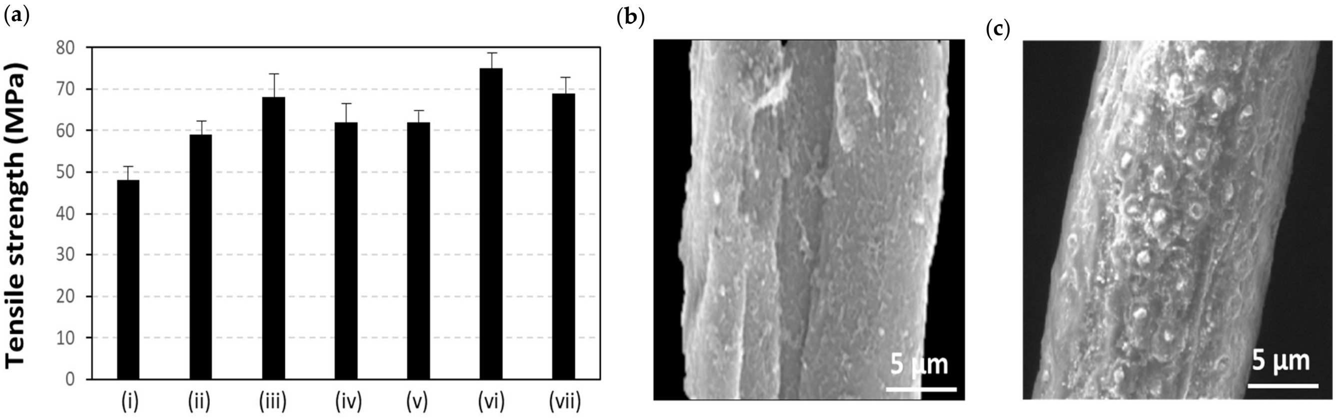

Figure 3. Evaluation of composite properties with modified cellulose fibers: (**a**) maximum tensile strength for (i) epoxy matrix, (ii) epoxy+Cell20, (iii) epoxy+Cell-DA20, (iv) epoxy+Cell-PDA20, (v) epoxy+Cell30, (vi) epoxy+Cell-DA30, and (vii) epoxy+Cell-PDA30; (**b**) SEM picture of modified cellulose fiber Cell-DA20; and (**c**) SEM picture of modified cellulose fiber Cell-PDA20.

3.3. Composite Debonding

The recovery of cellulose fibers after grinding and chemical dissolution at pH = 9.5 was quantified via weight measurement of the recovered fibers, together with qualitative imaging of the recovered fibers from the epoxy composites with 20 wt.% Cell, Cell-DA, or Cell-PDA (Figure 4). After dissolution, the unmodified fibers remained clogged within the epoxy matrix, while the Cell-PDA fibers were only partially recovered with large fractions of the epoxy matrix remaining sticking at the cellulose surface. Better fiber recovery was noticed for the modified Cell-DA fibers, with >50% recovery yield and smooth surface topography of the recovered fibers. The DA layer provides reversible interaction near the cellulose surface and allows the detachment of the epoxy. The experiments with dissolution at pH = 4 did not yield favorable recovery, with fibers being equally clogged in the epoxy matrix.

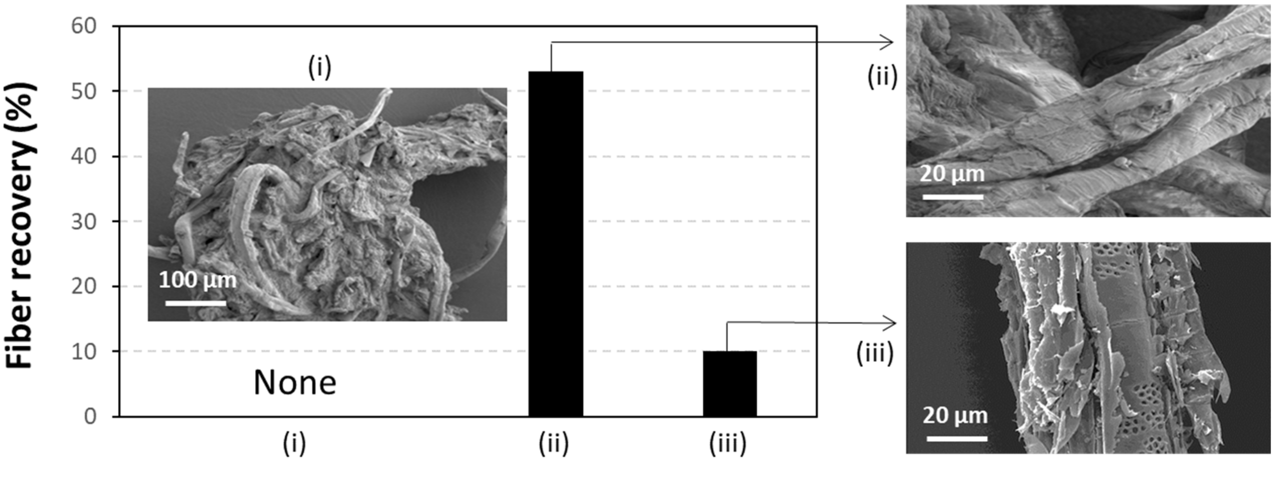

Figure 4. Experimental observation for fiber recovery and respective morphologies after mechanical grinding and chemically dissolving epoxy/cellulose composites in a buffer solution at pH = 9.5: (i) epoxy+Cell20, (ii) epoxy+Cell-DA20, and (iii) epoxy+Cell-PDA20.

4. Conclusions

This feasibility study demonstrated a route for the design of composite interfaces with reversible bonding between cellulose fibers and epoxy resin, improving both interface strength and debonding. The idea for bio-based adhesive surface modification of fibers through mussel-inspired functional groups was transferred into a synthetic material.

The intrinsic adhesive bonding between catechol groups and cellulose fibers was pH dependent, with strong adhesion at a low pH and weak adhesion at a high pH, in parallel with the oxidation of the catechol groups into quinone. The nanoscale adhesion could be employed for surface modification of cellulose fibers and tuning the macroscale interaction with an epoxy resin, by comparing the interface characteristics after surface modification of fibers with a dopamine (DA) or polydopamine (PDA) coating. The interaction with DA maximized the strength in the composite material while simultaneously allowing for the better recovery of fibers after grinding and solvent treatment at a high pH.

The results are promising in enhancing the recyclability of composite materials, where the separation between fibers and matrix constituents is often a hurdle when aligning composite designs within a circular economy. Only one case study for thermoset materials is presented here, which, in future research, should be further broadened towards thermoplastic composites.

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