

# BIO-BASED WATER-REPELLENT COATING FOR WOOD

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## Abstract

Wood is one of the oldest building materials and is currently becoming increasingly popular again due to the present growth in awareness in society regarding environmental issues. Wood is hygroscopic and porous, i.e. it not only absorbs moisture from the atmosphere, but also actively and quickly sucks up large amounts of water through its capillary system particularly via the end grain. This leads to dimensional changes, but above all the wood becomes susceptible to rot. As a result, for many applications wood needs to be protected from moisture. Besides a large number of well-established petrochemical products, there are still some traditional, natural finishes available. The most prominent ones are linseed oil and tung oil. Due to their large content of linoleic acid, both harden in air via autooxidation. However, to achieve a decent degree of protection, both oils need to be applied in multiple layers and the final coating requires at least several days to harden completely. In addition, linseed oil interferes with the food chain and tung oil is said to be toxic in some publications.

We have recently developed an alternative coating for wood based on chitosan, which can be obtained from food-industry waste. The coating is applied from an aqueous solution and adheres nicely to wood surfaces due to the structural similarity of chitosan and cellulose. The polymerised film reliably seals the end-grain of wood against liquid water. Currently, the polymerisation requires the films to be heated to 70 °C in an oven, but a method for UV curing is being worked on.

## Keywords

Chitosan, bio-based coating, water-repellent, biopolymer

## 1 INTRODUCTION

Wood is an abundant, renewable, and highly versatile natural material that has been used by humans for thousands of years [1]. Notably, it is responsible for the majority of captured carbon in the environment above the earth's surface [2]. Being a natural resource, wood is widely used as a building material because of its easy processability and good mechanical properties, as well as its aesthetic appeal [3]. However, despite its many advantages, wood as a building material presents major challenges. The chemical structure of wood renders it susceptible to biodegradation, which is primarily caused by fungal infestation [4], bacteria [5], or insect-induced decay [6]. Moreover, wood surfaces are prone to greying when exposed to sunlight, a consequence of UV-induced lignin degradation [7]. In terms of sustainability, the focus is therefore also shifting to previously unusable waste materials. Among other things, the natural polymer chitin stands out as a source of raw materials. It remains largely unused as a waste product of the fishing industry in the form of crustacean shells and is available in large quantities. After glucose, chitin is the most abundant naturally occurring polysaccharide, with a mass of more than ten gigatonnes constantly present in the biosphere [8]. The largest proportion of chitin is contained in the structural components of the exoskeletons of arthropods or in the cell walls of fungi [9]. Chitosan is derived from chitin by partial *N*-deacetylation and has favourable properties, such as solubility in dilute acids and improved modifiability due to the amino function.

Herein we present an alternative approach to wood coatings that combines a number of positive effects and desired properties. The coating based on chitosan, a waste material from the food industry, can be applied from aqueous solution and polymerises on wood surfaces into water insoluble, hydrophobic, and stain-protecting films.

## 2 METHODOLOGY

### Materials

Chitosan flakes (200–600 mPa·s, 0.5% in 0.5% acetic acid at 20 °C) were purchased from TCI Deutschland GmbH and lyophilised to a constant weight. The degree of acetylation was determined by elemental analysis to be 11.99%. Aqueous hydrochloric acid (1 mol·L<sup>-1</sup>) and sodium hydroxide were purchased from Sigma Aldrich. Itaconic acid was purchased from Alfa Aesar. Potassium peroxydisulphate (PPS) was purchased from Thermo Scientific. Planed and cut wood samples (beech and spruce) were purchased from Rocholl GmbH.

### Methods

Milling of the chitosan was performed with a Fritsch Pulverisette 14 Premium Line. For this purpose, a sieve insert with a 0.2 mm hole size was selected. The elemental analyses for the determination of the degree of acetylation (DA) of the finely milled and dried chitosan were performed using a Vario EL Cube (Elementar Analysensysteme GmbH, Langensfeld, Germany). The DA was calculated from the mass ratio between the detected carbon and nitrogen atoms  $w_{C/N}$  following the procedure of dos Santos et al. [10] For the chitosan, the average of a quadruplicate determination gave a degree of deacetylation of 11.99%. Being a high-performance dispersing unit, the T 25 digital ULTRA-TURRAX® from IKA, Germany, was used to disperse the solutions, which in some cases were highly viscous. The solutions were sheared at 25000 rpm. Contact angle measurements were performed on a Krüss G-1 contact angle meter. For this purpose, water drops were placed in focus on a coated wood sample with the use of a syringe, and the contact angle was determined over the span of 1–3 seconds. The samples were each measured in triplicate, and the average values calculated. NMR mouse measurements were performed on a MOUSE® model PM5 (Magritek GmbH, Aachen, Germany) and a minispec analyser (Bruker Corporation, Billerica, USA). The coated wood samples were placed directly on the sample table, and measured with 512 scans each in 200 µm increments to a measurement depth of 2000 µm. The used frequency was 18.15 MHz at 1000 T2 echoes, with a 30 µs echo time and 0.5 s recycle delay.

**Preparation of 2.5 wt.% chitosan itaconate solutions.** 250.0 mmol (32.525 g) of itaconic acid was dissolved in 500 mL of deionized water. The exact concentration of the solution was determined by potentiometric titration with a 0.1 M sodium hydroxide solution. To prepare a monosodium itaconate solution, 125 mmol (5.0 g, 0.5 equiv.) of sodium hydroxide was added to the itaconic acid solution and the mixture was stirred until the sodium hydroxide had dissolved. A second solution was prepared by dissolving 42.163 g of chitosan (1 equiv. of free amino groups based on the amount of itaconic acid) in 220 mL of 1 M hydrochloric acid (1 equiv. relative to the amount of free amino groups in chitosan) and 924 mL of demineralized water. The two solutions were mixed using an IKA T25 digital ULTRA-TURRAX disperser at 25000 rpm for about 1–2 min to obtain a final concentration of 2.5 wt.% solution. A viscous, colourless solution was obtained. Due to the limited shelf life of chitosan itaconate solutions, they were freshly prepared for each experiment, and used on the same day.

**Preparation of chitosan itaconate films.** 12.0 mmol of potassium peroxydisulphate (PPS, 5 mol% relative to the free amine groups of chitosan) was added to the above 2.5 wt% chitosan itaconate solutions. Then, 500 µL of the solution was applied to polyimide-coated glass slides, which were subsequently dried at 60 °C for 24 h.

**Preparation of chitosan itaconate-coated wood samples.** The coating solution was prepared by adding 12.0 mmol of PPS (5 mol% relative to the free amine groups of chitosan) to the obtained chitosan itaconate solutions. The solution (120 mL·m<sup>-2</sup>) was then smoothly applied to a sample wood (beech or spruce) using a bristle brush. Immediately after applying the coating solution, the wood samples were placed in an oven at 60 °C for 24 h. After that, the samples were stored at 23 °C and 50% relative humidity for 48 h before being used for further investigations.

**Cross-cut & pull-off test.** The test was performed according to DIN ISO 2409:2020-12 [11]. A grid was scratched into beech and spruce wood samples coated with 2.5 wt% chitosan itaconate. Adhesive tape was applied to the cut grid with a finger under light pressure. The tape was then removed with a smooth peeling motion.

**Stain test.** To investigate the stain resistance of the coated wood surfaces, 10 mL of mayonnaise was dropped onto a wood surface (beech or spruce) coated with chitosan itaconate. This was allowed to soak in for 10 minutes, and then wiped off with a sponge and soapy water. Finally, the wood surfaces were dried at 80 °C.

### 3 RESULTS

#### Preparation of the aqueous chitosan itaconate solution

To prepare the chitosan itaconate, chitosan was first dissolved in hydrochloric acid and then mixed with a solution of monosodium itaconate Fig. 1. Upon mixing, sodium chloride formed as a by-product.

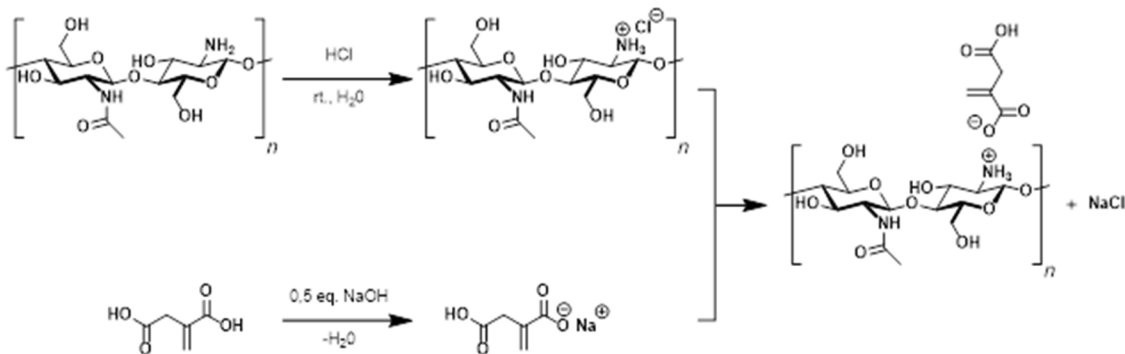


Fig. 1 Procedure for the preparation of chitosan itaconate.

#### Application and film properties on wood

The properties of the chitosan itaconate coatings were assessed on spruce and beech wood samples. For this purpose, the wood samples were treated with chitosan itaconate solution. The solutions were evenly distributed across the whole surface with a brush. The samples were placed in an oven until they were completely dry, after which the surface of the wood was found to be water-repellent.

The layer thickness can be determined by single-sided proton nuclear magnetic resonance, which records a depth profile of the proton density. Changes in the proton density over the depth after application of the coating can be used to determine the penetration depth and thickness. The coating thickness was found to be approx. 400–600  $\mu\text{m}$  for beech and 800–1000  $\mu\text{m}$  for spruce (Tab. 1).

Tab. 1 Thickness of the chitosan itaconate coating on beech and spruce wood.

Coating thickness of chitosan itaconate-coated wood [ $\mu\text{m}$ ]	
Beech	Spruce
400–600	800–1000

The surface adhesion of the chitosan itaconate films was tested using the cross-cut & pull-off test. It can be observed that the chitosan itaconate coating does not detach from the wood surface and no additional damage to the coating can be seen after pulling the tape off (Fig. 2).

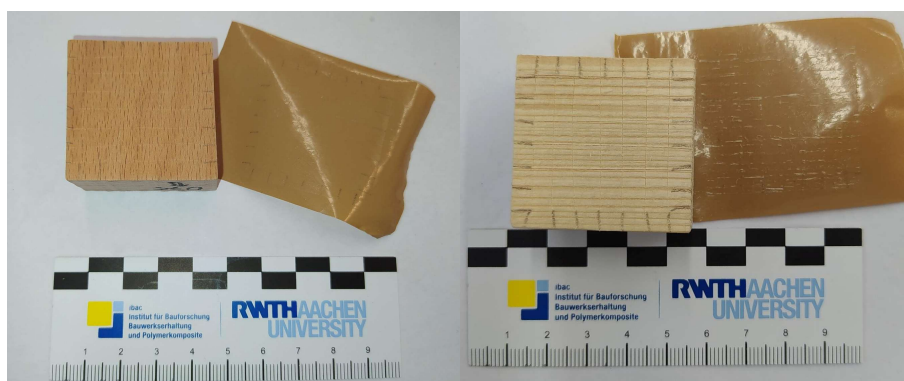


Fig. 2 Cross-cut & pull-off test of chitosan itaconate-coated beech wood (l.) and spruce wood (r.) samples.

When drops of water were placed on the surface, these did not spread on the surface or seep into the capillary system, both of which were behaviours observed for uncoated wood. The contact angle of water on the coated wood samples exceeded  $90^\circ$  in all cases, which indicates a hydrophobic surface (Fig. 3).

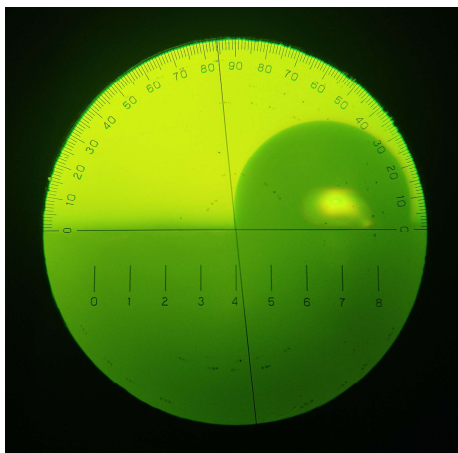


Fig. 3 Contact angle of a water droplet on chitosan-itaconate coated wood.

To test the stain resistance of the present chitosan-itaconate films, mayonnaise was selected and applied to coated and uncoated beech surfaces Fig. 4. A direct comparison between the uncoated Fig. 4-A and coated wood surface Fig. 4-B showed that the mayonnaise was absorbed directly into the wood. The wood shows a dark discoloration directly around the stain. The mayonnaise was removed from the wood surface after 10 minutes with a moistened cleaning cloth. After cleaning the surfaces, it was found that in the case of the untreated wood, the mayonnaise was completely absorbed and left stains Fig. 4-C.

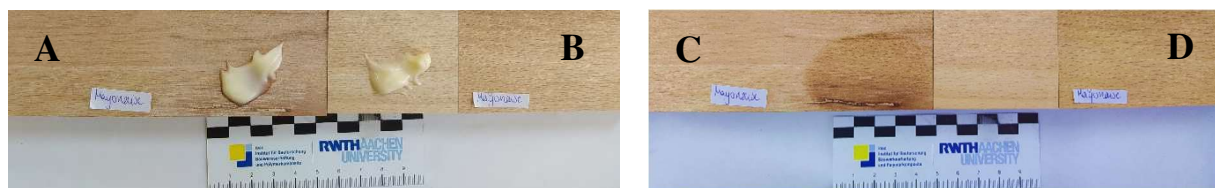


Fig. 4 Staining by mayonnaise on untreated wood (A) and wood coated with chitosan itaconate (B) directly after application, and after ten minutes of soaking, washing off and drying on untreated (C) and treated wood (D).

## 4 DISCUSSION

The solubilisation of chitosan in water generally occurs via the protonation of its free amine groups. As described in a previous article, this requires a sufficiently strong acid with a  $pK_A < 5$  [12]. Although the first carboxyl group in itaconic acid fulfils this requirement, chitosan does not dissolve in itaconic acid solutions. However, in hydrochloric acid solution, chitosan is susceptible to acid-catalysed cleavage of the acetal bond, [13] which is why special care was taken to ensure an equimolar ratio of hydrochloric acid to the free amino groups of chitosan [12]. To reduce the residence time in the hydrochloric acid solution, the solutions were combined as soon as possible after preparation. Upon mixing, sodium chloride forms as a by-product, which can be selectively removed by dialysis. This is, however, not necessary for this application, and was, therefore, not performed in the present study.

The cross-cut test shows that the coating adheres strongly to the wood surface. With consideration to the single-sided proton nuclear magnetic resonance measurements, it can be assumed that the strong adhesion of the coating to the wood is achieved by anchoring in the material lying below the surface of the wood. However, since the aqueous chitosan itaconate solution applied initially is able to cause the wood to swell, ingress into the volume below the surface is highly likely and thus the reported coating thickness includes this penetration depth of the coating in the wood. It is also observed that the amplitudes in beech wood are generally higher than in spruce wood. This is due to the higher density of beech wood, which directly relates to the proton density.

Oily liquids often cause dark stains on wooden surfaces, and such stains are difficult to remove. The chitosan coating completely protected the wood from the oily mayonnaise and prevented any kind of staining. Fig. 4-D.

## 5 CONCLUSION

Chitosan itaconate solutions can be polymerised on wood to form clear and transparent, approx. 400–1000  $\mu\text{m}$  thick films depending on the species, although parts of such films appear to have formed in the volume below the surface. Ion pairing between the two polyelectrolytes makes the polymerised coatings water insoluble and renders the surface hydrophobic. This is advantageous for wood coatings, since moisture is a major factor in the proliferation of mould or fungi. Thus, a hydrophobic coating can significantly prolong the wood's lifespan, and protect it from biological degradation. The coating was found to

- adhere very well to the wood surface,
- anchor in the material below the surface of the wood sample as indicated by NMR,
- hydrophobise the surface and seal the end grains of the wood effectively,
- provide excellent protection against oily liquids.

Currently, the polymerisation requires the films to be heated to 70 °C in an oven, but a method for UV curing is being worked on. Although the source substances themselves are all biodegradable, the biodegradability of the film still needs to be tested in detail.

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