HYDROXYL ACCESSIBILITY AS A TRANSFERABLE DESCRIPTOR IN MODIFIED WOOD PROPERTY PREDICTION

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Annotation: Chemical, thermal and impregnation-based modification of wood are studied in separate literatures, each with its own process descriptor: weight percentage gain, mass loss, or retention. These record what was done to the timber rather than what changed inside the cell wall, and do not convert between routes. This work argues that the concentration of accessible hydroxyl groups, determined by deuterium exchange in a dynamic vapour sorption apparatus, offers a route-independent chemical descriptor on a single scale. Published evidence is collated to establish where it accounts for hygroscopic behaviour and where it does not, and leave-one-route-out validation is proposed as the test of transferability. The outcome is a minimum reporting set that would make modification data poolable.

Keywords: wood modification; hydroxyl accessibility; deuterium exchange; dynamic vapour sorption; equilibrium moisture content.

Introduction

Modified wood is not one material but a family. Acetylation substitutes cell-wall hydroxyls, furfurylation fills the wall with a polymerised furanic phase, thermal treatment rearranges the wall polymers, and impregnation deposits an agent that may not enter the wall at all. All four raise service performance, and all four are reported using descriptors belonging to the process rather than the material.

The consequence is that results do not accumulate. A weight percentage gain of twenty per cent describes acetyl groups bonded to the wall in one study and salt deposited in lumina in another. Because the descriptors are incommensurable, a model fitted to one route cannot be applied to another, and the dataset for any single route stays too small to support more than interpolation.

The problem is the absence of a descriptor that is chemical rather than procedural, measurable by one method across all routes, and mechanistically tied to the properties of interest. The aim is to evaluate accessible hydroxyl concentration against those criteria and to specify how it would be validated, continuing two earlier lines of the author's work.

Literature review

Reviews of modification technology retain route-specific descriptors throughout, each being the natural bookkeeping quantity for its own route. Measurement of hydroxyl accessibility, by contrast, has matured into something route-independent. Deuterium exchange in a dynamic vapour sorption apparatus, where hydroxyl hydrogen is replaced by deuterium from D_2O vapour and the mass increase measured gravimetrically, gives the concentration of hydroxyls reachable by water. Protocol parameters for sample mass, exposure time and drying regime are established, which makes values from different laboratories comparable.

The relationship between hydroxyl accessibility and hygroscopicity is strong within a route and weaker across routes. Both decline with treatment severity, yet where both are measured on the same specimens the correlation is looser than the mechanism predicts. Work separating extraction from thermal treatment showed that removing amorphous carbohydrates lowers sorption through site loss, whereas heating acts additionally through matrix annealing. Wood-water physics has long held the mechanical constraint of the wall on swelling to be a distinct contribution.

Data-driven prediction has meanwhile entered materials chemistry, including flame-retardant systems [8], and feature attribution makes such models interpretable [4]. The limiting factor in wood applications is the feature set, not the algorithm: models built on process parameters inherit their non-transferability, as encountered in the author's earlier work.

Methodology

This paper is analytical rather than experimental. Studies were collected from Scopus, Web of Science and ScienceDirect, retaining those reporting accessible hydroxyl concentration by deuterium exchange together with at least one property measured on the same material; studies giving only weight percentage gain or mass loss were excluded. Values were normalised to millimoles of accessible hydroxyl per gram of oven-dry unmodified mass, so that bulking does not distort the comparison, and paired with equilibrium moisture content, anti-swelling efficiency or strength retention.

The framework treats accessible hydroxyl concentration as a mediating variable rather than a direct predictor: process settings act on the descriptor, the descriptor acts on the property. A model expressing property as a function of descriptor, species and a residual route term is fitted and the residual term tested. If route stays significant once the descriptor is included, a second variable is needed. Analysis of covariance provides the test, feature attribution the diagnosis [4].

Transferability is assessed by leave-one-route-out validation: a model is fitted on all routes except one and evaluated on the excluded route. This is stricter than the random splits usual in this literature, because it asks whether the descriptor carries meaning beyond the dataset in which it was measured.

Analysis and results

The routes divide by what their descriptor records. Acetylation, furfurylation and resin impregnation report weight percentage gain, which counts added mass without separating substitution from bulking; thermal modification reports mass loss, a net figure over competing reactions; impregnation reports retention, which does not show whether the agent entered the wall or stayed in the lumina; densification reports compression ratio, which records deformation but no new bonding. Three observations follow.

First, accessible hydroxyl concentration is measurable on the same scale for every route, whereas no other quantity is: weight percentage gain is undefined for thermal modification, mass loss for acetylation, retention only for impregnation. The descriptor therefore satisfies route independence, a necessary condition for pooling.

Second, the descriptor is chemically interpretable in a way process quantities are not: a decrease corresponds to a definite event, whether substitution, shielding or hemicellulose removal. It therefore serves as a mechanistic hypothesis, not only as a regression input.

Third, and decisively, the descriptor is not sufficient alone. A residual effect of route on hygroscopic response persists after hydroxyl accessibility is accounted for, attributable to the mechanical constraint the modified matrix imposes on swelling [1, 2]. Any framework built on this descriptor must carry a second variable for matrix constraint; sorption hysteresis area and the bulking coefficient are the best candidates, since both come from measurements already made.

For published data to be poolable at all, a minimum reporting set is required. The following items are sufficient and are all obtainable within a standard characterisation programme:

– accessible hydroxyl concentration by deuterium exchange, with the protocol parameters stated;

– oven-dry mass and volume before and after treatment, giving weight percentage gain and bulking coefficient;

– species and initial density per specimen, not as a batch average;

– sorption isotherm in both directions, so that hysteresis can be quantified;

– one mechanical property on the same material, since stability gains and strength losses are coupled.

Adopting this set costs little: most quantities are already measured, and what is usually missing is the deuterium exchange determination and specimen-level reporting. Averaging over a batch removes exactly the variance a regression needs to separate density from treatment.

Conclusions

Four conclusions follow. Accessible hydroxyl concentration measured by deuterium exchange is the only descriptor currently available that applies on one scale to chemical, thermal, impregnation and densification routes, and it is chemically interpretable rather than procedural. It is nevertheless insufficient alone, because a route-dependent residual persists in hygroscopic response and reflects the mechanical constraint of the modified matrix. A second descriptor for that constraint, derived from sorption hysteresis or the bulking coefficient, is therefore required. Leave-one-route-out validation, not random splitting, is the appropriate test of whether a model has learned chemistry or memorised a dataset.

Two recommendations follow. Groups reporting modification studies should include the minimum set above, since the marginal cost is small and the gain in comparability substantial. Groups building predictive models should treat hydroxyl accessibility as a mediating variable rather than one entry in a flat feature list, because that structure is what lets a model fitted on one route be applied to another.

The framework will next be applied to fast-growing Populus species of Central Asia, whose compositional baseline and response to thermal modification are being established.

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