Polypyrrole
Additional functions to bio-based façades

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Abstract

Due to the crisis of 2008 the construction and real estate market became more demand-driven. Architects, builders and developers are looking for high-quality solutions for the realization of sustainable buildings. Supplying SMEs experience an increasing demand for bio-based materials with lower environmental impact and additional functionality including smart functions. The development of sustainable products with higher added value is required to increase the innovation potential of the building and construction industries.

Polypyrrole is a biopolymer with very interesting and yet relatively unexplored features for construction. By applying PPY to bio-based carrier materials, like wood, bamboo or bio-composites, environmentally friendly building products can be realized with multiple features. In this paper an inventory will be given of potential (smart) functions that can be added to bio-based building materials treated with PPY. Functions discussed will be the protection against micro-organisms and UV-radiation. It will allow the realization of biological multifunctional building façades without using environmentally harmful substances.

Finally the adding of (smart) functions will be discussed as strategy to introduce new bio-based building components to the market. Here they will have to compete with existing products already known by the different building professionals.

Key words: Polypyrrole, bio-based building materials, market introduction strategy, potential applications for PPY

1. Introduction

There is an increasing demand for bio-based materials with lower environmental impact and with additional functionality. After the crisis the construction and real estate market became more demand-driven. It is now more obvious that sustainable buildings do not only contribute to objectives in the field of responsible social business. Sustainable buildings are also more easily rentable, generally have lower operating costs and provide improved comfort, health and productivity [1]. Architects, builders and developers are therefore looking for quality solutions for the realization of sustainable buildings. The supplying SMEs realize that they should respond to this, but do not really know how to do that. These companies realize that the development of sustainable products with more added values is not anymore a choice but necessary. The need for them is created by the increasing globalization and the increasing competition from low-wage nations around bulk products. The development of more quality products, make it an obvious way for these suppliers to achieve a competitive position. In case of failure shrinkage and further substantial job losses might be otherwise the result. The companies also feel the pressure of increasing regulation. In the area of e.g. environment performance or fire safety increasing demands are faced with the consequence that there is hardly any new material on the market that meets all these requirements. That has the effect that a number of current building products often do not meet the required combination of all requirements arising from existing regulations.

An important aspect of biomaterials is the environmental performance, which need to be protected against external impacts like UV-radiation or degradation by micro-organisms. These degradation factors frequently cause higher maintenance costs and limit the functionality as well as the aesthetics in building skins. Adequate sustainable solutions are therefore wanted especially since the use of toxic substances (biocides) is being increasingly restricted by legal regulations [2]. In coatings heavy metals may no longer be used. Many countries prevent the use of CCA (copper-chromium-arsenic) and the use of impregnated wood is more and more restricted [3]. Because there are (still) not sufficient sustainable solutions, the use of indigenous renewable resources such as wood is limited. Without technically and economically viable alternatives the ambitions have to be adapted to the technological available possibilities. This happens despite the fact that different governments are trying to encourage the use of sustainably produced materials [5].

The uniqueness of the use of PPY is that it combines two strategies of decoupling: environmentally friendly protection of bio-based materials (less environmental impact per kg of material) and cascading. These aspects are relevant in the context of the reduction of material usage while increasing added value in order to achieve sufficient economic growth, which is currently aimed for in the EU [5]. The combination of multiple functions into a single biobased material can be a construction related option. With the aid of cascading more different bio-based materials can be used on a higher quality level [6][6][7]. Construction industry will be more and more motivated to deploy products with extra value based on the principle innovation-by-reduction-while-adding. The question however arises how can we build with environmentally friendly materials and achieve at the same time additional technical functions at reasonable costs? The biological origin is no longer enough to survive economically as supplying business in Europe. This paper intends to describe the potential additional functions of PPY in general and highlighting the building and construction related applications of with PPY treated wood.

2. Potential functions

2.1 What is polypyrrole?

Pyrrole was first detected by F. F. Runge in 1834 [8], as a constituent of coal tar. Later it was isolated from the pyrrolysate of bones. The name comes from the Greek pyrros (“fiery”), from the colour reaction used to detect it (figure1), since red is the colour that it imparts to wood when moistened with hydrochloric acid [9]. The concentration of natural occurring pyrrole in substances of biological origin is in most cases relatively low. This fact stimulated the development of chemical synthesis processes to improve the reaction yield. There are several processes to synthesize pyrrole like e.g. the Knorr or Hantzsch synthesis [10]. Pyrrole is also made from furan, which is made from furfural extracted from the polysaccharide hemicellulose. Since hemicellulose is a "crop residue" and a wood component no displacement of the food market takes place. The properties of pyrrole make it a frequently occurring molecule in many biological compounds like e.g. chlorophyll of heme [11], vitamin B12 [12], or bilirubin [13]. Secondary metabolites which include pyrroles are e.g. lamellarin or makaluvamine M or prodigiosin [14] substances with a biological activity. Due to their biological activity pyrrole based substances are therefore frequently found in therapeutically drugs with e.g. antimalaria activity [15] or frequently used

Figure 1 Dried pyrrole on wood which was impregnated with HCl

as anti-cancer agents [16]. Although pyrroles are often occurring in nature they can be poisonous in higher concentrations [17].

Polypyrrole (PPY) is formed by pyrrole, which is a heterocyclic molecule. In the beginning PPY was besides other polymers mainly known for its electrical conductivity. In 2000 Heeger, MacDiarmid and Shirakawa were awarded the Nobel Prize in Chemistry for their pioneering work on conductive polymers including PPY [18]. There is a large number of properties of the biopolymer PPY, which make this compound interesting for various technical applications.

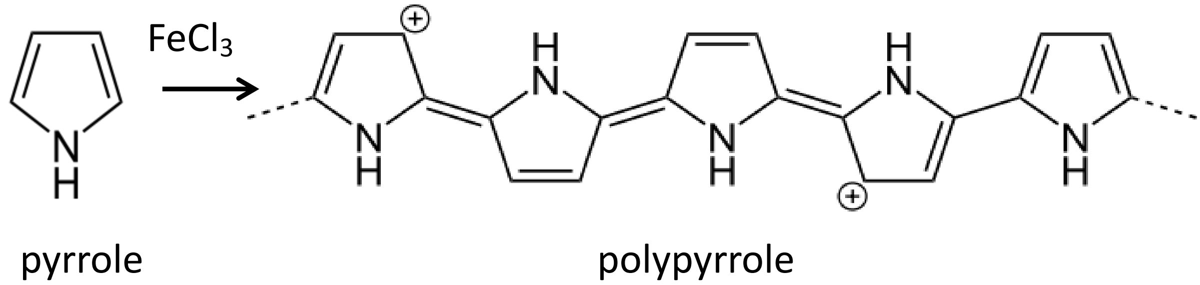

Figure 2 Reaction schema of PPY with an oxidizing agent

Pyrroles react with oxidisers, like e.g. ferric chloride ($FeCl_3$) [19] and form PPY (figure 2). Polypyrrole has a good biocompatibility [20] and is not harmful for the environment [21]. Wang *et al.* (2004) thoroughly evaluated PPY using a series of toxicity tests according to ISO 10993 and ASTM F1748-82 standards with encouraging results for the use in technical applications. PPY is a polymeric chemical compound that consists of 2,5-linked pyrrole units. The process of oxidation (p-doping) is used to create conductive PPY [22] but also (n-doping) by chemical or electrochemical means exist however mostly used in research since oxygen has to be excluded from reaction. There are publications assessing the role of n-doping for CO_2 capturing e.g. [23].
An interesting property is the possibility of colour change of PPY. It can change from yellow to black depending on the state of oxidation or reduction and reaction conditions [24].

2.2 Scientific state-of-the-art

Research on PPY is frequently carried out because of the potential smart functions which are triggering researchers and users in different fields. PPY has therefore become by far the most studied conducting polymer and is also potentially interesting for smart building applications.

Figure3: Detail of a polypyrrole treated façade of spruce (Picea abies).

One of the most dynamic fields for PPY are medical applications which is indicated by an increasing number of research reports and publications. The combination of the potential responsivity and biocompatibility make PPY a candidate par excellence for advanced biopolymer research. DNA-PPY biosensors for the detection of micro-organisms [25] are used to identify contaminations in an early stage whereas other biosensors will be available to determine e.g. glucose in a more efficient and cheaper way [26]. The creation of functional properties can be realized using the electrically addressable potential (in vivo electric fields) for e.g. tissue/cell support (e.g. bone re-growth and wound healing) [27][28]. New implants suitable for neural prosthetics [29], drug delivery [30] and electromechanical devices for "artificial muscles"[31][32] are other medical applications. Biologically functional macromolecules like proteins, polysaccharides or living cells form in combination with PPY valuable biological/medical research areas potentially contributing to a new generation of smart biomaterials [33][34].

Many non-medical research fields focus on the electrical properties of PPY. Conductivity is still one of the most assessed properties of PPY. In several publications topics related to different energy aspects are discussed e.g. energy storage as well energy production or transport. The ability to produce high-efficiency rechargeable batteries [35][36], electro catalysis for the activation of hydrogen [37], creation of anti-static materials [38], infra-red polarizers [39] or the use in solar panels instead of ITO glass [40] are further examples of high-tech energy related research issues using PPY or PPY derived substances.

Its radiation absorbing properties qualify PPY for radar absorbing coatings and therefore as a potential candidate for military stealth research [41] or protection in the field of electromagnetic interferences [42] properties also potentially useful for building related applications. Other properties useful for the construction- and building industry can be found e.g. in the production of UV-stable coatings. Recently Yazhini and Prabu (2015) published a study on flame-retardant and UV-protection properties of cotton fabric based on a PPY–nanocomposite [43], Eversdijk and Sailer described the in-situ polymerization of PPY on wood resulting in improved -properties against UV- and fungal degradation [44] (figure 3).
In connection with steel and metal protection the corrosion inhibition properties of PPY were frequently assessed e.g. [45] and recently reviewed by Deshpande *et al* (2014) [46].
Sasso *et al.* (2011) [47] give an overview on biobased materials like wood and cellulose derivatives describing several possibilities to create additional functionalities. The good biocompatibility, the possibilities to interact with other biopolymers and textiles [48] stimulate research efforts to combine PPY with wood, paper or other celluloses/lignin related materials [49][50].
In this context fire resistance and thermal stability of PPY treated biomaterials become an increasingly important issue which is reflected in recent publications [51][52].

3. Building- and construction applications

3.1 Technical properties of polypyrroles

As mentioned, PPY possesses potential properties useful for building applications. For the protective use at building skins several properties should be available at the same time. In order to keep and protect the esthetics performance good UV absorption, long term mechanical resistance, thermal stability as well as colour stability are prerequisites for a functional protective (film forming) layer. Resistance against leaching and protection against micro-organisms or other biological degradation factors is relevant in combination with different carrier materials. The UV-stability and resistance against biological degradation of PPY treated wood, as well as the leaching behaviour is well tested. In contrast to applications which are requiring long-term oxidation or reduction properties, the use as an UV-protective agent does not need extra protection, and is stable under outdoor conditions. PPY has the potential to be used as an adjustable window tint ("smart window”). It can be used as a window-pane, whose tone color and transparency can be changed by applying a voltage [53][54]. Thin films of PPY show in the oxidized state the colour brown to black and in the reduced state yellow to green. Only some voltage has to be applied to change the oxidation state. Application would technically be possible in principle, but it will probably suffer from the lack of a long-term stability [55]. This problem probably applies equally in applications requiring properties of PPY which are sensitive to acids, bases, oxidizing or reducing substances, anions, cations, inorganic or organic gases. In order to protect the functionality, e.g. conductivity or colour effects from degradation, additional protection for PPY needs to be developed.

3.2 Process of wood treatment

As a starting point to introduce potential smart functions to biobased construction materials, a dedicated treatment technology was developed to treat timber with PPY together with a Dutch wood processing company[1]. As a starting point a simple treatment process for façade elements was chosen providing the (basic) functionalities required for typical outdoor applications. The ability of pyrrole to penetrate wood and react with biopolymers like e.g. lignin or celluloses allows a treatment process using an in-situ polymerisation with an oxidizing agent (figure5). During the polymerization process a

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dark thin functional PPY layer is created on the wood. The functionality comprises an UV- stable bio protective coating with a good adhesion to the wood surface and hardly any leaching. The long term stability enables the creation of the basic properties for smart composites providing more functions with higher added value.

The process is basically characterised by the use of a simple 2-step process (figure 4) starting with dipping the wood in pyrrole dissolved a water solution. In this first step it is important to create a good penetration of the pyrrole into the wood matrix to ensure a good adhesion of the PPY coating. In a second step the pyrrole treated wood is dipped into the oxidizing agent relevant for the polymerization. After some time a dark PPY functional layer is created on the wood. In order to achieve a reproducible quality of the treatment a very high degree of control of the process parameters is required.

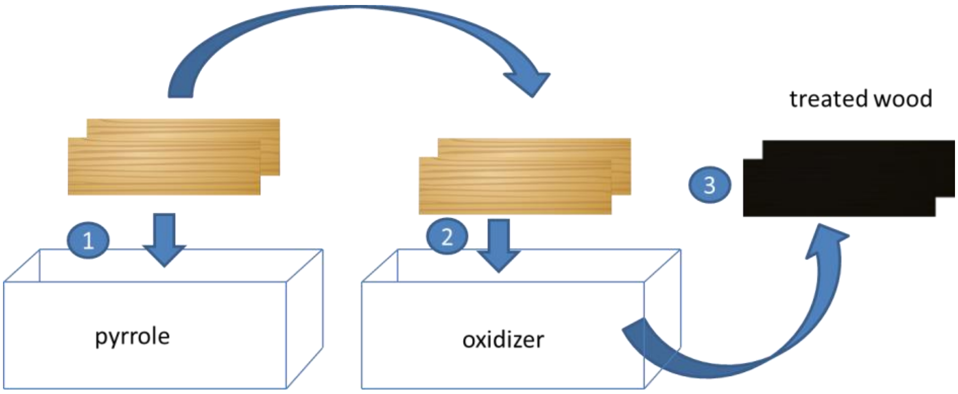

Figure 4: In situ polymerization process

3.3 Performance and environmental aspects

The performance of such a PPY coating depends on several factors like wood specie, wood surface and / or treatment conditions. After the polymerization has taken place a dark UV-stable coating is created (Figure 5). During initial in- and outdoor UV-tests hardly any leaching or visible changes were noticed. These results suggest that the surface will remain esthetically stable after several years of exposure, which allows the creation of wooden façade elements with long term robustness creating reduced maintenance and consequently less costs. The performance against degrading micro-organisms is assessed in several laboratory and outdoor tests with exposure at facades as well as in ground contact. Initial test results show that the PPY treated wood is difficult degradable for fungi although fungi are able to grow on the treated wood. This is indicating that the protection mechanism is not based on toxicity but rather on other protection mechanisms. Through the ion exchange properties of PPY, cells of potential degrading micro-organisms could be affected in a way that they are not able to degrade the PPY treated wood. Similar effects are described for antifouling in membranes [56]. If this will be verified the performance of PPY as a nontoxic biological prevention system is strongly depending on the treatment conditions and requires a good process and quality control. The water and moister regime of PPY treated wood does not seem to influence degradation, since PPY did not reduce the moisture content significantly compared to untreated wood. PPY treated wood created only slightly water repellent effects.

Figure 5: Polypyrrole treatment at the façade of a pilot

A critical factor in the PPY application is the sensitivity of the process. The reaction of the pyrrole is e.g. strongly dependent on the wood species used. This means that for each wood species the specific process parameters have to be developed. Furthermore the whole treatment process has to be controlled exactly since slight changes in the pyrrole solution caused e.g. by impurities put in by the timber influence the properties of the treatment. This can cause e.g. leaching of the polypyrrols or influence on the required colour or other properties. Especially in the process upscaling these factors have to be considered.

4. Market introduction strategies

The combination of two biobased materials with first a relative high potential to create a higher value and second the potential of a relative huge bulk market is asking for an adapted market introduction strategy. The starting point is the acceptance of the market and the technology level available in the producing industry. This allows initiating the production with a relatively simple process to serve existing markets for bulk materials (figure 6) which are in fact e.g. applicants of treated wood for functional facades. Practice shows that the process development can go along with this application. In the meantime additional properties like optimised fire resistance and process optimization can be realized opening the door for further additional smart functionalities. This approach creates the option for the realisation of an initial production within a relative short time to market without hampering further developments.

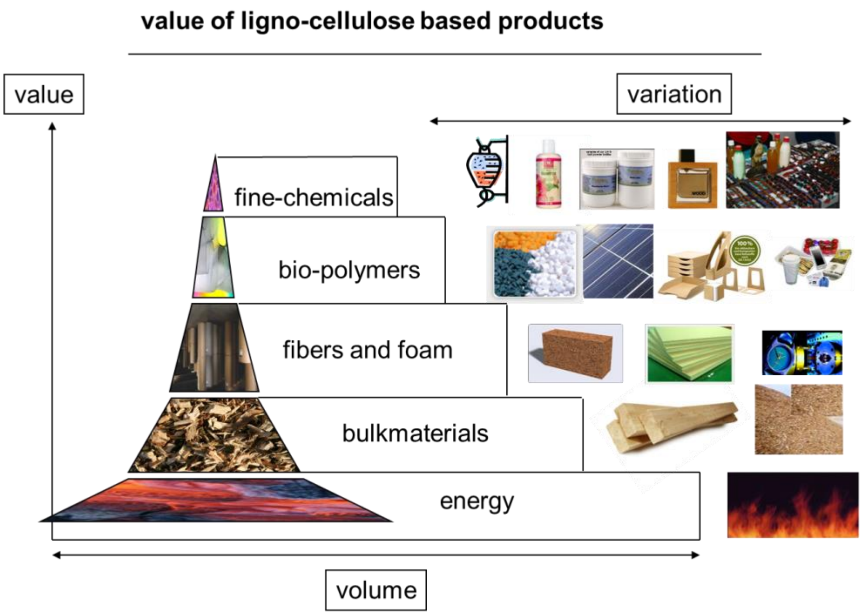

Figure 6: Value pyramid, - indicating the value relation of biopolymers and biobased carrier materials

5. Conclusions

Although there is a long research history in relation to pyrrole and PPY it took a long time from initial knowledge about PPY to realize practical applications in general, not only in construction. In the course of time, more and more properties of PPY became known. The application of PPY however did mostly not go above laboratory scale. Reasons for that are mainly based on difficulties in upscaling the processes which require a good control of the treatment process and lack of long term stability for high end applications relying on oxidation/reduction processes. Recently progress is visible in the technically most advanced area which is found in medical applications. Improved treatment processes and adapted application fields allow an increasing use of PPY in practice.

For building skins the basic functionalities like protection against UV, biodegradation or improved penetration and fixation are realized in a pilot, in which wood was treated with PPY. The in situ polymerisation with the related improvement of properties and relatively low costs of the process make this manner of wood treatment suitable for building skins. Further properties have been already introduced although the long-term stability has to be proven for these additional characteristics of with PPY treated timber. In the future medical research can be a valuable source of inspiration to create additional value for smart biobased materials in the building industry. It requires however multidisciplinary research and creativity to transmit existing solutions for smart building skins.

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