6th WORKSHOP

Green Chemistry and Nanotechnologies in Polymer Chemistry

July 15-17, 2015

Polytechnic Institute of Bragança | PCT-TMAD Brigantia EcoPark

Bragança · Portugal

WORKSHOP PROCEEDINGS

Eds. - M. F. Barreiro, O. Ferreira, A.I. Pereira

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Following the success of the previous five Workshops held in Pardubice (CZ) 2010, Riga (LV) 2011, Cracow (PL) 2012, Pisa (IT) 2013 and San Sebastian (SP) 2014, the **6th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry** took place in Bragança (PT) on 15-17 July 2015.

The conference aimed at exploring and discussing the latest trends in research and technology covering the following topics:

- Bio-based monomers and polymers
- Bio-based blends, composites and hybrids
- Bionanofillers and nanocomposites
- Nanostructured polymeric materials
- Nano- and microencapsulation
- Advanced functional polymers
- Biodegradation, LCA, safety and environmental issues

We hope that you have enjoyed the Conference and the hospitality of Bragança.

The Organizing Committee

Temporary exhibition at **Centro de Arte Contemporânea Graça Morais, Bragança** (Photo by Pedro Silva)

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P41. MELAMINE-FORMALDEHYDE RESINS MODIFIED WITH GLYCEROL

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Introduction

Melamine-formaldehyde resins represent an important class of aminoplastic resin and are made by the reaction of formaldehyde with mainly melamine.

Melamine-formaldehyde resins are used as adhesives for plywood and particleboard for use in humid and exterior conditions and are also used for the impregnation of paper sheets in the production of self-adhesive overlays for the surface of wood-based panel products and of self-adhesive laminates [1].

During the last decade the interest in using raw materials based on bio-renewable resources for synthetic polymers and composite materials increased largely [2]. Recent developments in eco-efficient bio-based adhesives for wood bonding include the use of tannins, lignin, proteins, and carbohydrate derived natural binders.

The main goal of this work is the partial replacement of melamine in melamine-formaldehyde resins by glycerol, yielding a stable resin with potential for use in impregnated paper based laminates.

Experimental

Resin synthesis

Modified resin was synthesized by substitution of 7.5 wt% of the melamine content by glycerol in four different stages, namely: Stage A) at the beginning of the synthesis; Stage B) after total solubilisation of melamine; Stage C) at the beginning of condensation phase; Stage D) at the end of the reaction.

Viscosity

The kinematic viscosity was determined with a flow cup viscometer according to the DIN standard cup at 25 ºC. (DIN EN ISO 2431) In this method, the time required for a sample of liquid resin to flow from a cup of defined volume is measured and used as an estimate of the viscous behaviour of the tested liquid.

Paper impregnation and pressing

Papers were impregnated with modified MF resin through impregnation process, where the papers were soaked in the modified melamine resin, and then dried at 130 ºC.

Impregnated sheets are laid with the desire number of plies and submitted to a hot pressing, where the rage of pressures varies from 5.5 to 10.3 MPa, with the layers consolidates at temperatures of 120-150 ºC.

Results and discussion

In comparison with the melamine standard the modified resins show the same translucent aspect as the standard.

However, the melamine formaldehyde resin is considered usable for impregnate papers if its flow time is less than 25 s (measured by the DIN cup) and it remains translucent. The initial tests show that the addition of glycerol, without the use of additives, reduced significantly storage stability of all modified resins whereby it will be need to add additives to the resin in order to increase the storage time.
When used as impregnation resins, the modified resins show a comparable performance to the standard resin in terms of penetration and distribution in the paper matrix.
Standardized surface quality tests were used to characterize the performance of the HPL, and it was verified that the modified melamine resin show better performance in terms of resistance to immersion un boiling water and resistance to water vapour.

Conclusions

Because of the promising performance of glycerol-modified resins, further tests will be performed using stabilization agents in order to increase the stability of the resin.
Other tests will be performance, to check the technical performance of the new resins.

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P49. NATURAL ADDITIVES FOR REDUCING FORMALDEHYDE EMISSIONS IN UREA-FORMALDEHYDE RESINS

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Introduction

Wood has followed mankind throughout its evolution. The development of science has led to the emergence of wood based products, whose main raw material is wood waste/residues and a binder system usually called resin or adhesive. One of the most important classes of wood based panels is particleboard, which is mainly produced with urea-formaldehyde (UF) resins.

UF resins represent 80% of the total production of amino resins due to their various advantages, such as good performance, low cost and high reactivity. However, these resins and their products emit formaldehyde, both due to the presence of non-reacted formaldehyde and due to the hydrolytic degradation of the polymer [1, 2].

In 2004, this problem became even more pertinent due to the reclassification of formaldehyde by the International Agency of Research on Cancer (IARC) as a carcinogenic to humans, Group 1 [3]. This way, methods such as lowering the molar ratio of formaldehyde to urea (F/U) of the resins, one of the most used at the industry level, have become insufficient to meet the market requirements [4]. Thus, new efforts have been taken to deal with this challenge. The use of formaldehyde scavengers both in the synthesis of resins and in the production of the wood-based panels has been one of the most studied methods [5].

In the past 10 years, the concept of bioadhesives has emerged, which, in a very simplified way, is based in the incorporation of bio molecules in the synthesis of resins [6-9] or in the production of the particleboards or, in a more radical approach, in the synthesis of a bio-based resin, as, for instance, soy or casein, among others [10].

The main goal of this work is the incorporation of soy or, more specifically, soy protein, either directly in the production of wood panels or in the synthesis of urea-formaldehyde resins, used in the production of panels.

Experimental

Soy protein solution

The soy protein solution was obtained through the dissolution/dispersion of the soy protein in water at 70 ºC under agitation, adding afterwards 3 ml of 50 wt% sodium hydroxide solution and keeping it for 1 h.

Resin preparation

The resins were synthesized according to the so-called alkaline-acidic process, which consists of three steps: the methylolation under alkaline conditions, followed by the condensation reaction under acidic conditions and the addition of the final urea. The incorporation of the soy protein, as a solution (13,5 wt%), was performed in each of the three steps, to analyse the effect of the addition phase. Percentages of 5%, 10% e 15% of soy protein incorporation were studied, based on the total quantity of resin.

Resin properties determination

Viscosity, pH and solids content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at 25 ºC. The resin pH was measured using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 ºC.

Production of particleboard panels

The production process of the particleboards is divided into three steps: blending of wood particles with the adhesive system, mat forming and pressing. The panels are composed by three layers: two face and one core layers. In an initial approach, particleboard panels were produced only with a commercial resin, supplied by the company *Euroresinas – Indústrias Químicas S.A.*, and 5%, 10% and 15% of soy protein powder was added to wood particles, during the blending process of the core layer. Three-layer particleboard were hand-formed in an aluminium container with 220x220x80 mm and boards were then pressed at 190 ºC during 150 s in a laboratory scale hot-press controlled by computer. In a second approach, panels were produced with the resins synthesized with the incorporation of soy, which were subjected to the same pressing conditions and the resin was used in both layers.

Board testing

After pressing, boards were tested according to European standards. The internal bond strength was determined according to NP EN 319 (tensile strength perpendicular to the plane of the board) and formaldehyde content was determined according to NP EN 120 (perforator method).

Results and discussion

This work consisted of two stages: addition of soy protein powder in the production process of the panels and synthesis of UF resins with addition of soy protein as a solution for later manufacture of panels.
In the first stage, where soy protein powder was mixed with the core layer particles, it was observed that, in fact, an increase in the percentage of added soy protein leads to a slight decrease in the formaldehyde content from the particleboard, without any significant change in its properties, namely the IB (Figure 1).

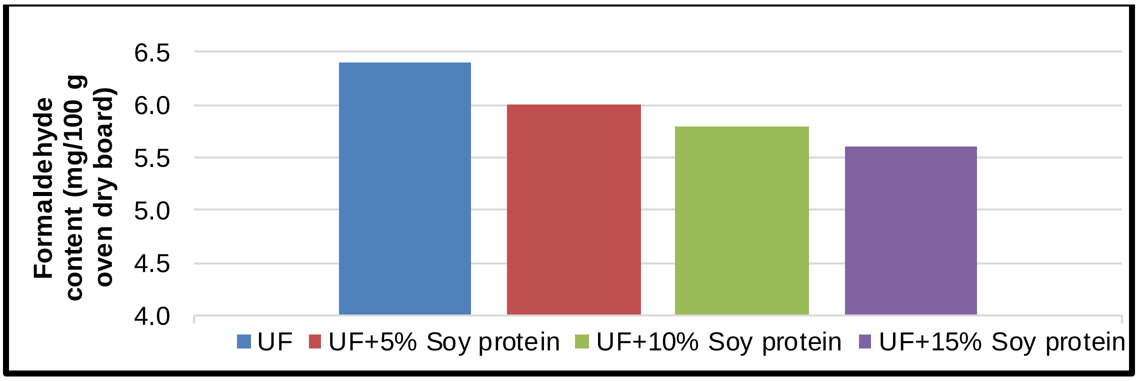

Fig. 1. Formaldehyde content (mg/100 g oven dry board) of particleboards produced with soy protein powder in the core layer

The second part was the synthesis of a UF resin (control) and 3 resins with soy protein and the difference between these was the phase of the addition of the soy protein solution (methylolation, condensation or final step). It was observed that, when the addition of soy protein is performed in the methylolation step, there is a small reduction in the formaldehyde content when compared to the panels produced with the other two resins (Figure 2). Once again, the mechanical properties of the particleboard did not experience any significant changes.

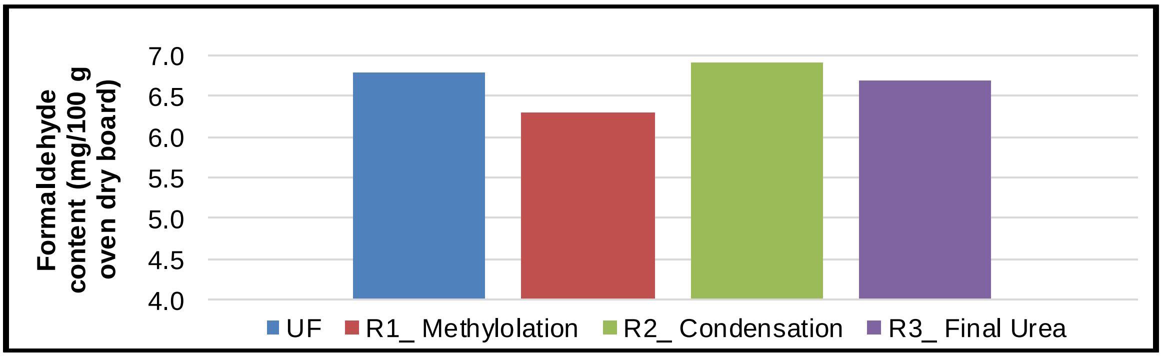

Fig. 2. Formaldehyde content (mg/100 g oven dry board) from particleboards produced with UF resin with soy protein solution in the two layers

Conclusion

With this work, we can conclude that the incorporation of soy protein can contribute to a decrease in the formaldehyde content of particleboard panels and also that it is possible to produce UF resins with the incorporation of natural compounds, namely soy protein, without changing their production process, as well as without any significant change in their properties.

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