Chitosan: a Novel Bio-based and Bio-degradable Formaldehyde Scavenger

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Introduction

The most important bonding adhesive in wood-based panels industry is the urea formaldehyde (UF) resin since last decades. This is mainly attributed to its adequate adhesive characteristic, good stability, lower cost and fast curing (Hemmila et al. 2017). The International Agency for Research on Cancer (IARC) officially classified formaldehyde as a “definite human carcinogen” for nasopharyngeal cancer in 2004 and for leukemia in 2012. Furthermore, formaldehyde has been classified under hazard classes Carcinogenicity/Category 1B and Mutagenicity/Category 2 in the 6th adaptation to technical progress of the classification, labelling and packaging regulation. Therfore, the further reduction in the formaldehyde emission (FE) from wood-based products made by formaldehyde-based adhesives to a level which is as close as possible to that of wood or wood particles has been taking place gradually for many years (Salthammer et al. 2010; Pizzi and Mittal 2013). Therefore, a lot of efforts have been made toward minimizing formaldehyde emission of wood-based panels (WBPs) or replacing with formaldehyde-free adhesives (Shalbafan et al. 2017).

Among all of the techniques used for the reduction of FE, developing of formaldehyde scavengers (FS) show a great potential in the industry to cope with the abovementioned limitations (Hassannejad et al. 2020). FS absorbs formaldehyde either by chemical linkage (e.g. urea, melamine, tannins etc.) or physical interaction (e.g. active carbon etc.). Moreover, most of the scavengers used have a fossil-based origin (Ebnesajjad and Ebnesajjad 2013). However, due to the growing awareness on environmental issues as well as the scarcity and increase in price of fossil resources, particular attention and efforts have been given to the bio-based and bio-degradable materials and technologies (Duan et al. 2015; Hassannejad et al. 2020). In this context, the development of bio-based formaldehyde scavenger gained a lot of interest in recent years for the wood-based panels industries.

Recently, the authors have developed and patented a novel bio-based scavengers for reducing of FE based on chitosan (Shalbafan et al. 2020). Chitosan is a natural, renewable, biodegradable, environmental friendly and a liner amino polysaccharide that is derived from chitin, the second most abundant polysaccharide in nature after cellulose. The scavenger was further modified to enhance its absorbency by nanosizing technology. The efficiency of developed FS was investigated with the production of medium density fiberboard (MDF).

Materials and Methods

Un-resinated wood fiber supplied from Kimia Chob Ltd, Iran were used to produce MDF. Wood fibers were a mixture of hardwoods species, mainly poplar and willow. Urea formaldehyde (12%) resin (Amol Resin Ltd., Iran) with a solid content of 62% and ammonium chloride (1%) as hardener were used as adhesive. Target density and thickness of the panels was kept constant at 750 kg/m^3 and 10 mm, respectively. The press pressure, temperature and time were 3 MPa,180 ˚C and 200 seconds, respectively.

Low molecular weight chitosan of 100 kDa, deacetylation degree of 90% and viscosity of 20cps was obtained from Sigma-Aldrich, Munich, Germany. Glacial acetic acid (Sigma-Aldrich, Munich, Germany)

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with 99.85% assay and distilled water were used to prepare all the solutions. The amount of chitosan as FS used was 1, 2 and 3% based on the solid content of UF resin. The amount of nano-chitosan was 1% based on solid content of the resin.

Formaldehyde emission from MDF samples were measured according to desiccator method (ISO12460-4). The board specimens (150 × 50 × 10 mm^3) were placed in a glass desiccator around the outside of a container of distilled water. After a specified time (24-hours) the concentration of formaldehyde in the distilled water was determined. That concentration, in mg/L, is termed the desiccator value of the board. The number of samples (n=9) was determined in accordance to sum of the areas of the ends, sides and faces that were close to 1800 cm^2. The samples were conditioned at 65±3% RH and 20±2˚C for one week prior to testing. Two repetition was performed for each panel variation. The third repetition only performed if the differences between two measurements was more than 20%.

Results and discussion

The influence of chitosan as FS on the formaldehyde emission (FE) of MDF board is illustrated in Figure 1. The results showed that the FE is significantly decreased with addition of chitosan particles. The higher the FS, the lower the emitted formaldehyde from the MDF board. FE for the reference sample was about 0.54 mg/L while it was reach to below 0.25 mg/L in panels having 3% FS. A reduction of about 55% in FE of MDF board obtained due to the absorbance capacity of chitosan. Chitosan has a lot of functional groups (e.g. amine and hydroxile) in its structure that can be linked with the free and hydrolozed formaldehdyde (Shalbafan et al. 2020). Formaldehyde emission values obtained were compared to those of JIS A 5908 & 5905 standards to get an impression of the board class. Reference panel belongs to the F** which is more or less equivalent to European E1 class. Panels produced with 3% bio-scavenger can be categorized into the class F**** which is more or less equivalent to European SE0. It is worth mentioning that the emission level of F**** is close to the emission of sloid untreated wood.

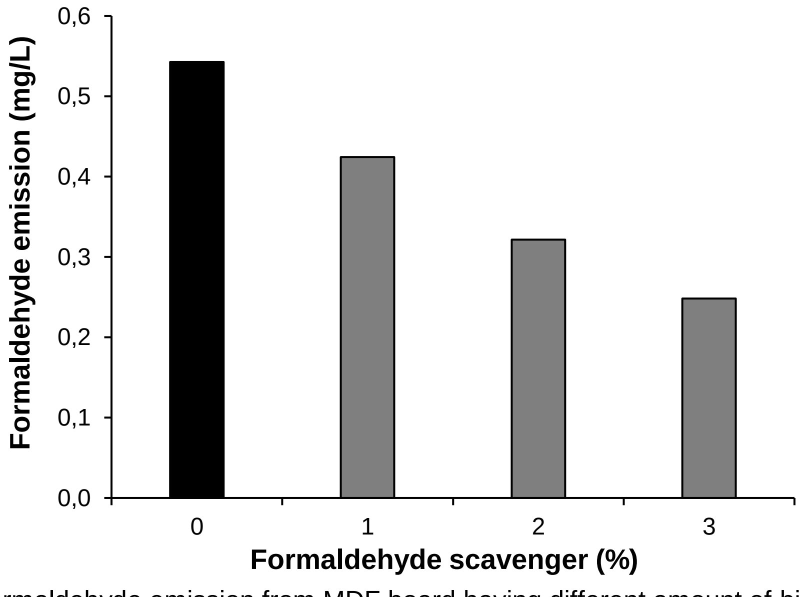

Figure 1. Formaldehyde emission from MDF board having different amount of bio-scavenger

The effectiveness of chitosan as FS were increased with its transformation into the nano-particle size. A corresponding comparison was applied between different forms of chitosan (with the same amount (1%)) on the formaldehyde emission and the result is presented in Figure 2. It can be seen that the efficiency and effectiveness of the nano-chitosan is much higher for the reduction of formaldehyde emission. Formaldehyde emission is 50% more reduced in case of using nano-chitosan as FS. Nano particles have higher specific surface area which means more possibilities to absorb free and hydrolyzed formaldehyde. It can also be said that the panels having 1% nano-chitosan can be categorized to the F**** classes which is the lowest level of formaldehyde emission.

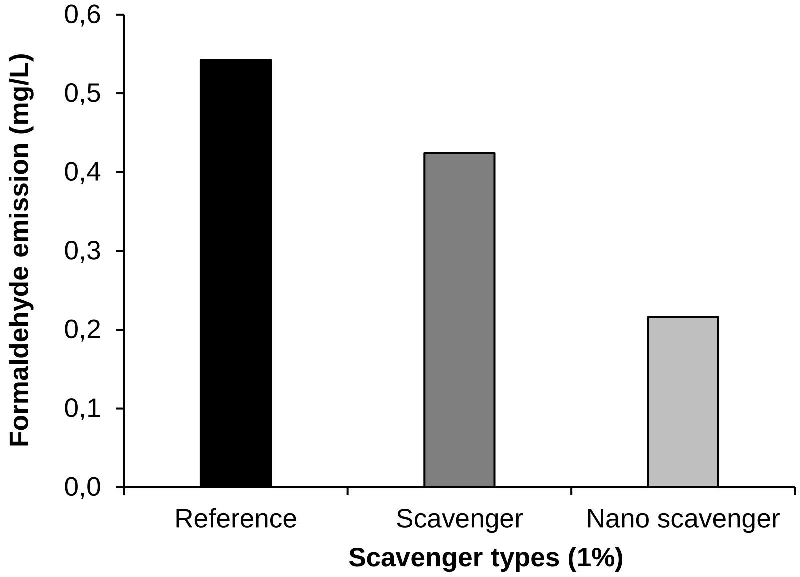

Figure 2. Formaldehyde emission from MDF board having different types of bio-scavenger

Conclusion

In the present study, a novel bio-based and bio-degradable formaldehyde scavenger was developed based on chitosan as the second most abundant polysaccharide in nature after cellulose. The results showed that the formaldehyde emission was significantly reduced using chitosan as FS. Addition of 3% chitosan was resulted to 55% reduction of formaldehyde emission. Nano-particles of the chitosan showed higher efficiency compared to those of conventional chitosan. This means that reaching a lower level of FE can be achieved using scavenger in nano-particles size with the lower dosage. Generally speaking, wood-based panels can be produced having a FE class close to the emission of solid untreated wood using developed bio-scavenger based on chitosan.

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