International Symposium on New Horizons in Forestry 18-20 October 2017 | Isparta - Turkey



Oral presentation

D

Surface properties of biopolymer nanocomposites coated wood and wood panels

Kezban Kıy¹, Deniz Aydemir^{1,*}

Bartin University, Faculty of Forestry, Forest Industrial Engineering, 74100, Bartin, Turkey * Corresponding author: *denizaydemir@bartin.edu.tr

Abstract: The aim of this study was conducted to determine the effects of biopolymer nanocomposite films on the surface properties of the wood based substrates. Today, many resins or paints with different chemical contents and allergic effects are used on surfaces of wood panels to obtain more aesthetic furniture. This status had led people to be affected by these surface coating components on products. In this study, the biopolymer nanocomposite films were prepared by solvent casting method with using polyhydroxybutyrate (PHB), a biodegradable and non-allergenic polymer. In order to improve the combustion and UV resistance of the PHB, 1% of nanobor nitride (BN) and nano titanium dioxide (Nano-TiO₂) were added to the biopolymer matrix, separately. The all blends were prepared in chloroform medium at 90°C for 30 min with speed mixer. SEM characterization, color changes of the coated wood and wood panels, and thermal analysis with TGA of the biopolymer coating solutions were determined. The obtained results showed that pure polyhydroxybutyrate and their composite films with TiO₂ and BN are suitable for using as coating solutions. The addition of fillers such as TiO₂ and BN was found to improve adhesion among the filler and the polymer matrix.

Keywords: Biopolymer, Nanocomposite films, Polymer coating, Polyhydroxybutyrate (PHB), Nanoparticles

1. Introduction

Surface coating for wood and wood panels are generally based on petroleum based or synthetic polymers due to low-cost and easy availability. These polymers have a significant barrier against water and oxygen permeation, and exhibit high mechanical properties. However, they are disfavored by limitations in petroleum reserves, difficult recyclability toxic and allergic effects, and lack of biodegradation (Rastogi and Samyn, 2015). Therefore; bio-based polymers have been widely studied as alternative to petroleum polymer. The replacing the petroleum coatings with biopolymer films and solutions might provide both a competitive advantage and more sustainable/greener image (Vartiainen et al., 2014; Vieira et al., 2011). Biobased coatings for wood and wood panel have high potential to replace petroleum based coating. Bio-based coatings obtained from renewable resources also have the numerous advantages such as biodegradability, easy recyclability, non-toxicity and biocompatibility, etc (Cha and Cinnas, 2004; Tang et al., 2012; Khwaldia et al. 2010; Uzun and Aydemir, 2017). Some biobased polymers have used as coatings for wood panels, such as starch and cellulose derivatives, casein, soya, gluten, carnauba wax, fatty acids, polyhydroxyalkanoates (PHA) and polylactic acid (PLA) (Schaller and Rogez, 2007; Khwaldia et al., 2010; Kugge and Johansson, 2008). Moisture resistance of bio-based polymers is the most important issue because poor barrier properties of many biopolymers, thus excessive water vapour transmission can diminishes the hardness and strength of the coatings. Thermal behavior and UV-resistance also other important issues for bio-based coatings thus various fillers can be added to improve the disadvantages (Johansson et al., 2012; Vartiainen et al., 2010). This study investigated feasibility of biobased coatings on the surface of the wood and wood panels to their potential for use in the sustainable and green coating applications. The effects of nano sized BN and TiO₂ on the thermal properties were also determined.

2. Materials and methods

2.1. Materials

Polyhydroxybutyrate (PHB), which is a biodegradable and bio-syntheses polymer was used as polymer matrix for preparing of coating solution (PHB was supplied from GoodFellow, UK). Nano sized boron nitride (BN) (Bortek Inc., Turkey) and nano sized Titanium dioxide (TiO_2) (MKNano, Canada) were added to polymer matrix for improve the thermal properties and UV-resistance. The sizes of BN and TiO_2 were 85 nm and 15-35 nm, respectively. In this study, particleboards, fiberboards, heat-treated and un-treated ash wood were used, and the panels and woods were bought from a market.

2.2. Preparation of the biopolymer nanocomposite films

5 g Polyhydroxybutyrate (PHB) pellets dissolved in 100 mL chloroform was mixed to 30 min at 25 ± 2 °C with a magnetic stirrer. The melted PHB were applied to the surface of wood and wood panels, and all samples were dried at room temperature for a day. In the preparation of the PHB nanocomposites; BN and TiO₂ at 2% loadings were suspended in chloroform under magnetic stirring for 15 min. The blends were then sonicated for 15 min at room temperature with an ultrasonic mixer at 50 W

and 50% frequencies. The solutions containing 2 wt% of BN and TiO₂ were added to the prepared PHB solution and then stirred vigorously for 15 min, with a magnetic stirrer. The blends were sonicated for another 15 min, and the blends were applied with a brush on the surface of the samples, respectively. The rest of the coating solutions with BN and TiO₂ were put to petri, respectively to determine the thermal behavior. Both the coating solution and the coated samples were put to the climatic chamber for curing

2.3. Methods

The coating thickness and particle dispersion on the surface the coated samples were determined with scanning electron microscopy (Tescan, Poland). The color changes of the coated samples were measured with Minolta color device, and the results were exhibited with Δ Eab. Thermogravimetric analysis of the coating solutions also were performed with Perkin Elmer TGA-DTG analyzer. The TGA analyses were conducted from 25°C to 900 °C with 25°C heating rate.

3. Results and discussion

3.1. Surface Characterization of the Samples Covered with Coating Solutions

The SEM images of the samples coated with pure PHB, PHB-TiO₂, and PHB-BN blends were given in Fig. 1, 2 and 3. The each coating solutions were applied with a brush the surface of the samples for 3 times. After coating with the blends, the surface of the samples were provided to white layer. Thickness of the layer generally was found to be different according to the SEM images. The surface of the samples was determined to be wavy for all samples, and some porous layers found to the samples coated with pure PHB and PHB+TiO₂ blends. The roughness of the layer were found to be similar to all samples. According to particle dispersion analysis, some aggregates was determined on the surface of the coated samples. EDAX analysis exhibited that TiO₂ and BN were dispersed on the surface of the samples. In a study, PHB was used to cover the surface of the paper with solvent casting, and the obtained results showed that the origin and distinctive molecular weight and their composite films with various fillers proved to be suitable for coating formation and the requested thickness. Addition of fillers to polymer matrix was found to improve adhesion among the filler and the polymer matrix and formation of a homogeneous structure of the obtained films, and also the surface of the materials (Erkske et al., 2006).

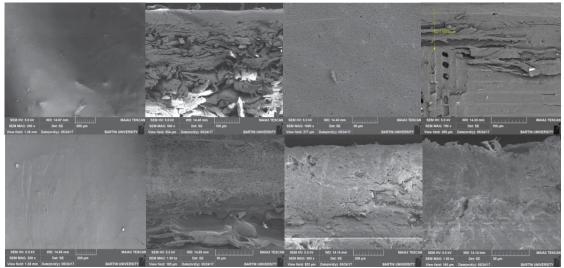


Figure 1. SEM images from surface and cross-section of the samples coated with pure PHB.

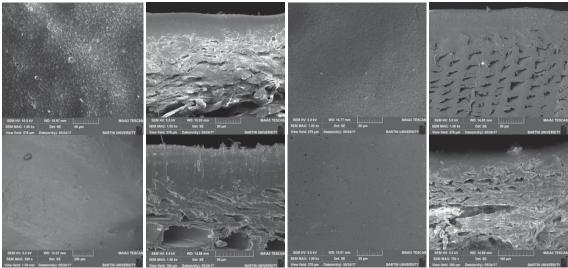


Figure 2. SEM images from surface and cross-section of the samples coated with 1%TiO₂-PHB blends.

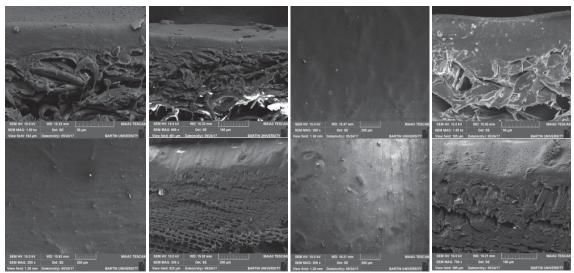


Figure 3. SEM images from surface and cross-section of the samples coated with 1%BN-PHB blends.

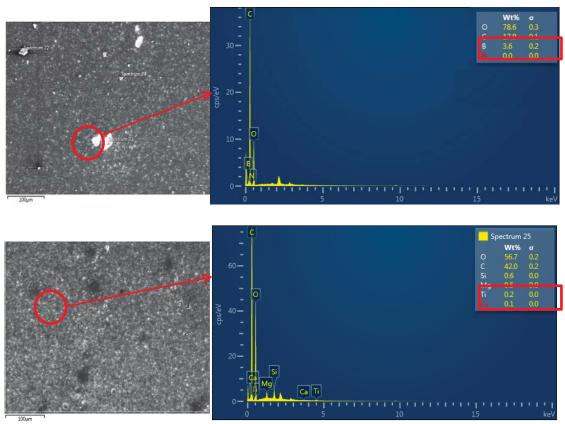


Figure 4. SEM Mapping on the surface of the samples coated with TiO₂/BN-PHB Blends.

The color changes of the coated samples were given in Fig. 5. According to Fig. 5, the Δ Eab values were generally found to be lower than the samples coated with pure PHB. The addition of the fillers such as BN and TiO₂ generally decreased to the Δ Eab.

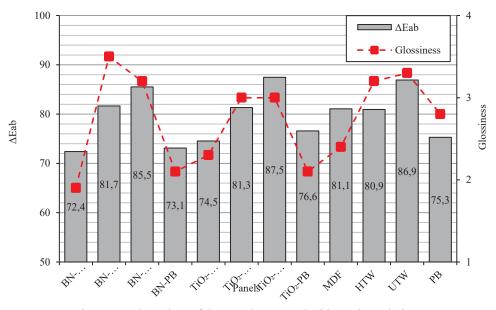
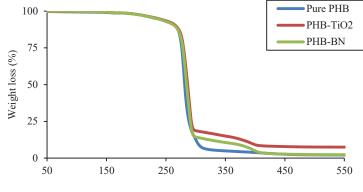


Figure 5. Color values of the samples covered with coating solutions.

3.2. Thermogravimetric analysis of the coating solutions

The thermogravimetric analysis of the coating solution were determined with TGA-DTA device, and the curves and the summary of the all TGA data were given in Fig. 6, 7, 8, and Tab. 1.



Temperature (°C)

Figure 6. TGA Graph of the Coating Solutions.

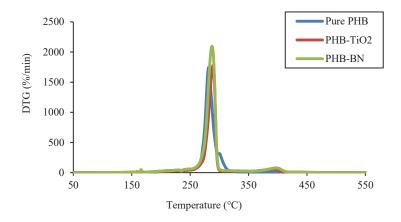
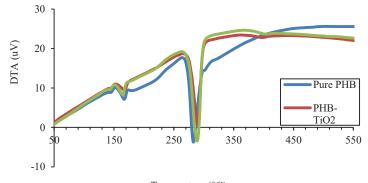


Figure 7. DTG Graph of the Coating Solutions



Temperature (°C) Figure 8. DTA Graph of the Coating Solutions.

Table 1. Summary of the Curves of Thermogravimetric Analysis of the Coating Solutions.

Coating	Tonset	T _{10%}	T _{50%} (°C)	T _{85%}	DTG _{max} (°C)	Residue	Tm (°C)	Td
Solutions	(°C)	(°C)	$1_{50\%}(^{\circ}C)$	(°C)	$DTG_{max}(^{\circ}C)$	(%)	$\operatorname{Im}(\mathbf{C})$	(°C)
Pure PHB	274.4	266.5	281.5	297.8	281.4	99.8	166.2	281.4
PHB-TiO ₂	276.5	267.8	286.5	357.7	288.0	92.9	166.9	286.3
PHB-BN	277.3	266.0	284.9	299.4	288.3	98.9	165.7	286.0

As seen as TGA curves of the coating solutions in Fig. 6, all curves for the coating solutions were found to be similar and near to each one. Tonset was found at 274.4°C for pure PHB, 276.5 °C for PHB-TiO₂, and 277.3 °C for PHB-BN. Fig. 7 showed the DTG peaks of the coated samples, DTG max peaks were determined at 281.4°C for pure PHB, 288.0°C for PHB-TiO₂, and 288.3°C for PHB-BN. Fig. 8 exhibited the DTA curves, which obtained to the melting temperature (Tm) and the degradation temperature (Td). Tm and Td values were found as 166.2°C and 281.4°C for pure PHB, 166.9°C and 286.3°C for PHB-TiO₂, and 165.7°C and 286°C for PHB-BN. According to Tab. 1, the maximum temperature was determined to $T_{10\%}$, $T_{50\%}$ and $T_{85\%}$ for PHB-TiO₂ blends. Uzun and Aydemir (2017) found that the addition of the fillers to polyhydroxybutyrate polymer matrix improved the thermal properties.

4. Conclusion

In this work, the feasibility of use of the PHB biopolymer films to the coating of the surface of the wood and wood panels, and also the effects of the fillers such as TiO2 and BN on the thermal properties were investigated. The coating performance of the PHB films on the surface of the wood and wood panels were characterized with SEM, EDAX, and SEM-mapping. SEM analysis showed that PHB layers were determined on the surface of the all samples, and especially the thickness layer were seen the cross-section of the all samples, but the thickness of the PHB layers were found to change at 50-100µm for all the samples. The addition of the fillers improved the thermal behavior, and improving effect of TiO2 was found to be higher than those of the BN. Tm and Td values increased with incorporation of the both fillers into PHB.

References

Rastogi, V.K., Samyn, P. 2015. Bio-Based Coatings for Paper Applications: Review. Coatings, 5(4), 887-930.

- Schaller, C., Rogez, D. 2007. New approaches in wood coating stabilization. Journal of Coatings Technology and Research. 4 (4): 401–409.
- Vieira, MGA, Silva, MA., Santos, LO., Beppu, MM. 2011. Natural-based plasticizers and biopolymer films: A review. European Polymer Journal, 47 (3): 254-263.
- Uzun, G. and Aydemir, D. 2017. Biocomposites from Polyhydroxybutyrate and Bio-fillers with Solvent Casting Method. Bulletin of Materials Science 40(2):383-393.
- Erkskea, D., Viskere, I., Dzene, A., Tupureina, V., Savenkova, L. 2006. Biobased polymer composites for films and coatings. Proc. Estonian Acad. Sci. Chem., 55(2): 70–77
- Tang, X.Z.; Kumar, P.; Alavi, S.; Sandeep, K.P. 2012. Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials. Crit. Rev. Food Sci. Nutr., 52, 426–442.
- Khwaldia, K.; Arab-Tehrany, E.; Desobry, S. 2010. Biopolymer coatings on paper packaging materials. Compr. Rev. Food Sci. F., 9, 82–91.
- Cha, D.S.; Chinnan, M.S. 2004. Biopolymer-based antimicrobial packaging: A review. Crit. Rev. Food Sci. Nutr., 44, 223–237.
- Kugge, C.; Johnson, B. 2008. Improved barrier properties of double dispersion coated liner. Prog. Org. Coat. 2008, 62, 430– 435.
- Vartiainen, J., Vähä-Nissi, M., Harlin, A. 2014. Biopolymer Films and Coatings in Packaging Applications—A Review of Recent Developments. Materials Sciences and Applications, 5, 708-718.
- Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon, P., Gregor Svetec, D., Virtanen, S., Giacinti Baschetti, M., Breen, C., Clegg, F. and Aucejo, S. 2012. Renewable Fibers and Bio-Based Materials for Packaging Applications—A Review of Recent Developments. BioResources, 7, 2506-2552.
- Vartiainen, J., Tammelin, T., Pere, J., Tapper, U. and Harlin, A. 2010. Biohybrid Barrier Films from Fluidized Pectin and Nanoclay. Carbohydrate Polymers, 82, 989-996.