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Strategies to Preserve Bio-Based Antimicrobial Agents During Extrusion and Injection Molding

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Abstract. The reduction of bacteria-caused disease transmission gains importance in medicine as well as in areas of public life. As part of a project, a bio-based compound was developed which combines the advantages of plastics processing and the natural bactericidal effect of heartwood. A Polylactide polymer and bactericidal pine heartwood chips were mixed to a compound and injection molded into specimens, to create a plastic material with antimicrobial ingredients. An aim of this work was to preserve the bactericidal ingredients of pine heartwood chips (Pinus sylvestris) during compounding and injection molding into Polylactide wood compound specimens. Additionally, it was necessary to ensure the efficiency of the bactericidal ingredients especially at the surface of the specimens and the increase of the mechanical compound properties. Therefore, the specimens were tested with an antibacterial test method based on the ISO 22196:2011. Influences of different conditions such as temperature, chip size and chip content on the antimicrobial efficacy and mechanical properties were tested using a Design of Experiment. The specimens were tested for antibacterial activity, Charpy impact strength, surface hardness, Young's modulus and yield strength. The results show significant dependencies between varied parameters and measured material properties.

Keywords: Polylcatide, mechanical properties, wood flour, wood chip, bactericidal, antibacterial, injection molding process, temperature behavior, impact strength, bio-based, biodegradable.
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INTRODUCTION

Bio-based and biodegradable plastic materials reduce the dependency on depleting fossil fuels. Polylactide has high modulus, strength and can be readily fabricated and is one of the most promising bio-polymers for varied applications [1]. Mixtures of bio-based and biodegradable plastic materials with fibers or chips of sapwood lead to a well-known increase of compound strength and stiffness [2-10]. Heartwood chips (HWC) are uncommon because of higher oil and tree resin contents, but some of these ingredients cause bactericidal effects [11-14]. Fekih et al. analyzed an antibacterial extract made from pinus halepensis. It showed bactericidal effects against various bacteria [11]. Välimaa et al. compared 30 extracts of pine wood and other trees with the result that pine wood is the most efficient one [12]. Strategies to preserve bactericidal ingredients of HWC in compounding and molding processes are not mentioned. Influences on bactericidal effects and the fragility of antibacterial ingredients during compounding and molding processes are unknown. Temperatures, mixing rates and chip sizes are investigated of the influences on antimicrobial surface efficacy.

The aim of this work is to ensure bactericidal effects at the surface of injection molded products out of HWC-Polylactide compounds to create a compound with high mechanical properties and antibacterial surface efficacy. Thus, this study uses HWC combined with Polylactide in various mixing ratios and process settings.

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EXPERIMENTS

Materials

A Polylactide (PLA) type is used which is suitable for injection molding. The density of the PLA granulate is 1,24 g/cm³ and its melt flow rate is 14 g/10 min by 210 °C and a load of 2.16 kg. It has a tensile strength of 68.0 MPa, a Young's Modulus of 2.96 GPa, a ball indentation hardness of 107.8 MPa at a test load of 358 Newton and a Charpy impact strength of 19.5 kJ/m².

In this study the fillers are pine heartwood chips (HWC) of Pinus sylvestris and their shape is defined by the average size of a HWC fill measured by a sieve shaker with various mesh sizes from 63 µm up to 2,000 µm.

Compounding and Injection Molding Setup

Heartwood chips and PLA are mixed in a co-rotating twin-screw extruder and formed to a string. The extruder has an L/D ratio of 38 and a screw diameter of 40 mm. The Compound string gets separated into granulate. Afterwards the granulate is handed over into the hopper of an injection molding machine. Injection molding parameters are varied and for each variation five up to ten specimens are molded (Figure 1).

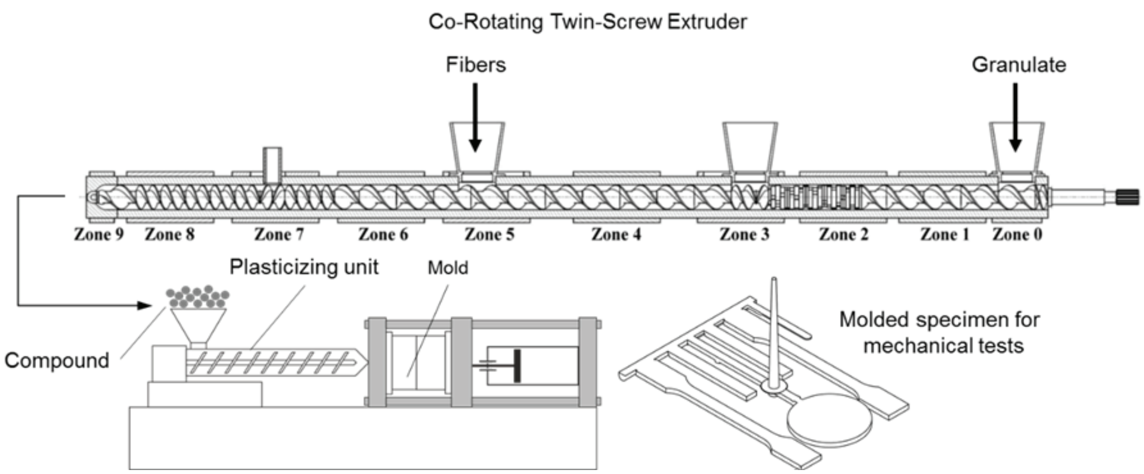

Figure 1. Experimental setup to create compound test specimens out of heartwood chips and Polylactide

The temperature of the melt is controlled by the barrel wall temperatures of zone two to four out of four. The temperature near the hopper is held lower to ensure the feed behavior. Variation ranges are determined by pre experiments.

Test Methods of Mechanical Properties and Antibacterial Efficacy

The mechanical properties are measured according to specific norms. Tensile strength and Young's Modulus were measured using the DIN EN ISO 527-1 and -2. The Charpy impact strength is measured according to DIN EN ISO 179-1. The ball indentation hard-ness is measured according to DIN EN ISO 2039 by a test load of 358 Newton. The antibacterial efficacy is determined using ISO22196:2011 test method and staphylococcus aureus bacteria.

RESULTS AND DISCUSSION

Figure 2 shows significant dependencies between filler contents and resulting antibacterial efficiencies on the specimen surfaces. The specimens with HWC contents of 20 weight percent or higher completely reduce the bacteria on the surface, thus after 24 h the specimen surface is freed from staphylococcus bacteria. A specimen group is also bacteria-free and contains only 10 percent HWC.

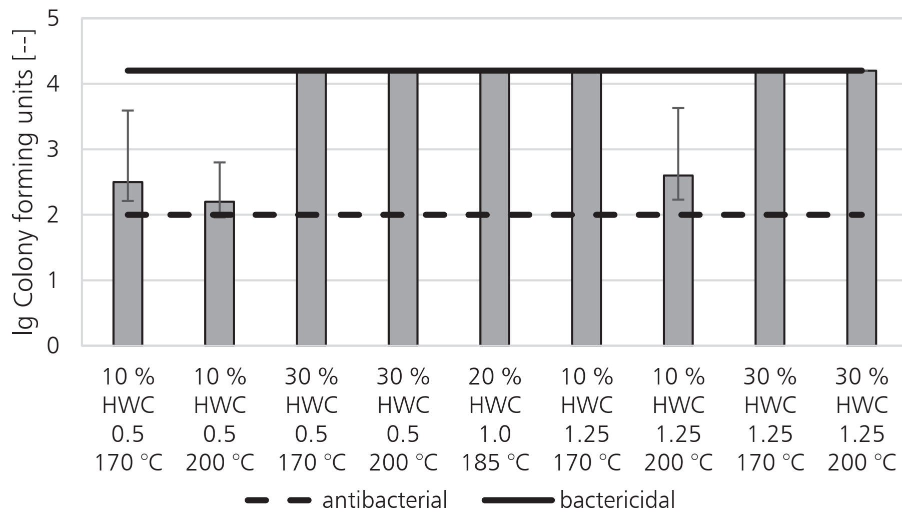

Figure 2. Antibacterial efficiency of PLA compounds with varied average chip size, content and process temperature.

Changes in average filler sizes also affect antibacterial activity. Small chips reduce antibacterial surface activities. This relation can be found comparing PLA + 10 % HWC0.5 at 170 °C with PLA + 10 % HWC1.25 at 170 °C as well as between PLA + 10 % HWC0.5 at 200 °C with PLA + 10 % HWC1.25 at 200 °C.

PLA + 10 % HWC1.25 with process temperatures at maximum 170 °C. In comparison to PLA + 10 % HWC at 200 °C a significant deviance is reached. Antibacterial efficacies of PLA + 10 % HWC0.5 is reduced as process temperatures rise to 200 °C. Thus, process temperatures effect antibacterial surface efficacy. Reductions in antibacterial surface efficacy can be explained by weight losses of HWC in the TGA at 200 °C, shown in Figure 3.

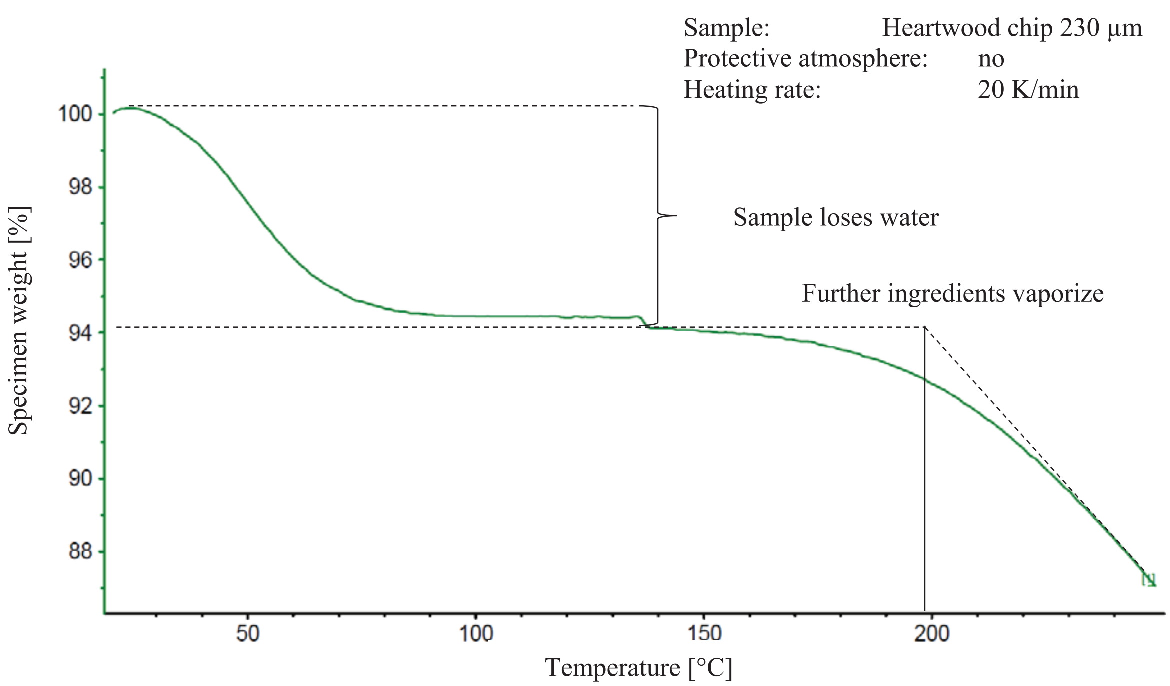

Figure 3. Thermogravimetric analysis of a pine heartwood chip sample

To maximize antibacterial intensities, low process temperatures need to be combined with increased chip sizes and high percentages of HWC content. To reach antibacterial properties, ten percent of HWC are sufficient.

In terms of mechanical properties, varied average chip sizes affect Charpy impact strengths. In Figure 4, the impact resistance of specimens, injection molded at a maximum temperature of 170 °C, were compared. The bactericidal PLA + 10 % HWC1.25 has a halved impact resistance compared to neat PLA with 19.5 kJ/m². In contrast smaller chip sizes keep the impact strength on an acceptable level of circa 14.1 kJ/m² which is 70 % of neat PLA. Thus, decisions can be made regarding antibacterial efficacy or impact resistance.

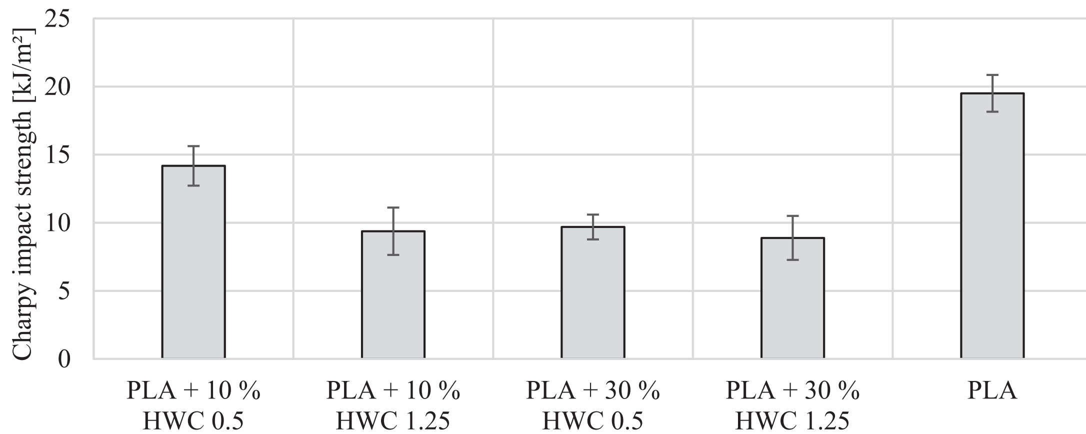

Figure 4. Comparison of different Compounds to the Charpy impact strength

In Figure 5 the bactericidal and brittle PLA + 10 % HWC1.25 at 170 °C is compared to PLA + 10 % HWC0.5 at 170 °C. Just the Young's Modulus of the HWC1.25-compound is higher. The HWC0.5-compound show higher tensile strength, Charpy impact strength, as well as an increased ball indentation hardness.

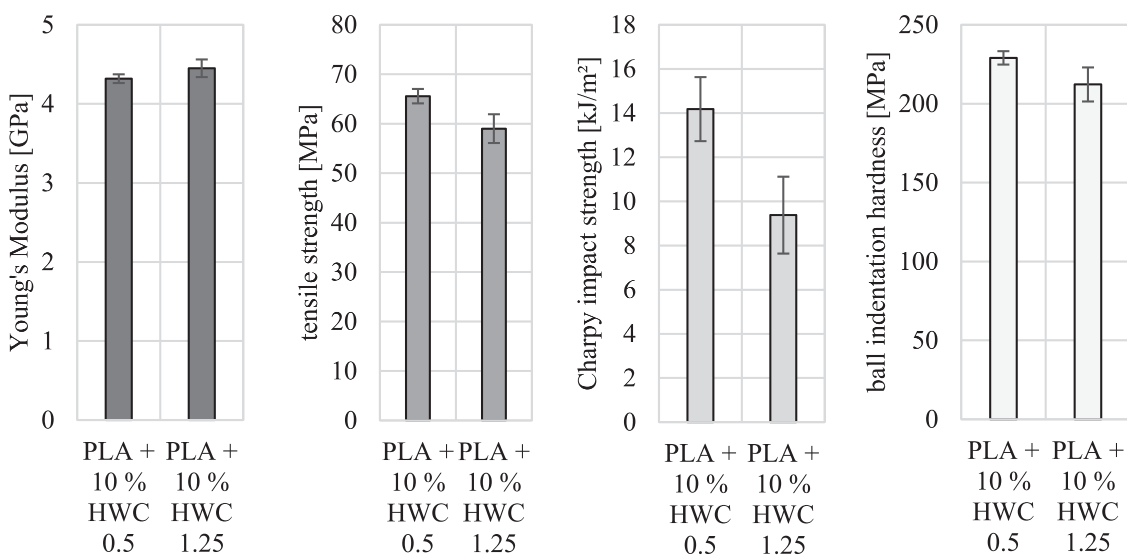

Figure 5. Direct comparison of mechanical properties to a bacterial and a bactericidal efficient compound

To reach antibacterial surface efficacies in combination with high mechanical properties like impact resistance PLA + 10 % HWC0.5 need to be chosen. If bactericidal surface efficacies are requested, higher HWC contents or bigger HWC sizes need to be used.

CONCLUSION

Antibacterial ingredients of HWC can be preserved during compounding and molding processes. Temperatures, average chip sizes as well as contents influence the surface efficacy against staphylococcus aureus bacteria. Productions of antibacterial efficient and tough materials are reachable. Highly antibacterial efficient compounds lead to low impact resistances. On the one hand high HWC contents and on the other hand increased average particle sizes lead to embrittled compounds.

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