In pursuit of degradation - seeking beneficial effects of thermal and thermomechanical modification of plant-based materials used in polymeric materials

A. Hejna[1], M. Barczewski[1], A. Bartnicki[2], J. Andrzejewski[1], J. Aniśko[1], R. Malinowski[2]

[1]Institute of Material Technology, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland
[2]Łukasiewicz Research Network - Institute for Engineering of Polymer Materials and Dyes, M. Skłodowska-Curie 55, 87-100 Toruń, Poland
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Presenting author email: aleksander.hejna@put.poznan.pl

Wood-polymer composites (WPCs) are a particular group of composite materials consisting of one or more plant-based fillers and one or a mixture of polymers. Over the last decades, research works on their development aim to address the main problems related to their processing: (i) variations in the quality of plant-based materials (PBMs); (ii) limited thermal stability of PBMs, narrowing the processing window for WPCs; and mostly (iii) limited compatibility between often hydrophobic polymer matrix and hydrophilic fillers (Olakanmi and Strydom, 2016).

The insufficient thermal stability of PBMs noticeably limits the range of polymers potentially applied as a matrix for composite. Numerous works indicate that the melt blending temperature of 200 °C is the upper threshold for WPCs' processing (Ramesh *et al*, 2022), limiting or excluding the application of engineering plastics. To avoid unfavorable degradation during melt blending, fillers' pre-treatments aimed at the removal of components with insufficient thermal stability are required. Considering the compatibility, strong interfacial interactions are crucial for the satisfactory mechanical properties of WPCs. Their enhancement can be realized by providing possibilities for chemical bonding of filler with functional groups present in the polymer backbone or by changing the character of the fillers' surface from hydrophilic to hydrophobic, simultaneously enhancing the filler and matrix mutual affinity.

The most critical problems related to the WPCs' processing require an adequate selection or modification of introduced PBMs. Multiple works related to their chemical modification, mainly aimed at the enhancement of the performance of WPCs, have been published by different research groups (Li *et al*, 2020; Mohit and Selvan, 2018). The authors mentioned numerous filler modifications, whose goal was to enable covalent bonding with a polymer matrix or to reduce the hydrophilicity gap. However, most did not consider the other WPCs' processing limitations, variations in the quality of PBMs, and their limited thermal stability, which still require addressing.

Except for the chemical modification, thermal treatments can be applied to adjust the composition and performance of PBMs. Various PBMs, except for the most abundant cellulose, hemicellulose, and lignin, contain a significant portion of proteins, lipids, and phytochemicals that may be employed as functional additives for WPCs. Therefore, in the case of WPCs' manufacturing, it is crucial to increase the materials' thermal stability with minimal or controlled degradation of active compounds. Moreover, these compounds can undergo degradation-induced changes yielding highly beneficial effects, which, however, have been overlooked so far in the state-of-the-art.

Considering the upper-temperature limit for the WPCs' processing related to the PBMs' processing degradation and the currently emphasized chase for resource efficiency, a paradigm shift in WPCs' manufacturing is required. Instead of trying to avoid PBMs' decomposition during melt processing by applying additional treatments, only the sequence of processes could be changed by excluding the degradation out of melt blending and proceeding it by torrefaction with desired conditions prior to melt mixing. Such an approach would enable conducting biomass' thermal degradation and melt blending in a controlled manner. Performing controlled thermal degradation of PBMs before the processing is the most straightforward approach. Afterward, fillers will be stable at WPCs' processing temperatures, enabling conducting the melt blending without damaging the composite.

Inspiration and direction can be taken from the food sector, which often uses PBMs similar to those applied in WPCs and makes the best of their degradation, often turning them into works of art. Thermal degradation is integral to food processing, like cooking, baking, or roasting. It is considered a preservation method, like smoking meat, roasting coffee, or even sun-drying fruits. These examples clearly indicate that degradation can be treated as a positive and desired phenomenon, contrary to materials engineering, where degradation, suggesting performance deterioration, is always pejorative and in opposition to the spirit of this field.

The first potential food-inspired benefit originating from PBMs' deliberate is the possibility of WPCs' color adjustment resulting from the non-enzymatic browning reactions (NEBRs): caramelization and Maillard reactions. Our research work indicated that thermomechanical treatment enables adjusting the color of modified BSG (Hejna *et al*, 2021a), which varied with the extrusion parameters. The impact of screw speed and throughput was not straightforward due to contradictory effects related to the shear forces and the residence time of material in the extruder barrel. Higher shear forces increase interparticle friction, stimulating NEBRs, simultaneously enhancing particles' grinding, and boosting lightness due to the higher specific surface area and more reflection of light.

Except for color appearance adjustment, NEBRs' products are characterized by potent antioxidant and antimicrobial activity, which can be potentially transferred to WPCs, inducing their stabilization. Our previous works (Hejna *et al*, 2021a,b) indicated that the browning of the extrusion-modified BSG and the increase of its antioxidant activity were attributed to the Maillard reactions resulting from the high protein content in BSG. The browning extent was proportional to the extrusion temperature and shear forces inside the extruder barrel, and detailed analysis showed that it depended on the particle size of

BSG. It suggests that the antioxidant activity of modified fillers may be enhanced by proper fractionation and adjustment of particle size distribution, which was confirmed by Aniśko and Barczewski (2023). Taking inspiration from the food sector, such an effect may beneficially impact the PBMs' stabilizing activity toward the polymer matrix. Our research (Hejna *et al*, 2022c) indicated that NEBRs' products generated during BSG thermomechanical treatment enhanced the stability of poly(ε-caprolactone). The UV-induced mechanical performance deterioration was inversely proportional to the extent of Maillard reactions. For WPCs with BSG modified at 180 and 240 °C, the crystallinity degree was maintained or reduced after UV exposure, confirming the BSG protective impact. In our other work (Hejna *et al*, 2022b), modified BSG shifted Mater-Bi-based WPCs' thermal decomposition onset under an oxidative atmosphere from 142-143 °C to 152-165 °C. Mater-Bi-based WPCs' were subjected to soil biodegradation (Hejna *et al*, 2022a), whose extent differed with BSG modifications. Despite their stabilizing impact, the biodegradation of WPCs was not detained but only inhibited. The described treatments could be efficiently applied to develop sustainable WPCs with the engineered stability driven by the PBMs' treatment.

The WPCs' limited compatibility can be also addressed by the PBMs' thermal modifications, as they shift the character of PBMs toward hydrophobicity due to the removal of bound water, masking accessible hydroxyl groups, hemicellulose decomposition, and generation of melanoidins considered moderately hydrophobic due to the glycation of amino-bearing compounds with reducing sugars. Analysis of the Mater-Bi/BSG composites developed in our previous work (Hejna *et al*, 2022b) in terms of microstructure and rheological properties revealed the enhancement in the interfacial interactions with the increasing BSG treatment temperature.

Furthermore, what can be even the most important, thermal or thermomechanical treatment procedures developed during the project would enable removing the least thermally stable components, shifting the decomposition onset towards higher temperatures, and broadening the application window for PBMs. Our preliminary work (Hejna *et al*, 2021a) indicated that higher temperatures (180 and 240 °C) of BSG extrusion also resulted in the enhancement of the thermal stability of BSG samples, which was related to the reduction of moisture content and possible partial decomposition and evaporation of its products.

Herein, in the presented work, we would like to highlight the potential benefits yielding from the controlled degradation of PBMs in the WPCs' manufacturing and discuss them based on our preliminary research works. We believe the transdisciplinary look inspired by food technology can induce a vital paradigm shift, boosting the performance of WPCs and broadening their potential application range.

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