100 % RENEWABLE HIGH-VALUE PHB-BASED COMPOSITE MATERIALS

TURNING INDUSTRIAL BY-PRODUCTS INTO ADDED-VALUE PRODUCTS

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The ERA-NET project PHB2Market is developing 100 % renewable, high-value composite materials made of sustainable industrial by-products or biomasses using eco-efficient industrial biotechnology and chemical processes. We combine the bio-polymer polyhydroxybutyrate (PHB), cellulose nanofibers (CNF) and bio-based, multifunctional plasticisers (BMP) to create a fully biobased composite material with enhanced properties. PHB2Market composites will be an alternative to conventional petroleum-based polymers in various applications.

PHB2Market developments in cellulose nanofibers

Cellulose nanofibers (CNF) are mainly produced in the form of an aqueous suspension. They can therefore easily be used as a filler in a matrix of hydrophilic polymers. However, for thermoplastic polymers, a dry form of nanocellulose is necessary. The evaporation of water from the suspension of nanocellulose is accompanied by the phenomenon of hornification, leading to irreversible agglomeration of the microfibrils. This negatively affects the unique properties of nanocellulose that are associated with its huge surface area. In order to counteract hornification, various protective chemical compounds may be used, which are deposited on the microfiber surface and hinder their agglomeration during drying, while also changing their properties to partially hydrophobic.

Within PHB2Market, further investigations have been carried out on the preparation of a dry form of cellulose nanofibers derived from hemp stems by using a protective agent based on renewable raw materials. In a first step the CNF was extracted from pulp from hemp stalks. Partially saponified methyl esters were then mixed with an aqueous suspension of CNF in different ratios and dried using a GEA MOBILE MINOR™ spray dryer with a specific temperature profile. Following this approach, a powder of cellulose nanofibers with a particle size in the range of 1-10 µm and a solids content of 96.0% was obtained which, after being re-dispersed in water, retained the fibrous structure of CNFs. Thermal analyses indicate that dried functionalized CNFs are stable in the processing temperature range of PHA polymers such as PHB and PHB-V.

PHB2Market developments – biobased multifunctional plasticizers

Usually plasticizers are added to a polymer matrix to overcome the mechanical drawbacks of PHA polymers and particularly improve the material ductility and elongation at yield properties. For this reason, new fatty acid-based plasticizers, so-called biobased multifunctional plasticizers (BMPs), have been developed by the partner ICSO. In a first step the effectiveness of these BMPs in the context of the PHA plasticization were investigated with thermal and mechanical characterization methods. The developed BMPs consist of a linear structure and particularly differ in the amount and type of functional polar end groups. The characterization of the BMPs was carried out using ATR-FTIR, GC, TGA and physiochemical characterization.

The results show that the structure of the plasticizer strongly influences the compatibility between plasticizer and polymer as the amount of the unsaturated bond in the fatty acid hydrocarbon chain affects the miscibility of the PHA and BMP. For example, the maximum BMP content of methyl esters of oleic acid is only 10 percent, while the maximum content of methyl esters of stearic acid is already overdosed at 8 percent. Additionally, the studies indicated that the presence of a free hydroxyl group significantly changes the properties of the ester and thus increases miscibility in the PHA compounds. The reason for this is that the free hydroxyl groups form a hydrogen bond with the carbonyl groups of the polyester and thus enhance the compatibility of the plasticizer with the polymer.

PHB2Market PHA compound development

The synthesized plasticizers were compounded in different ratios into the PHA matrix. Due to incompatibility between the polymer melt and the plasticizer not all PHA compounds could be produced. Some compounds led to inhomogeneous melt flow and phase separation of the components. For subsequent material characterization the samples were mechanically and thermally analyzed. Before injection molding the granulates were pre-dried and injection molded into Campus A test bars for tensile and impact tests.

The thermal test results show that the implementation of the BMPs into the PHA matrix leads to a reduction of the crystallization and melting temperature. This indicates that the plasticizers adversely affect the crystallization kinetics of PHA, tending to result in a lower crystallization temperature. The mechanical test results clearly show that the BMPs generally increase the impact strength of the notches samples. In comparison to the neat PHA the increase in ductility is up to 193 %, reaching a value of 4.1 kJ/m². In terms of tensile strength and Young modulus values the effect of the plasticizers leads to a slight deterioration in the properties with increasing plasticizer content.

Upscaling and part production using PHB2Market compounds

Based on the results of the compounding studies the most promising mixtures were up-scaled using industrial compounding equipment. After processing, all materials were tested on their mechanical properties and positively evaluated.

Impact modified (plasticized) PHA compound developed in PHB2Market

In the next step these compounds were successfully injection molded into small containers, technical parts and cutlery (knives and forks).

Picture: PHB containers and cutlery

The next step will be to further optimize the material properties and particularly to improve the processing of the material for injection molding and 3D-printing applications to achieve a competitive fully biobased compound.

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