

## FINAL PUBLISHABLE SUMMARY REPORT

**Project title: Novel Nano-Reinforced Biodegradable Composites: Design and Characterization (NanoBioComp)**

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The short-running of mineral oil<sup>1</sup>, the increasing waste problem and growing consciousness of our society for environmental aspects lead to an increasing interest in biopolymers. Hereby, the term biopolymer refers to plastics, which are either biobased or biodegradable (or both). In recent years, production capacity of biopolymers is increasing strongly with a growth rate of roughly 20% for the European market.<sup>2</sup> However, applications of biopolymers are still limited, because some of these materials still suffer from poor mechanical and thermal properties or high prices. There exist different possibilities to improve polymer property profiles, among them blending with another polymer<sup>3,4</sup> and reinforcement with fillers, such as fibres or particles<sup>5,6</sup>. The topic of this Intra-European-Fellowship is the design and characterization of nano-reinforced biodegradable composites, which could be employed e.g. in packaging, agriculture or throw-away products.

This project focusses on two biopolymers, the biobased and biodegradable poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)<sup>7,8</sup> and the petroleum based but biodegradable poly(butylene adipate-co-terephthalate) (PBAT)<sup>9</sup>. Furthermore, reinforcement of these polymers by different nanoclays, i.e. natural and organomodified montmorillonite and bentonite, is investigated. Since clay is a natural abundant material, its addition to the biopolymers does not affect their green character.

In the first part of the study, both polymers are filled with different particle contents of 1, 3, and 5 wt% of each nanoclay type by melt mixing using an internal mixer. Properties of the resulting materials regarding thermal stability, crystallization behaviour by differential scanning calorimetry and dynamic mechanical analysis are performed. It turns out, that

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<sup>1</sup> J.P. Gerling, F.-W. Wellmer: Wie lange gibt es noch Erdöl und Erdgas; Chem. Unserer Zeit 39 (2005) p. 236-245

<sup>2</sup> <http://en.european-bioplastics.org/market/>, date accessed: 04/10/2013

<sup>3</sup> L. Han, C. Han, H. Zhang, S. Chen, and L. Dong, Polym. Compos., 33, 850 (2012)

<sup>4</sup> J.M. Raquez, Y. Nabar, R. Narayan, and P. Dubois, J. Appl. Polym. Sci., 122, 639 (2011)

<sup>5</sup> E. Zini and M. Scandola, Polym. Compos., 32, 1905 (2011)

<sup>6</sup> F.P. La Mantia and M. Morreale, Compos. A, 42, 579 (2011)

<sup>7</sup> K. Sudesh and Y. Doi, "Polyhydroxyalkanoates," in Handbook of Biodegradable Polymers, C. Bastioli, Ed., Rapra Technology Limited, Shawbury, 219 (2005)

<sup>8</sup> I. Chodak, "Polyhydroxyalkanoates: Origin, Properties and Applications," in Monomers, Polymers and Composites from Renewable Resources, M. Belgacem and A. Gandini, Eds., Elsevier, Oxford, 451 (2008).

<sup>9</sup> K.O. Siegenthaler, A. Künkel, G. Skupin, and M. Yamamoto, "Ecoflex and Ecovio: Biodegradable, Performance-Enabling Plastics" in Advances in Polymer Science, Synthetic Biodegradable Polymers, B. Rieger, A. Künkel, G.W. Coates, R. Reichardt, E. Dinjus, and T.A. Zeveco, Eds., Springer, Berlin, Heidelberg, 91 (2011).

reinforcement with 3 wt% of organomodified clays (both montmorillonite and bentonite) lead to the best property profile.

In the second part of the study, the two biopolymers are blended with different weight ratios of 30/70, 50/50 and 70/30 and material's thermal and mechanical properties are tested. As a result, it is found, that the addition of 50% or more PBAT to PHBV enhanced its thermal stability. Moreover, blending low crystalline PBAT with higher crystalline PHBV affects the crystal growth of the latter. Fig. 1 shows polarized optical microscope pictures of PHBV, PBAT and their blend with weight ratio 50/50 when cooling down from 200°C to ambient temperature at cooling rate 30 K/min. These biopolymers are immiscible and an interlocking structure can be observed. For PHBV the growth of very big and perfect crystals can be appreciated. By contrast, PBAT possesses very small crystals and in the 50/50 blend are only some crystalline regions. It is assumed that addition of PBAT retards crystallization PHBV, which is also confirmed by differential scanning calorimetry. These investigations furnish knowledge about the processing-structure-property relationship of the biopolymer composites, which later is of interest for their processing and applicability.



Fig. 1: Polarized optical microscopy images of PHBV, PBAT and their blend with ratio 50/50 after cooling down from 200°C to room temperature

Considering the results of part one and two of the study, biopolymer composites with 50% PBAT, 50% PHBV and the reinforcement of 3% of organomodified montmorillonite and bentonite are manufactured. Furthermore, these materials are filled with propolis as natural antimicrobial agent as well as a commercial antimicrobial additive as reference. Materials are characterized regarding their thermal stability, water absorption, antimicrobial activity and weathering behaviour. These results of the materials stability and degradation behaviour furnish information about their suitability for applications like packaging or agriculture foils and about the product's lifetime.