Compatibility of Polylactic Acid with MaterBi

Bioblends. As oil prices rise and problems with CO_2 grow, bioplastics are moving increasingly into the focus of users. Particularly, blends based on various organic materials are playing an increasingly important role in meeting the required performance properties. A comprehensive study was made of the influence of the compatibility of the materials on the properties and processing of such bioblends.

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Plastics based on renewable raw materials (bioplastics) are increasingly capturing markets that can no longer be labelled as niches. Thus, the packaging sector, where biodegradability is frequently a strategic important marketing factor, is increasingly resorting to bioplastics. The applications of bioplastics now range from film right through to beverage bottles. Fairly often, mixtures or blends of different organic materials are used for this purpose. Their compatibility among themselves as well as the resultant mechanical and thermal properties are thus frequently crucial to processing and application. The results of a comprehensive study of the full mixing range of two selected bioplastics are presented below.

Starch Derivative and Polylactic Acid

When it comes to plastics based on renewable raw materials, starch-based bioplastics have essentially made all the running in recent years. As a biopolymer, the starch is used in either modified or unmodified form. Unmodified starch, unlike its modified counterpart, is treated only with additives that are needed for improving processing or meeting special application requirements. For example, if biodegradability is a criterion, the corresponding additives are chosen or adapted. Modified starch is made by chemical modification, such as reactive extrusion. Changing the molecular structure in this way affects not only the biodegradability, but also makes it possible at molecular level to affect the mechanical, thermal and user-specific properties of the starch derivatives.

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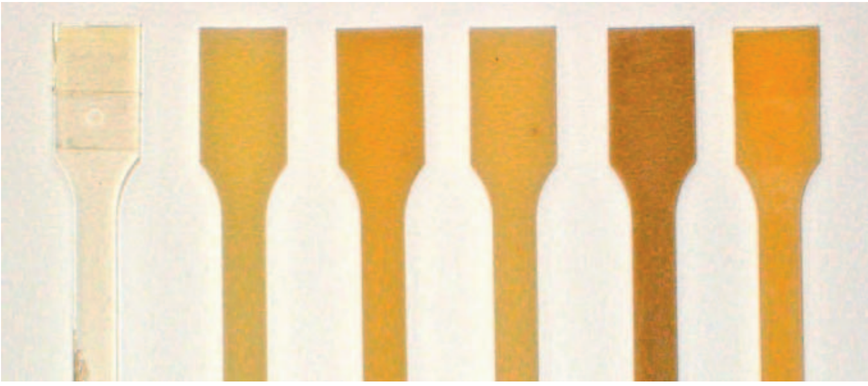

Fig. 1. The figure shows the colour change in the test specimen made from different mixtures of PLA (polylactide or lactic acid) and MaterBi (starch); from left to right: PLA/MaterBi = 100/0; PLA/MaterBi = 80/20; PLA/MaterBi = 60/40; PLA/MaterBi = 40/60; PLA/MaterBi = 20/80; PLA/MaterBi = 0/100

MaterBi YI 01 U, a product from Novamont, SpA, Novara in Italy, is one such starch-based bioplastic. It contains selected cellulose derivatives and special plasticisers in addition to starch. It is intended primarily for the injecting moulding of catering articles, packaging material and products for agriculture and horticulture. A short overview of the key technical characteristics of this bioplastic are provided in the study "Bioplastics – Processing Parameters and Technical Properties" [1].

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In the broadest sense, polylactic acid (polylactide, PLA), the most sought-after bioplastic at the moment, is a polymer derived from starch. This assertion is based on the fact that the monomer of polylactic acid is essentially produced in a fermentation process. The monomer for PLA has a very broad raw material base because, not only starch, but also sugar and a variety of waste materials and plant-based raw materials may serve as the raw material. Since the choice of monomer exerts major influences on the subsequent polymer, the mechanical, thermal and processing properties of the polylactic acid can be modified in various ways by specifying a certain isomer (D- or L-lactic acid), isomer ratio or by targeted copolymerisation with other hydroxy acids. PLA made from pure D- or L-lactic acid, is semi-crystalline. As the proportion of the other monomer increases, the degree of crystallisation decreases until, at a 50/50 mixture of both isomers, no more crystalline structures are present. This has consequences for the mechanical and thermal properties.

PLA is a hydrolysis-sensitive polyester, whose molecular weight distribution can be strongly affected by degradation or transesterification reactions. That, in turn, impacts the thermal, mechanical and application technology properties. Thus, it is vital that the material be dried appropriately before it is extruded or injection moulded.

Lacea H 100, a product based on polylactic acid from Mitsui Toatsu chemicals, Inc., Tokyo, Japan, is a crystal-clear bioplastic that is manufactured by direct polycondensation and lends itself to injection moulding. Further technical properties of Lacea are to be found in the study [1] specified above.

Bioblends

Material systems, such as polymer blends, are manufactured for the purpose of enhancing properties such as thermal stability, resistance to environmental stress corrosion, paintability, electroplatability, along with mechanical properties, such as tensile strength, tensile elastic modulus and impact strength. Blending makes it possible to diminish, enhance or linearly interpolate properties. Of the miscible (homogeneous) and immiscible (heterogeneous) systems that exist, the latter are the more common. However, heterogeneous systems can be rendered homogeneous to a certain extent by means of compatibilisers. The compatibility studies presented below refer to blends of the aforementioned starch-derived bioplastics starch (MaterBi) and polylactic acid (Lacea).

In order that the properties could be studied over the full blending range (and not just on the pure components, namely 100 % MaterBi and 100 % Lacea), the following four blends were also studied:

- 80 % MaterBi + 20 % PLA,
- 60 % MaterBi + 40 % PLA,
- 40 % MaterBi + 60 % PLA and
- 20 % MaterBi + 80 % PLA.

Before the individual blends were compounded, they were dried for 24 h at 80°C. They were compounded in a twin-screw ZSE 40 GL 40D extruder from Leistritz, Nuremberg, Germany, and then cooled and granulated in the water bath. The blends containing 80 % and 60 % MaterBi proved to be very brittle and readily frangible, properties that make it more difficult to granulate these strands in continuous processing.

By intensive drying process of the granules with 80°C during one period of 48 h it is ensured that the granules are sufficiently drying despite water bath cooling of the extruding strands. The granules manufactured and prepared in this way were moulded on an Arburg, Loßburg, Germany, 420 C 1000-250 injection moulding machine to yield Campus "shoulder" specimens and standard test specimens for the impact and notched impact strength tests. Demoulding of the test specimens from the mould proved to be more difficult at a high MaterBi proportion, but this was resolved with an appropriate mould release agent.

All plastic mixtures are processed with the same injecting casting parameters. The polymer blend granules were processed at an injection pressure of 1300 bar, a holding pressure of 800 bar and a back-pressure of 4 bar. Figure 1 shows the colour change in the test specimens made from different blends of PLA (polylactide) and MaterBi (starch).

Before the properties were determined, the samples were conditioned, as per standard, for 16 h in a conditioning cabinet under standard conditions of 23°C and 50 % rel. humidity.

The data for the pure materials were taken from the relevant data collection [1]. Shrinkage of the blends (Fig. 2) was determined by measuring the mass of each of the shoulder specimens after treatment in the conditioning cabinet. The total shrinkage (ts) in the blends studied varied from -0,32 % (pure PLA) to 0,65 % (pure MaterBi). The negative value (elongation instead of shrinkage) of the pure PLA was caused by water absorption after the injection moulding. Overall, it may be stated that shrinkage increased with increase in MaterBi content. The comparatively low shrinkage of the blends may have been responsible for their poor demouldability. Good demouldability can be expected shrinkage levels of 1.3 to 2.0 %.

The tensile tests were performed with a Tira test 28100 tensile tester from Tira, Schalkau, Germany. The test results show that the tensile elastic modulus (Fig. 3) fell with rising MaterBi proportion, except in the case of the 60 % MaterBi blend. The slopes of the graphs of the stress-strain curves show that embrittlement of the blends rose with increasing proportion of MaterBi. Furthermore, it is clear that the elastic modulus values of the blends barely changed over the range 40 to 60 % MaterBi. A pronounced change in elastic modulus values is discernible only in the boundary regions of the blend diagrams.

Apart from the tensile test, tensile strength (Fig. 4) and elongation at break

More Information

More information on bioplastics will be presented in the August and October editions of *Kunststoffe international*.

Bioplastics Study

The study by the Institute for Recycling, Wolfsburg, Germany, presents a global overview of the current market for bioplastics. It surveys products by approx. 30 suppliers and lists the respective material and processing data by product. This information is supplemented by experimental data obtained in-house on over 40 materials.

The study is being marketed together with the internet portal www.bioplastics24.com. The publication is available in English and may be obtained both in electronic (PDF format) and printed form.

Shrinkage

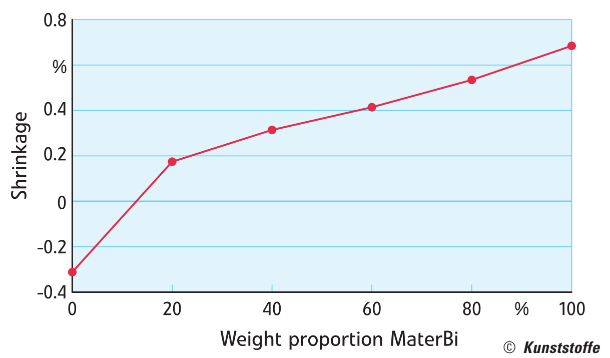
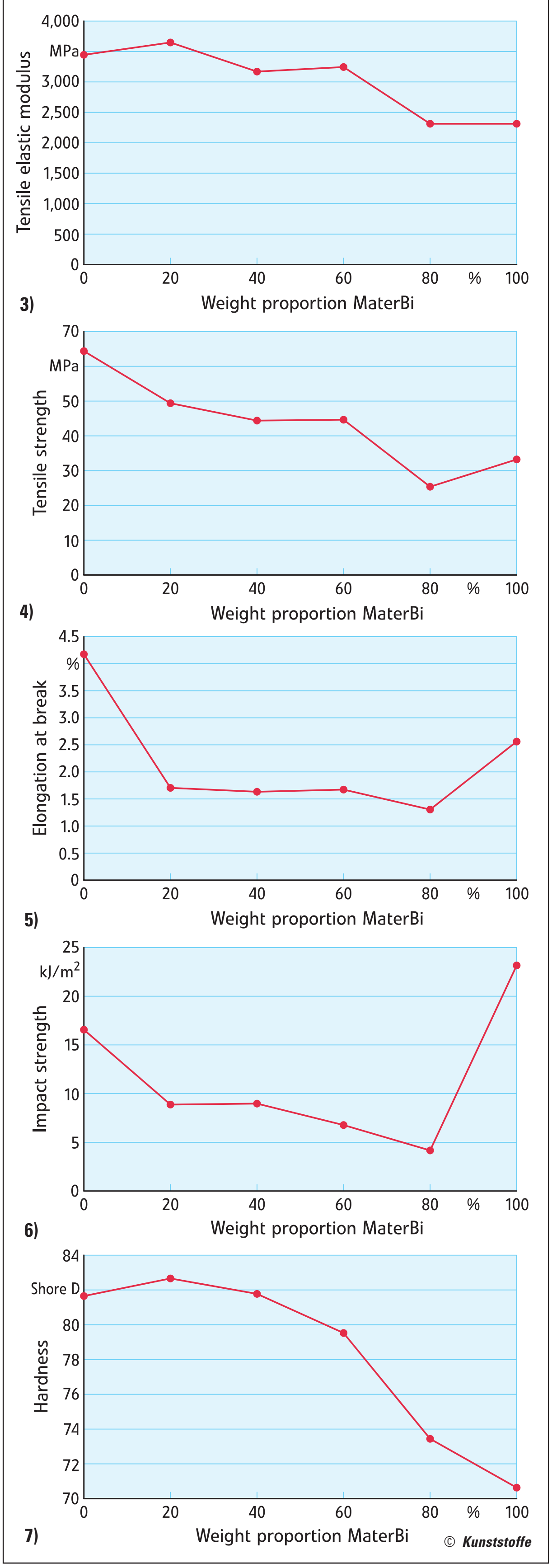


Fig. 2. Determination of shrinkage in the various (PLA+MaterBi) blends

Tests



Figs. 3 to 7. Determination of tensile elastic modulus, tensile strength, elongation at break, impact strength and hardness of the various (PLA+MaterBi) blends

(Fig. 5) were determined as a function of the composition of the blends. Here, again, there was hardly any difference in the figures for elongation at break and tensile strength in the range 40 to 60 % MaterBi. Only at low and high MaterBi proportions did large differences in the characteristic values occur, a fact which indicates major structural changes in these blends.

The impact strength test was performed with the aid of a testing device from Zwick, Ulm, Germany, in accordance with ISO 179/1 EU (unnotched samples). Proceeding from a PLA blend containing 20 % MaterBi, the impact strength started to drop considerably only when the MaterBi proportion was 60 % and higher. The experimental values are plotted in Figure 6.

Figure 7 shows the results for the hardness test performed on the blends. Initially, there was a slight increase in Shore D hardness, but this decreased markedly as the proportion of MaterBi rose.

In summary, this was the first time that a bioplastic blend had been studied comprehensively. The test series showed that, although the system was largely inhomogeneous, there were isolated beneficial properties. Future projects will be aimed at studying the influence of compatibilisers. ■

REFERENCES

1 Marek, A; Otten, A.; Widdecke, H.: Bioplastics – Processing Parameters and Technical Characteristics. www.bioplastics24.com, 2006

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