



Bioplastics such as polylactide can be injection molded to yield on-spec articles

(figure: David Carreno Hansen)

Naturally Cost-Effective

Quality Assurance. Cost-effective manufacture of on-spec bioplastic components begins before the actual start of production. For example, pellets composed of hydrolyzable biopolyesters, such as polylactide, need to be pre-dried. Stabilizers can protect against loss of quality during processing and use in technical applications. Studies support this approach.

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It is well known that hygroscopic pellets must be sufficiently dried prior to injection molding in order that process disruptions or moisture-induced damage to the material may be avoided.

Especially susceptible to thermally induced hydrolysis during injection molding are biopolymers that contain ester linkages, such as biopolyesters (e.g. PLA and PHA). Material manufacturers therefore make recommendations about the amount of moisture that can be tolerated during processing and indicate the ap-

propriate drying conditions, such as drying temperatures and times. The recommended drying always incurs a certain amount of energy consumption and additional costs, e.g. for storage, floor space, equipment, personnel and labor, which

in turn have to be factored into the end product. Processors and product manufacturers therefore need to consider not only these additional process-related costs in times of constantly rising energy costs and raw materials shortages, but also how they might be minimized.

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Reducing Costs

Proper material handling and storage is often underestimated as way of reducing or saving on costs. In particular, the moisture content prior to injection molding is a key influence on pre-drying. The wetter the material is before processing, the more effort (drying time/temperature) is needed to obtain the corresponding tolerable residual moisture content (typical-

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ly 0.01 to 0.025 %), which is usually specified by the manufacturer. The downside of this is that gentle drying at low temperatures is usually time consuming and so is rarely done.

For processors of bioplastics, it is not only the manufacturer's recommended drying temperatures and times of the materials to be processed which are hugely important, but also the moisture content of the pellets before processing and the period during which, after drying, the material should be processed. An oft-neglected factor is the storage of pellet sacks. For the most part, the moisture content of sealed sacks usually exceeds the tolerable moisture content and the goods need to be additionally dried. This problem is all the more acute where open sacks are left exposed to ambient humidity, because, if the polymers are hygroscopic, the moisture damages the material during processing and also complicates processing.

Moisture absorption was analyzed by selecting two commercial PLA copolymers from Nature Works LLC, Blair, Nebraska/USA that differ in their application and their molecular weight (h-MW = high molecular; l-MW = low molecular).

Uniform conditions (moisture content <0.01 %) were ensured by drying the pellets (60°C/10 to 12 h) on a laboratory scale in semi-industrial dryers in accordance with Nature Works' recommendations and storing them under standard conditions (23°C/50 % rel. humidity).

The results in **Figure 1** show that most of the moisture is absorbed in the first 24 to 48 hours. However, this may vary by location and storage. The dried material should therefore be processed immediately after drying in order that process downtimes and damage to the material may be avoided. Preventing the moisture content from rising again and choosing an appropriate storage location can thus save on additional costs and time outlay.

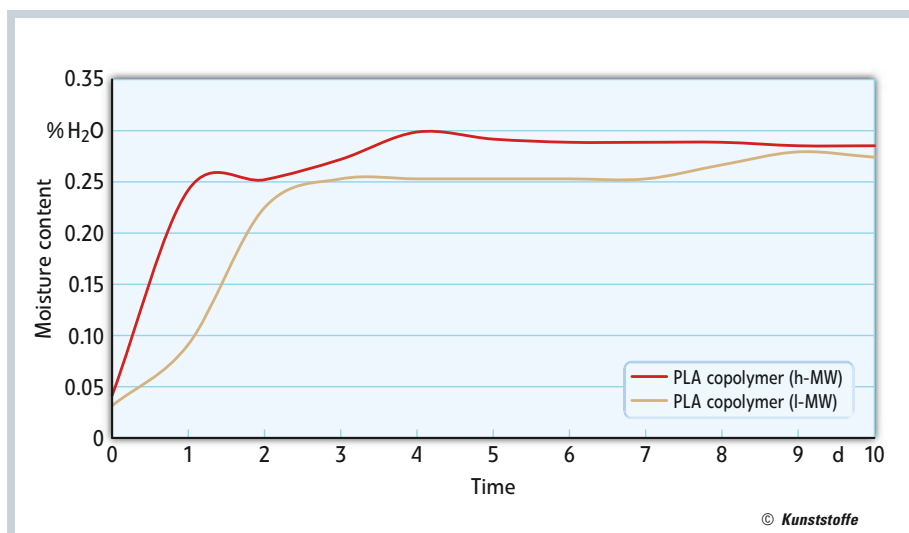


Fig. 1. Determining the moisture absorption of PLA copolymers (figure: UH – University of Applied Sciences and Arts in Hanover)

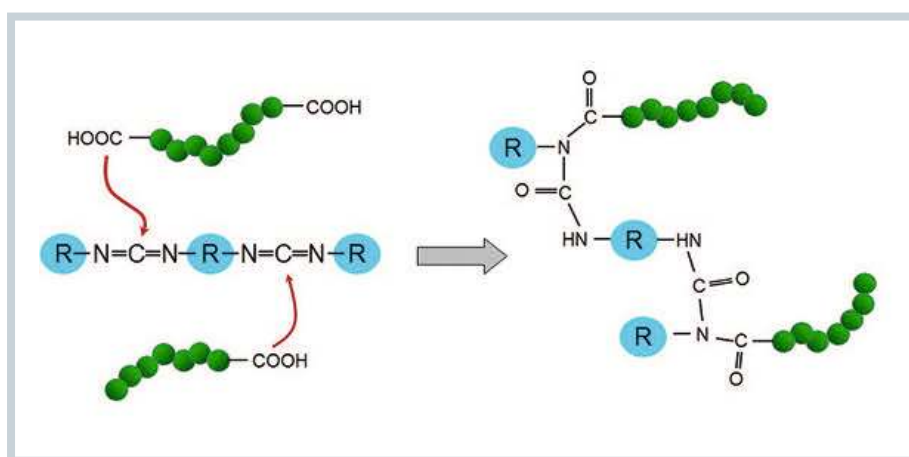


Fig. 2. Chemical mode of action of the polycarbodiimide BioAdimide 500 XT (figure: Rhein Chemie Rheinau)

Adequate Stabilization

Due to its poor hydrolytic stability, un-additivized PLA is rarely used in durable technical applications. Further stabilizers are therefore essential. A series of experiments aimed at inter alia studying hydrolytic stabilization and resistance to environmental stress testing for the automotive sector was performed on BioAdimide 500 XT from Rhein Chemie Rheinau GmbH, Mannheim, Germany.

This polycarbodiimide protects the biopolymer, both during processing and in the end product, from molecular chain degradation caused by heat, moisture and shear forces. It does so by reacting with the acid end groups of the PLA copolymer, thereby preventing acid-catalyzed hydrolytic ester hydrolysis and so reducing the extent of chain degradation (**Fig. 2**). Due to its polymeric structure, BioAdimide 500 XT exerts a chain-extending effect and so builds up the molecular weight.

The polycarbodiimide is added in various concentrations (1 to 1.5 wt.%) to the chosen PLA copolymers as a function of molecular weight; these were processed to standardized tensile test bars (Type 1A) and examined. The bars were then subjected to environmental stress tests to study long-term stabilization under constantly changing and extreme climatic conditions.

The acid value, as a comparative measurement, provides information about possible hydrolytic chain degradation. →

Material	Acid end groups before environmental stress test [mmol COOH / kg sample]	Acid end groups after environmental stress test [mmol COOH / kg sample]
PLA copolymer (h-MW)	26	> 190
PLA copolymer (h-MW) + polycarbodiimide	< 5	< 5
PLA copolymer (l-MW)	41	> 190
PLA copolymer (l-MW) + polycarbodiimide	< 5	5.3

Table 1. Acid number measurements before and after environmental stress tests (automotive sector)

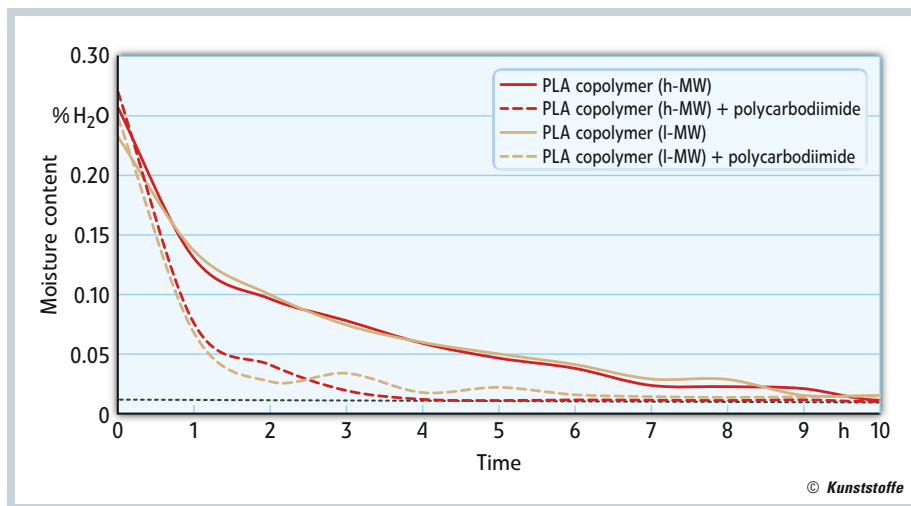


Fig. 3. Determination of the drying curve of two PLA copolymers at 60°C (figure: UH)

Any chain scission induced by cyclical climatic conditions leads to an increase in acid end groups; these were measured before and after cyclical climate testing.

Table 1 shows the molecular weight buildup resulting from the addition of BioAdimide 500 XT to both PLA copolymers. It can be seen that the acid number is reduced or the reaction between the acid end groups and the polycarbodiimide is diminished. Following environmental stress testing, unadditized PLA copolymers exhibit hydrolytic degradation due to a dramatic increase in acid end groups, whereas additivization conferred sufficient stabilization.

Another finding of this extensive study is that the requisite additive concentration is specific to the molecular weight of the polymer. Thus, a high-molecular PLA copolymer requires less BioAdimide 500 XT for adequate stabilization.

Wise Drying

Drying times and temperatures have been widely discussed with reference to biopolymers, particularly PLA [1] and they have been illustrated in detail with drying curves. How might this knowledge best be used to help processors and product manufacturers to minimize processing costs?

This question was investigated by studying the materials' drying behavior. First, drying curves were created by drying the pellets to constant weight (23°C, 50% rel. humidity) to produce a uniform initial moisture content. The initial moisture content was analyzed at the start of the experiment in the usual manner with a moisture analyzer and then the pellets were dried in semi-industrial dryers at different temperatures (60 and 80°C) and measured every hour. The drying curves

for the low-molecular (l-MW) and high-molecular (h-MW) PLA copolymer show a decreasing moisture content [% H₂O] over time in Figure 3. The target and generally recommended moisture contents of 0.01 and 0.025 wt.% are shown in red for the sake of clarity.

There is no substantial difference in the drying behavior of the PLA copolymers (h-MW/l-MW) at a mild temperature of 60°C. Both Nature Works PLA grades require 10 h to reach the guide figure of 0.01%. This result also mirrors the drying times specified by Nature Works. Optimal additivization with the polycarbodiimide can shorten the period spent at these low temperatures by 50%. The implication for injection molding is that gentle material drying at 60°C before actual processing does not necessarily extend the drying time or increase the costs. The shorter drying time, which also worked for larger quantities, as well as the lower drying temperature, could allow better and more efficient assignment of dryers and therefore of scheduled workers as well.

Conclusion

Proper handling of biopolymers, especially in terms of storage, drying and processing, can lead to cost savings. Additivization with BioAdimide 500 XT as a function of molecular weight can, in addition to conferring long-term stabilization (as demonstrated in cyclical climate tests), shorten the drying time and lower the drying temperature, which in turn lead to savings. ■

REFERENCES

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