Sustainable Solution for Coloration of Bioplastics

Coloration with Biodegradable Color Masterbatches

Plastics packaging is one of the main contributors to the global waste mountain. To avoid potential environmental problems, biodegradable bioplastics are increasingly being used for this application. But what about the additives and colorants? A masterbatch producer provides the answer.

Applications produced from biobased PHA colored with biodegradable masterbatches
(figures: Akro-Plastic)

In our everyday lives, we all encounter plastics applications produced from biobased plastics without really noticing them. Disposable carrier bags, bin liners, and refuse bags are currently the most common applications for bioplastics. In the food packaging sector, colored bioplastics are also used, for example, in the production of meat trays or disposable cutlery. There are many different applications for bioplastics in this sector and they all have to meet food industry specifications (i.e. comply with the requirements of, for example, the German Federal Institute for Risk Assessment – BfR – or the US Food and Drug Administration – FDA).

Colorants and Limit Values

The coloration of bioplastics is becoming increasingly important and is achieved today almost exclusively with the aid of color masterbatches based on polymeric carrier materials and suitable colorants.

The difficulty in producing color masterbatches lies in attaining the smallest possible residual particle size of the colorants used without employing additional dispersing agents. In film applications, particularly, extremely high dispersibility is required. When conventional, non-petroleum-based, biodegradable carrier

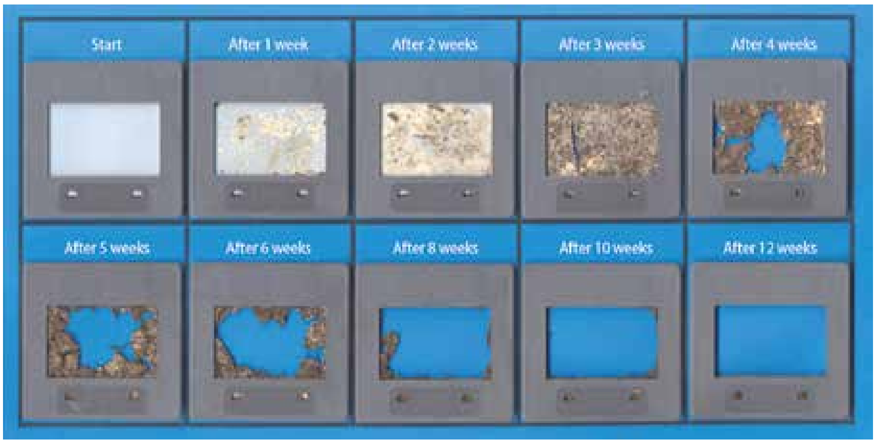

Fig. 1. The PHA carrier matrix is completed degraded within 12 weeks: the photos show the progressive degradation of a 100 µm film (disposable carrier bags usually have a thickness of about 50 µm)

Element	Concentration in the final article [ppm]
Zinc	150
Copper	50
Nickel	25
Cadmium	0.5
Lead	50
Mercury	0.5
Chromium	50
Molybdenum	1
Selenium	0.75
Arsenic	5

Table 2. Limit values for the heavy metal content in packaging applications according to DIN EN 13432

Table 1. Survey of carrier materials for masterbatches

	Petroleum-based	Biobased
Biodegradable	PBS PBSA PCL	**PHA** Cellulose Starch
Compostable	PBAT PGA PVOH	PLA
Non-biodegradable	Conventional polymers: PE, PP, PS	Bio-PE, PA11, PA6, PA10, PDO

materials are used, microparticles are released into the environment after complete degradation of the colored biopolymer. Although the amount of these microparticles is some 100 times less than that of the microparticles, this problem must be included in any strict ecological analysis and assessment in view of the large quantities of packaging waste generated.

Consumers expect a biodegradable packaging material to break down completely, including its color components. Consequently, the polymer carrier matrix must be just as biodegradable as the material being colored. But if this requirement is met, the colorant particles continue to be present as microparticles, since most available colorants have no biodegradable or compostable properties.

AF-Color, a subsidiary of Akro-Plastic GmbH, Niederzissen, Germany, uses only biodegradable and biobased PHA (polyhydroxyalkanoates) as the carrier matrix for its biobased color and additive masterbatches (**Fig. 1**, **Table 1**). Although PLA (polylactides) – a frequently used carrier material – have compostable properties and are also biobased, they are not biodegradable, i.e. they are not completely decomposed in sea water, for example.

To ensure compliance with requirements and regulations, suitable certification is of crucial importance. As with certification under UL (Underwriters Laboratories), specific requirements must be met. All formulation constituents (colorants, additives, and fillers) must comply with the prescribed standards. The applicable standard in Europe is DIN EN 13432, within which the relevant suppliers have to operate on the basis of appropriate tests. The certifying bodies (Vincotte, DIN Certco) in turn have approved laboratories that carry out the relevant tests.

The content of non-biodegradable fillers is limited by DIN EN 13432 to a maximum of 5 % in total and 1 % per individual filler. Heavy metal content, especially in packaging applications, is also regulated by this standard (**Table 2**).

The frequently used organic pigments of the copper-phthalocyanine family are particularly affected by this, since the copper content here is about 11 %. The maximum content of this colorant class in biodegradable applications according to DIN EN 13432 is thus limited to a maximum of 0.045 % in the case of pigment classes PB 15:1 and PB 15:3, and to 0.09 % in the case of PG7. The disadvantage of these colorants is that unfortunately they are not biodegradable, i.e. after degradation of the polymer matrix they potentially also enter the environment as microparticles. Mineral, i.e. inorganic, pigments – except for lead and cadmium pigments that have now fallen out of use anyway – are already contained in the relevant positive lists of various testing institutes because of their natural origin. These, among other pigments, are used as a basis by the above-mentioned certification bodies.

However, these colorants are preferably used to produce "earthy" shades and are less suitable for creating stronger, more brilliant shades, which restricts the use of bioplastics in the packaging sector.

Biodegradable and Nature-Identical

A still largely unresolved problem is the question of the biodegradability of the pigments required to color bioplastics. Organic pigments are not biodegradable and so the only option is to specify limit values (**Table 3**). The focus is on ensuring that these pigments are free from heavy metals.

"Natural" alternatives are only known from the ancient art of textile dyeing: pure purple from the purple snail, red from the cochineal insect, indigo from plants or Indian Yellow from cow's urine. Production of these colorants is of virtually no commercial importance today because of the cost and various animal protection aspects. In any case, these dyes would migrate from the bioplastic.

Some natural or nature-identical colorants can now be produced in part synthetically but they lack the properties required for modern plastics coloration in terms of light and heat stability. How- »

Color Index	Maximum concentration in the final article [%]
PY 214	0.500
PY 151	0.500
PY 155	0.500
PY 180	0.500
PY 191	0.500
PY 139	0.500
PY 181	0.500
PO 64	0.500
PR 285	0.500
PR 149	0.500
PR 53:1	0.500
PR 254	0.500
PR 170	0.500
PR 247	0.500
PR 48:2	0.500
PR 187	0.500
PV 19	0.500
PR 57:1	0.500
PR 122	0.500
PV 23	0.500
PB 15:1	0.045
PB 15:3	0.045
PG 7	0.090
PBr 25	0.500

Table 3. Limit values for the use of organic pigments in biodegradable applications as per DIN EN 13432

Fig. 2. Bin liners and disposable carrier bags produced by film extrusion from PHA and colored with biobased masterbatches

ever, if we compare the lifecycle of a plastic bag from the supermarket with our present requirement profiles, long-term preservation of color quality over a number of years would seem to be of lesser importance here.

AF-Color has already developed a color range based on its biodegradable carrier matrix and natural or nature-identical colorants (**Title figure**). Formulations specially tailored to customer requirements are also possible.

Temperature tests have shown a heat resistance of up to 150 °C for 5 min, which is sufficient for film extrusion of bioplastics from the PHA family (e.g. Mirel from Metabolix Inc., Cambridge, MA/USA) to produce items such as disposable or multi-trip plastic bags (**Fig. 2**). However, this colorant class cannot withstand the processing temperatures in masterbatch production (about 200 °C and more).

At Low Temperatures

The biodegradable plastic is supplied in pellet form, while the colorants are added as a premix and tend to decompose at temperatures above 150 °C.

Because of the colorants' low heat stability, manufacturing and processing operations must be adapted accordingly. AF-Color completely dispenses with the kneading elements and uses only mixing elements that meet this requirement. Despite a suitably adjusted temperature profile, the kneading blocks normally used in masterbatch processes would introduce too much thermal energy because of the high shear and so damage the colorants.

Through the use of special screw elements in the co-rotating twin-screw extruders (kneading block-free screw configuration, **Fig. 3**) designed by our affiliate Feddem GmbH & Co. KG, Sinzig, Germany, melt temperature peaks are significantly reduced (by about 20 to 40 %). The specific energy (kWh/kg) and hence the integral melt temperature are significantly decreased (10 to 15 % less energy, 10 to 25 °C lower melt temperature). As a result, with the kneading block-free technology used on Feddem extruders – as compared with screws with kneading blocks – speeds and hence outputs can be increased for the same melt temperature, i.e. it is possible to produce more economically, while achieving the same product quality.

This know-how is implemented by Feddem through innovative technologies in order to obtain good dispersion at low melt temperature. ■

Fig. 3. Mixing element in a kneading block-free screw for the production of biobased masterbatches at low temperature

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Service

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