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Color-Stable at High Temperatures

Polyamide 6, colored with a new pigment carrier system, does not change its color, even after exposure to a processing temperature of 320 °C (left: with a PAG-based carrier system, right: with a new carrier system) (figures: Akro-Plastic)

Polyamides. A heat-stable color system can only be achieved with a certain number of colorants. This is because many colorants reach their thermal stability limits at the high processing temperatures encountered.

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Polyamides are an important class of engineering plastics. For the vast majority of applications in which they are used, these plastics are colored black or left in their natural color, especially in the automotive sector. Other market segments for polyamides include electrical accessories, such as plugs, and food packaging film. A key reason for choosing polyamides is their excellent price/performance ratio. Their high impact strength and elastic modulus values coupled with excellent thermal stability make them particularly suitable for engineering applications in which good electrical properties are required. Their high

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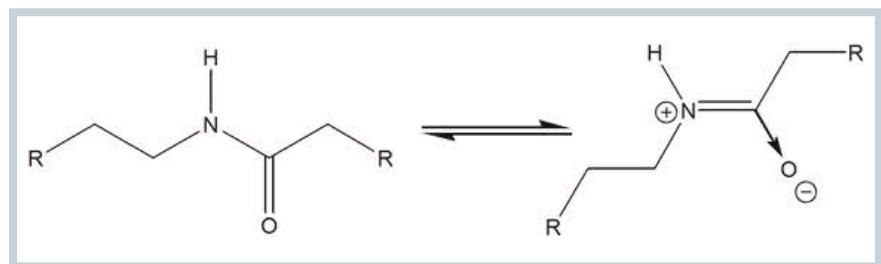


Fig. 1. Formation of the reactive center on the carbonamide group

filler loading capacity permits the use of reinforcing materials such as glass fibers, which significantly increases their rigidity and strength values. Polyamide (PA)6 and 66 are most commonly used to produce electrical and electronic plugs and various housing components.

To achieve clear recognition in a competitive environment, many components, especially housing parts, are colored in the house color of the original equipment manufacturer (branding).

The Right Colorant

To ensure that coloration of the materials described leads to the desired, reproducible result, it is very important to select the right colorants.

First and foremost, these colorants must comply with thermal stability requirements, since processing temperatures in injection molding can reach up to 300 °C. In the mold, additional short-term temperature peaks considerably

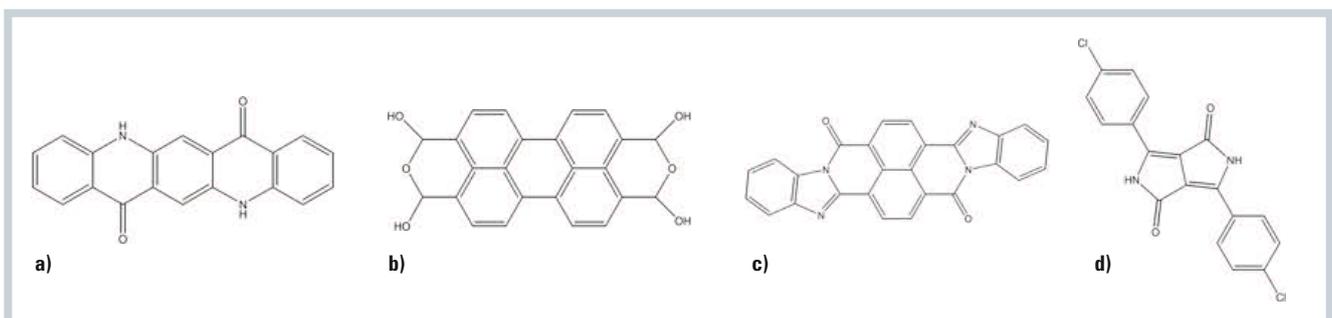


Fig. 2. Different base structures of the pigments and dyes used in polyamide coloration

higher than 300°C also occur. These depend on the design of the component, i.e. how many wall thickness and flow path transitions there are and what pressures and injection rates are used.

Many colorants succumb to high temperature at an early stage. The pigment breaks down, leading to undesirable discoloration of the component. This frequently shows up in the form of dark, brownish streaks or loss of opacity, since some pigments go into solution under the prevailing conditions. Many colorants lose their color effect entirely as a result of the decomposition process.

Some 15 years ago, this problem could be solved very easily and effectively with low-cost heavy metal pigments (lead- or cadmium-based). But the use of these colorants is no longer desirable in light of today's increased environmental awareness. A possible substitute has been found with the introduction of the rare earth metal, cerium sulfide, as a colorant. This pigment family – with shades varying from Burgundy red through red to a very brilliant orange – is highly suitable for coloration of polymers right into the high-temperature range and therefore also for

polyamide. But its price is relatively high and its market availability restricted. This pigment class also has very limited chemical resistance.

Generally speaking, all types of inorganic, i.e. in the broadest sense of the word mineral, pigments can be used for polyamide coloration. But when bright, brilliant colors are required, the limitations of this colorant class are very quickly exposed.

Colorists must therefore turn to organic, i.e. synthetically produced, pigments and dyes. Depending on their properties, i.e. their basic chemical structure, these colorants exhibit widely varying thermal stability.

Color Stability Is Important

The very reactive carbonamide group in polyamide favors physico-chemical processes that can lead to changes in the colorant molecule (**Fig. 1**). With some colorants, this is an irreversible process. This can be attributed to the formation of so-called electron donor-acceptor complexes. Under the action of atmospheric oxygen, the colorant reverts to its original structure and largely to its orig-

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inal color. Some pigments of the perinone type (**Fig. 2a**) exhibit this behavior, which is manifested in a brownish discoloration of the colorant during processing. In film extrusion, such color changes do not occur, because processing temperatures here are generally lower.

High-voltage plugs, for example, are often colored in a characteristic red. Here the use of colorants of the perylene type leads to very good results (**Fig. 2b**). In the violet range, pigments and dyes of the anthraquinone family can be used (**Fig. 2c**).

Other important criteria in selecting suitable colorants are the particle hardness and edge acuity of some inorganic pigments. Pigments of mineral origin of →



Fig. 3. PA66 test specimen with conventional color system based on a PA6 carrier (left) and formulation with a newly developed carrier system (right)



Fig. 4. Test parts colored with a diketopyrrolopyrrole-based pigment (left: with PA6 carrier, right: with new carrier)



Fig. 5. Colored test plaques injection molded from polyamide 6 after the polyamide melt has been exposed to a temperature of 320 °C for 4 min (left: PA6, right: with new carrier)

with injection molded plaques produced at 280 °C, i.e. without additional temperature stress (Fig. 3, Title picture). The CIELab values in Table 1 show the different color changes as a function of the two carrier systems.

It then became interesting to find out whether, on the basis of the new carrier, better thermal stability could be obtained with other colorants, e.g. those of the diketopyrrolopyrrole group (Fig. 2d). To this end, polymer melt containing a colorant of the aforesaid group was sim-

ten have a marked abrasive tendency, which damages the glass fibers in reinforced polyamides, causing drastic loss of mechanical properties. This is a particular problem with near-white colorants but also with many colored ones. These additional limitations compel colorists to turn to the previously described alternatives in the range of synthetically produced colorants.

To serve the market reliably therefore, further solutions are required that ensure suitable processing stability in the upper temperature range. But more far-reaching solutions have not so far been available.

New Carrier System

As described above, it is possible to go a certain way towards meeting the high requirements of polyamide coloration through the selection of suitable colorants.

Another approach is to add a suitable antagonist that positively influences the very reactive environment in the polyamide melt. AF-Color, a subsidiary of Akro-Plastic GmbH, Niederzissen, Germany, has developed a new carrier system that fulfills these conditions.

One specific challenge that colorists had to address was the coloration of a

PA66 in a very brilliant orange shade. Since all colorants are only as stable as their chemistry allows, in this particular case a solution had to be found that guaranteed the stability of the color system, even at temperatures of up to 320 °C. A conventional PA6-based formulation was compared with a formulation based on the new carrier system. In both cases, the same colorants were used: a colorant with a perinone base structure (main component) and a colorant of the anthraquinone type.

Polymer melt in the barrel of the injection molding machine was exposed to temperatures of 300 and 320 °C respectively for periods of 4 min. The test plaques molded from this material were compared visually and colorimetrically

ilarly exposed to temperatures of 300 and 320 °C respectively for 4 min in the barrel of the injection molding machine. The injection moldings were again compared with the test plaques molded at 280 °C. Figure 4 shows the test plaques molded at 280 °C (top row) and 300 °C (lower row).

Conclusion

The color system based on the new carrier showed very good stability results at 320 °C for 4 min as compared with a conventional PA6 carrier system (Fig. 5).

The carrier system described has already proven successful in some specific injection molding applications. This promising performance must be verified in further applications. The transfer of this concept to other color systems is the subject of current development projects. ■

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Temperature [°C]	CIELab	PA6-carrier	AFC-carrier
300	dL*	-1.37	-1.73
	da*	0.71	1.43
	db*	-2.68	-1.49
320	dL*	-3.26	-3.77
	da*	-1.78	0.17
	db*	-6.47	-3.84

Table 1. CIELab values for PA6 and the new carrier as a function of heat stress