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Whitening of polycarbonate requires special TiO_2 pigment grades

Abstract:

Polycarbonate, due to its unique properties, is a requested polymer for diverse applications. Apart from the automotive and consumer electronics industries, polycarbonates are also in demand from the packaging and construction industries. Electrical & electronics is estimated to be the largest segment, both in terms of value as well as volume, in 2015 with a market share of more than 21 percent of the total polycarbonate market. This segment is also projected to maintain its leading position till 2020[1]. Especially for these markets white polycarbonate compounds play an important role. Due to chemical interactions with this polymer classical TiO_2 grades are not appropriate to meet the high demands of bright white articles. The paper will compare coloristic effects as well as rheological and mechanical properties of dedicated titanium dioxide pigments with a general purpose grade.

Due to its excellent mechanical and electric properties polycarbonate even in combination with ABS, ASA or PET is a demanded resin for versatile applications. The branched molecular chain favors an amorphous crystal structure with glassily appearance reaching 89% optical light transmission. This property connected with a high impact strength make it the ideal material for safety glazing especially in the automotive and building industry but also for optical lenses and visors. In the form of CD´s or DVD´s polycarbonate founds even its place as data carrier for entertainment and office files.

But also in colored articles this polymer is appreciated because of easy processing characteristics, high temperature resistances, excellent dimension and mechanical stability, electrical properties and flame retardant performance. This includes, in particular, housings for smart phones, computers, food mixers, kettles, hair dryers etc. in short for everyday necessities.

Beside home appliances there is a wide variety of white goods for electrical and electronic applications. Examples are sockets, plugs, switches, coverings, LED reflectors. The possibilities to use white polycarbonate compounds are not limited to injection moulded parts, but are also spread to film and sheet products. Product examples of the PC calandering process are e.g. (ID) cards or (backlit) signages, reflective films for lighting etc. often as part of a multilayer composites.

In the Asia-Pacific region, China is the leading country in the consumption of polycarbonate as it is the manufacturing base of the top multinational and domestic PC manufacturers. It accounted for a market share of 1/3 of the global market share in 2014 and is expected to grow at a CAGR of 8.3% by 2019[2]. Despite the declining demand for optical data storages (CD/DVD) growth opportunities are seen in innovative lightening and light-weight automotive applications.
For white coloring of plastics mainly TiO_2 is used. In contrary to polyolefins or PVC engineering plastics like PET and especially PC interact with TiO_2 during compounding. One reason for this effect is the sensitivity of engineering plastics to hydrolysis (Fig.1), which basically requires predrying before processing. TiO_2 pigments display a hygroscopic nature and their moisture uptake depends on their chemical structure and the atmospheric humidity. This physically bound moisture is therefore in a chemical equilibrium of adsorption and desorption. Beside the physical there is also a chemical type of moisture which originates from the inorganic pigment surface treatment. This inorganic coating consists in most cases of precipitates of aluminia for improving dispersion and in case of durable TiO_2 grades additionally of silica or zirconium oxide. These compounds are not uniform as they have additionally free hydroxyl groups. At the elevated temperatures above 220°C, necessary for processing the engineering plastics, the hydroxyl groups separate water. Depending on TiO_2 volume and processing heat PC degrades. The degree of degradation can be determined by viscosity measurements.

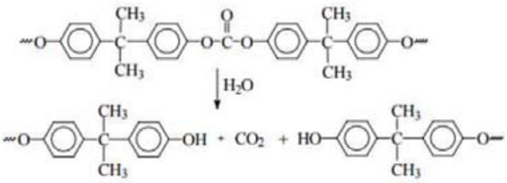
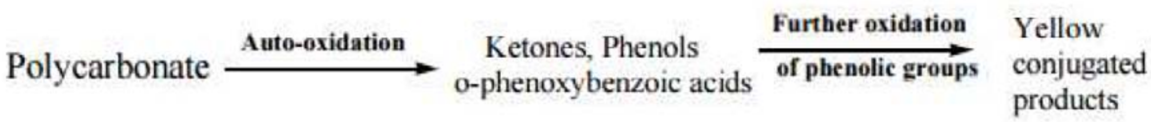


Fig.1 Degradation mechanism of polycarbonate

Shortening of the molecular chain length inevitably leads to impairment of mechanical properties, such as a decline in impact strength. In case of PC additionally a yellowish discoloration of the compound is observed as a consequence of oxidation reactions beside the hydrolysis. Bisphenol-A polycarbonate gradually degrades at temperatures above 310°C as detected by differential thermal analysis. The first stage of degradation of the resin is induced by oxygen.



The classical antioxidants cannot stabilize polycarbonate efficiently when TiO_2 is incorporated and therefore end products suffer damage. The discoloration is suspected to be caused by quinoid – structures and conjugated double bonds[4]

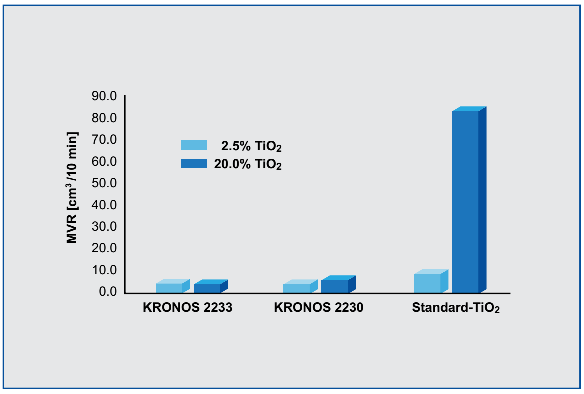


Fig.2 MVR values (300°C/1.2kg) as a function of TiO_2 content

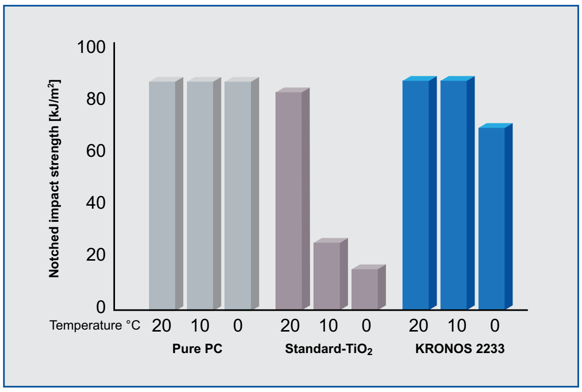


Fig. 3 Notched impact strength in dependence of temperature (ISO 180/4a)

These serious quality impairments can be extensively suppressed by using the special TiO_2 pigments KRONOS 2230 and KRONOS 2233. Both grades are functionalized TiO_2 pigments which provide an excellent stabilization (Fig. 2 and 3) and impart a bright white to polycarbonate products (Fig. 4 and 5).

Fig. 4 Color stabilising effect with KRONOS 2230 and KRONOS 2233

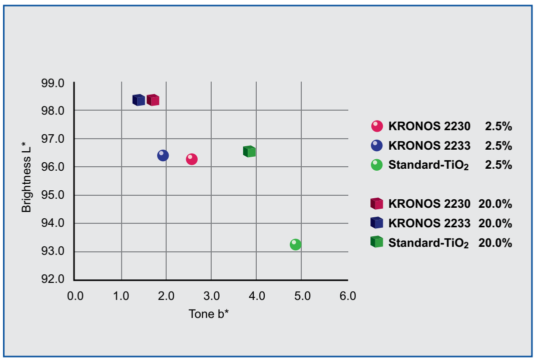


Fig.5 Color values of TiO_2 pigments in polycarbonate

The two pigments mutually complement each other as a result of their specific tones. KRONOS 2233 has a smaller mean particle size and gives grey specimens a more bluish tone. KRONOS 2230 appears more bluish in translucent films in transmitted light. Dosing volume of these KRONOS grades depends on application and may vary by average of 2.5% in up to 20% in high reflecting films.

Additionally a thermocatalytic effect on the TiO_2 surface cannot be excluded. Therefore it is not possible to gain PC products with a bright white color when using standard TiO_2 grades. Even white polyethyleneterephthalate compounds can be stabilized by both KRONOS TiO_2 grades. Measurements provide stable compound viscosities after extrusion what is not the case with standard TiO_2 pigments.
KRONOS 2230 and KRONOS 2233 are very successful since many years in quality products with a high demand in color, reflectivity and stability.

Dr. Tino Kuhn
Application and Product Manager
KRONOS INTERNATIONAL, INC
kronos.tsd@kronosww.com

[1] Business Standard, July 8, 2015
[2] Kunststoffe 10/2014, p. 78ff
[3] Kunststoff Information 11/2015, Nr. 2286
[4] ENVIRONMENTAL ASSESSMENT FOR BISPHENOL-A AND POLYCARBONATE by JIMMY T. CHOW B.S., Universidad de Costa Rica, San Jose, Costa Rica, 1991