

Chimia 48 (1994) 436–439  
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ISSN 0009–4293

# Electron-Microscopy Investigations of the Warping Effect in Pigmented High Density Polyethylene

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**Abstract.** The warping effect of high-density polyethylene (HDPE) articles produced by organic pigmentation has been studied by scanning electron microscopy. A warping pigment and its warp-free analogue obtained by surface treatment have been observed and compared to an inorganic warp-free pigment. The results indicate that the generally accepted nucleation theory is not sufficient to describe fully the warping effect. An attempt is made to describe this effect in terms of pigment-polymer compatibility.

## 1. Introduction

The coloration of bottle crates is a very interesting market for a pigment producer. Millions of crates with a lifetime of *ca.* ten years are produced each year all around the world. Apart from normal high-performance properties, like lightfastness, weatherfastness, and a heat resistance (up to 270°), the pigment needs a specific property to be used in high-density polyethylene application: it must not influence the crystallization process of the polymer. Such an influence can cause shrinkage or warping, showing as a deformation of the injected article and deterioration of the mechanical properties, which can lead to a

total failure of the article as depicted by the cracks on the bottle crate (Fig. 1).

There are several theories explaining why pigments produce distortion in polyolefins, the most widely accepted one involves the nucleating effect that some pigments have on semi-crystalline polymers such as polyethylene. After the injection, the polymer crystallizes very rapidly, during cooling. Temperature gradients which are present in the mould can produce different rates of crystallization and result in strains within the cooled material. The crystallization is mainly induced by seeding, but could also be induced by epitaxial growth on a crystalline surface [1–3]. Thus, crystalline particles

like pigments are likely to modify crystallization and crystallization rate, producing distortion in the injected article.

Inorganic pigments are particularly good in the coloration of polyethylene articles; they do not produce any deformation, because their chemical constitution and specially their surface properties have no influence on the mechanism of crystallization, and they have a good heat resistance. However, an important drawback appears at use: the high saturated colors – like red and yellow – can only be obtained with cadmium pigments. Ecological requirements recommend avoidance of their use. Their replacement by organic pigments, having the required stabilities, was always hindered by the warping problem – which is observed in a majority of organic pigments.

## 2. Surface Treatments

The important difference between inorganic and organics pigments lies in their surface: inorganics have a polar hydrophilic surface; high-performance organics are mostly lipophilic and apolar. A possible method to avoid the nucleating effect is to simulate the inorganic surface on the organic pigments by modification of the surface [4]. Typical treatments involve the precipitation on the surface of the organic particles of a thin layer of a metal oxide (*e.g.* zirconia, silica, or alumina) [5]. Another possible way to efficiently change the polarity of the pigment is to adsorb or to precipitate on the pigment surface some polar polymers like poly(vinyl alcohol), poly(acrylate), or cellulose derivatives [6].

## Testing

The efficiency of the treatment on the warping behavior is tested by injection of high-density polyethylene (HDPE) plaques. The pigmented plate is compared to a colorless one; typically, a warped plate shows a decrease in its length (DL) compensated by an increased width (DW). The Table gives the effect of two treatments on the commercial pigment *Irgazin DPP® Red BO*.

The treatment with inorganic material gives the expected results; the pigment is



Fig. 1. Example of deterioration on an injected bottle crate due to the influence of the pigment on the crystallization of the HDPE

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still not warp-free – the encapsulation with inorganics is certainly not homogeneous enough, and could also be destroyed during the dispersion step. Conversely, the treatment with the polymer shows a very good improvement of the warping behavior. These type of values represent an optimum, for dispersion reasons it is certainly not possible to go further – new naked faces are formed, when small aggregates are broken during the dispersion process.

The nucleating effect of the pigment is also regularly assessed by calorimetry and by optical microscopy. In the first test, the crystallinity and the crystallization rate of extruded HDPE sample containing 3.5% pigment are measured by DSC. In the selection of pigments discussed here, the measured differences are too small to be representative. The second test is a recrystallization at isothermal temperature. The observation of this process between two glass plates under an optical microscope does not give much more information. Normally, a non-warping pigment produces large and regular spherulites. In contrast, a warping pigment results in a very fine crystallization with irregular and numerous spherulites. In this case, untreated, as well as treated pigments present surprisingly similar crystallization behavior. All three samples show very fine crystalline structure and cannot be differentiated.

### 3. Scanning Electron Microscopy

The poor discrimination observed with these traditional investigations has led us to look at the microscopical level in order to study the area around of the pigment particle as well as the pigment-polyethylene interactions.

#### Samples and Preparation

The high-density polyethylene used in this study was a *Stamilan 9089V ex Hüls*. The pigments and the HDPE pellets were first mixed (3.5% w/w) in a *Turbula*-mixer and then extruded (dimension: 15 mm x 1 mm) three times for a better dispersion. The maximum extrusion temperature was 200°.

A 2-cm long piece of the extruded bar was then frozen to liquid N<sub>2</sub> temperature and fractured. One fractured face of each sample was etched for 4 h with an acid permanganate solution (0.7% KMnO<sub>4</sub> solution in 1:1 mixture of 98% H<sub>2</sub>SO<sub>4</sub> and 83% phosphoric acid) [7]. The other face was kept untouched. Both were observed simultaneously.

Table. *Warping Behavior*

Pigment	Surface treatment	DL	DW
C.I. Pigment Red 254 <sup>a)</sup>	none	-10.3	10.3
	metal oxide	-3.5	4.1
	polymer	-1.5	2.1
Cadmium Red <sup>b)</sup>		1.6	0.6

<sup>a)</sup> *Irgazin DPP® Red BO (Ciba)*.

<sup>b)</sup> *Cadmopur® Red BS (Bayer)*.

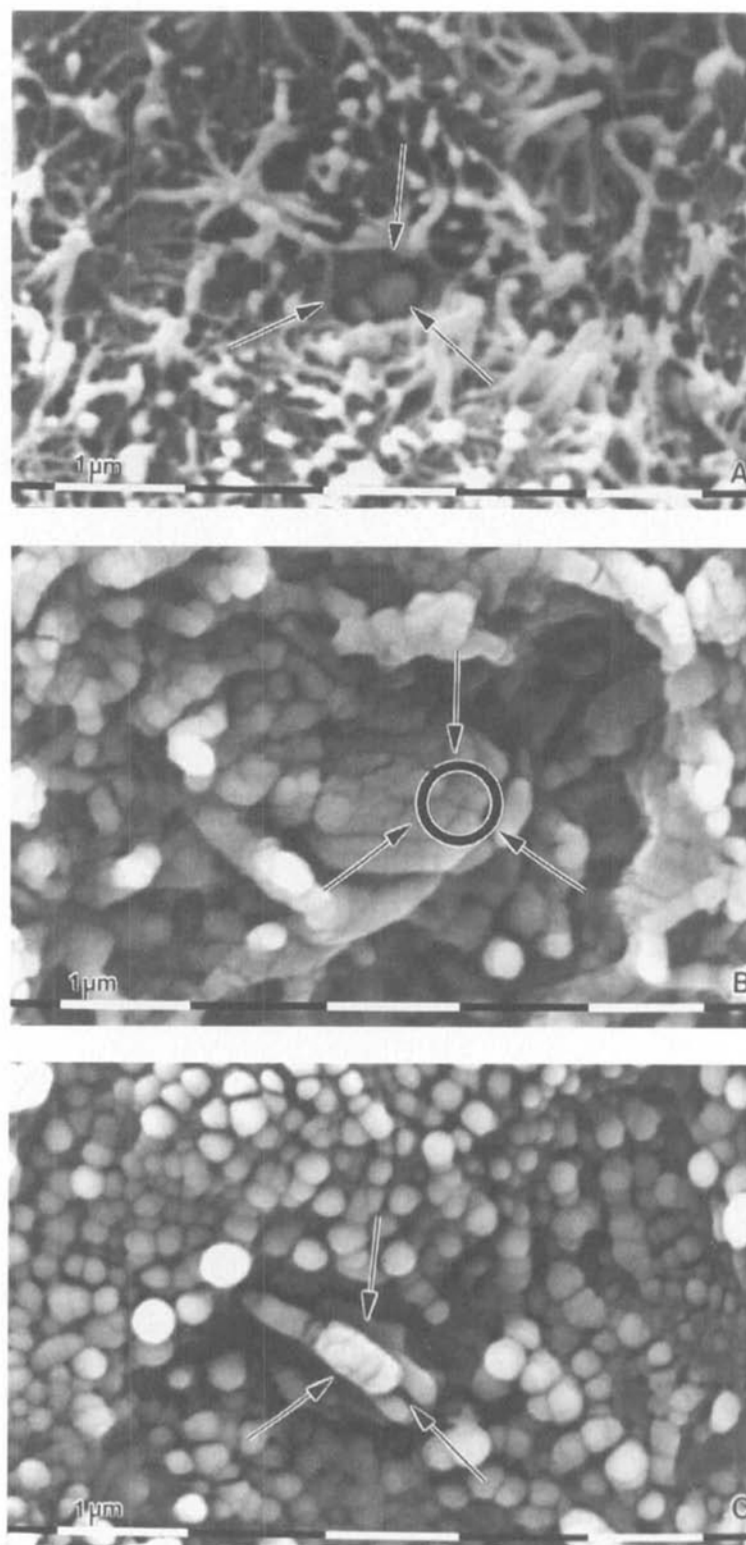


Fig. 2. Cryo-fracture of HDPE colored with A) Cadmium-Red particle isolated from matrix B) untreated organic pigment particle embedded in the matrix, found by EDX analysis. C) Polymer treated organic pigment particle isolated from substrate

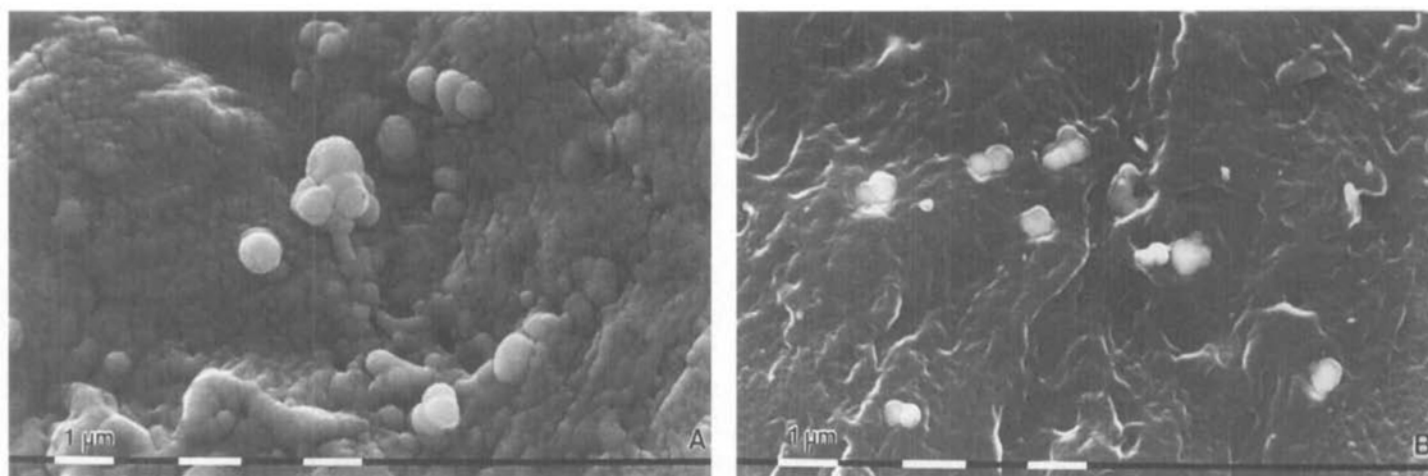


Fig. 3. Cryo-fracture of HDPE colored with A) an hydrophilic inorganic pigment ( $\text{CrTiO}_4$ ) B) hydrophobized inorganic pigment by silanization

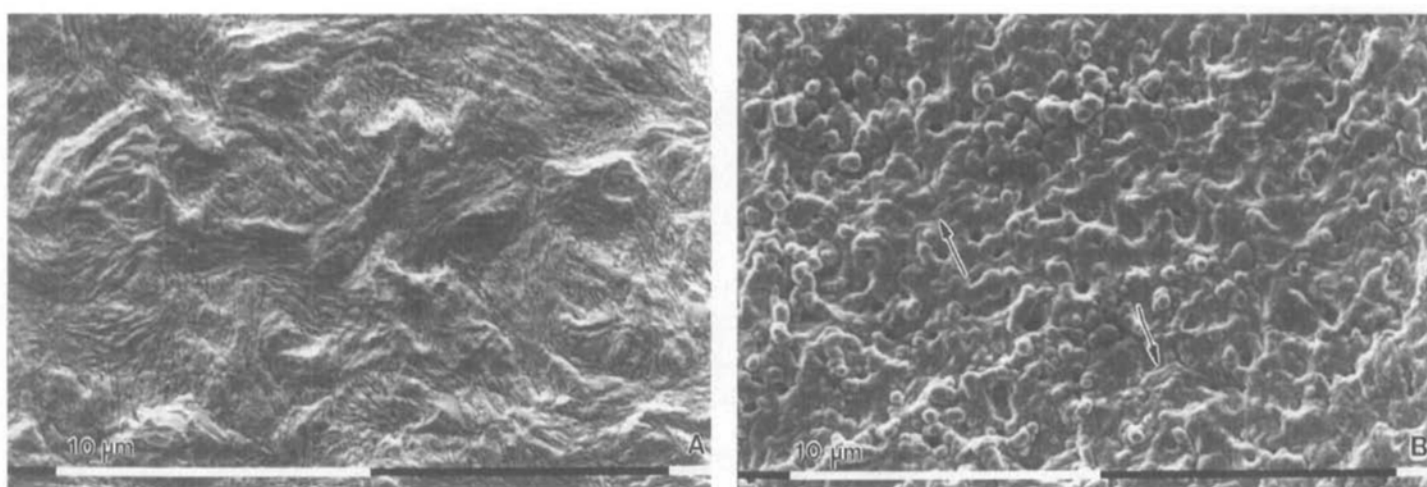


Fig. 4. A) Etched cryo-fracture of unpigmented HDPE B) same sample as in Fig. 2B, etched

The sample preparation was completed by a sputtered coating of the sample surface with 10-nm Au/Pd film in order to avoid electrical charging in the SEM. Samples were observed with a scanning electron microscope *Philips 525-M* equipped with an *EDX TRACOR TN5400*.

#### 4. Results

The observation of the effect of the different pigments on the polymer structure requires that the pigment particle themselves could be located with precision. For the inorganic pigments, it is not that much of a problem, because the difference in average atomic number between the polymer and the pigment is high enough to build a good contrast between the two. For organic pigments, however, there is very little difference, and hence very little contrast between the matrix and particle. By efficient use of the SEM-EDX (Scanning Electron Microscope coupled with an Energy Dispersive X-ray spectrometer) combination, we were able to find the pigment particles by localization of the X-ray emis-

sion of the Cl atoms contained in the pigments.

The results obtained are shown in *Figs. 2–4*. *Fig. 2A* depicts the behavior of a CdS pigment particle in the HDPE. The hydrophilic surface being totally incompatible with the polymer, the pigment particle is found sitting in a cavity built around it by the polymer. There is clearly no interaction between the pigment and the polymer. In *Fig. 2B*, the pigment is an untreated DPP with a hydrophobic surface, and, therefore, hence polymer-compatible. The capability of the pigment particle to blend into the polymer is well illustrated here. Only the X-ray Cl emission allowed us to identify the pigment position with precision. In *Fig. 2C*, the same pigment as in *Fig. 2B* was used, but its surface has been treated in order to render it hydrophilic. The situation is then comparable with *Fig. 2A*. The organic pigment that does not cause warping is treated like a foreign particle by the polymer and segregated outside the structure.

*Fig. 3* illustrates the same effect observed on the  $\text{CrTiO}_4$  – an inorganic pigment. *Fig. 3A* shows the original pigment

causing no warping. It behaves much like the CdS of *Fig. 2A* or the treated organic pigment of *Fig. 2C*. However, when its surface is chemically treated to make it hydrophobic, it blends in the polymer as it can be observed on *Fig. 3B*. In this case, the finished parts are warped.

In *Fig. 4*, the effect on the polymer structure can be clearly seen. *Fig. 4B* shows a chemically etched sample containing the same pigment as *Fig. 2B*. *Fig. 4A* shows the structure of the pigmentless reference sample. One can see that the crystalline structure of the reference is well resolved whereas in the pigmented sample, which exhibited strong warping, only very fine lamellae could be distinguished in a few areas (arrows). The structure of non-warped pigmented sample is not shown here. It is very similar as the one of *Fig. 4A* only much finer.

Finally, we observed that the addition of pigment in HDPE changes its microstructure in all cases. The pigments, where the warping is the most dramatic are also the ones where the structural changes are the most noticeable. This ability to strongly disturb the polymer's crystalline struc-

ture is due to the surface characteristics of the pigment particles. The hydrophobic, hence polymer-compatible, pigments play an active role in the structure development, whereas the hydrophilic ones have a typical impurity effect namely, they cause no observable structure modification.

## 5. Conclusions

The true explanation for the pigment warping is still unclear: not one of the different methods of analysis used has given the real evidence necessary to prove the mechanism of warping. However, the DSC results and the observation by optical microscopy indicate that this effect cannot be explained by the nucleation theory alone. The results obtained by the SEM and by other testing methods direct us to a new theory where the pigment compatibility is essential.

If a pigment is compatible with the polymer (by analogy: the polymer wets the pigment), the polymer chains will have

strong interactions with the pigment surface and the pigment particles will be linked (tied) together by the polymer chains to form a composite matrix. These interactions restrain the chain movement, meaning that mechanical relaxations are hindered, producing the warping (as with the untreated organic pigment). Conversely, incompatible pigments as inorganic pigments (CdS or CrTiO<sub>4</sub>) present no interaction with the polymer; the pigment particles and the polymer can behave as two separate phases, and mechanical relaxations after the processing are possible.

In all the methods investigated, the measured effect produced by the warping is small (*e.g.* the degree of crystallinity, the kinetics of crystallization, the change of yield *etc.*). This makes it difficult to understand fully the origin of warping, and it appears impossible to progress further in the study of warping with the analytical techniques used until now (SEM, TEM, DSC *etc.*).

From the point of view of the pigments' producer, even if the true explana-

tion of the warping was not definitely established, a good solution to the problem was found, and a commercial product is actually on the market. The treated product is commercialized under the trade name *Cromophthal DPP® Red BOC*.

Received: July 7, 1994

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*Chimia* 48 (1994) 439–442  
© Neue Schweizerische Chemische Gesellschaft  
ISSN 0009–4293

# Phasenumwandlung von 3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4-dithione für optische Speicherungsanwendungen

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**Abstract.** 'Diketopyrrolopyrroles' (DPP) are industrially important red pigments which resist bleaching. Thionation (replacement of the O- by the S-atom; the title compound (DTPP)) brings about an intense near-IR absorption in the solid state. Because of this, DTPP has recently attracted attention as a material for laser printers and optical information-storage systems based on GaAsAl laser diodes. Three crystal modifications I, II, and III are known to exist for DTPP. Among these, only modification III exhibits an intense near-IR absorption (860 nm), whereas the absorption band appears only at 690–710 nm in modifications I and II. The near-IR absorption is due to interplanar  $\pi$ - $\pi$  interactions of the alternating N-atom of one DTPP molecule and thiocarbonyl C-atom of the neighboring molecule along the stacking axis. The formation or blocking of the  $\pi$ - $\pi$  interaction ('phase change') by means of optical energy can be applied to an optical information storage system. The optical disk (structure: substrate/hydrazone/DTPP/Al) exhibits a reflectivity change from *ca.* 30 to 45% on writing with a power of *ca.* 9 mW at 780 nm.

## 1. Einleitung

'Diketopyrrolopyrrole' (DPP) sind bereits als wichtige industrielle Rotpigmente bekannt. Schwefelung des unsubstituierten DPPs ('Dithioketopyrrolopyrrol': DTPP, Formelbild in *Fig. 1*) bringt eine intensive, nah-IR-Absorption zustande. Die optischen Eigenschaften von DTPP im Festzustand sind ausführlich untersucht worden, besonders im Zusammenhang mit Anwendungen für Laserdrucker [1–4] und Informationsspeichersysteme [5] basierend auf der GaAsAl-Laserdiode. Diese Anwendungen beruhen auf der nah-IR-Absorption von DTPP. Wir haben bereits berichtet, dass es drei Kristallmodifikationen in DTPP gibt, unter denen nur die Modifikation III eine intensive, nah-IR-Absorption bei *ca.* 860 nm aufweist [6–8]. Ferner sind die elektronischen Eigenschaften von DTPP in der Lösung sowie im Festzustand sowohl vom Standpunkt intermolekularer Wechselwirkungen [9] wie auch der Molekular-Orbital-Berechnungen [10] systematisch untersucht worden.

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