

## The relationship between structure and properties in titanium dioxide filled polypropylene

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### Summary

The effect of a pigment grade of titanium dioxide on the morphology, crystallisation and mechanical properties of a typical grade of isotactic polypropylene are described. Pigment particles are able to nucleate additional spherulites, and are incorporated within spherulitic and lamellar morphologies. Measurements of isothermal crystallisation rates using differential scanning calorimetry and hot-stage microscopy show that bulk crystallisation rate is increased by addition of the pigment due to the larger number of spherulites, while the growth rate of the spherulites is unchanged. Addition of the pigment increased tensile modulus, and reduced yield stress. The elongation at break and impact resistance were increased by the addition of pigment, showing that particle debonding processes can lead to toughening of the polypropylene matrix.

### Introduction

This study [1] presents the effect of rutile titanium dioxide (TiO<sub>2</sub>) pigment on the morphology, crystallisation and deformation behaviour of an isotactic polypropylene homopolymer. Although TiO<sub>2</sub> is used widely as a pigment for polypropylene, there is very little information in the literature concerning the effect of TiO<sub>2</sub> upon the structure and mechanical properties of polypropylene and this present study represents the first major investigation in this area.

### Experimental

The polymer used was an isotactic polypropylene (Himont S-30-S) with a melting point of about 165°C and a degree of crystallinity of about 45% when injection moulded [2]. The pigment employed was a typical Ti oxide TiO<sub>2</sub> grade used in polyolefins, which had an alumina surface coating, and an organic surface treatment. The particle size of the pigment was about 0.25 μm.

Masterbatches containing 50% w/w of the pigment were made in a Banbury internal mixer. The masterbatch was diluted with pure polymer using a Brabender twin-screw extruder, to make compounds containing up to 40% w/w of pigment. Specimens for DSC crystallisation were compression moulded in the form of 0.75 mm thick sheets at 210°C [2]. Specimens for morphological studies and mechanical testing were injection moulded into rectangular bars (4 mm × 10 mm × 120 mm) using a Negri-Bossi NB60 [2]. The nozzle temperature was 220°C and the mould temperature was 30°C.

The etching technique of Bassett and co-workers [3] was used for morphological analysis. Specimens were cut from a parallel-sided injection-moulded bar with the surface for etching parallel to the direction of injection, and the surface flattened using a microtome. Specimens were etched using 1% w/w of potassium permanganate dissolved in a 1:1 mixture

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of concentrated sulphuric acid and orthophosphoric acid (88%) for one hour. Two-stage replicas were produced for examination by TEM, or specimens were examined by SEM, after sputter coating with gold.

Isothermal bulk crystallisation was performed using a Perkin-Elmer DSC-2, over the temperature range of 116 to 135 °C. The specimen was heated to 230 °C, and held for ten minutes at this temperature, before being cooled at 40 °C/min to the crystallisation temperature. The crystallisation of PP containing 2.5% w/w of pigment was compared with that of the unfilled PP. Radial growth rates of spherulites were measured using a Linkam THM 600 hot-stage, over the range of temperature of 116 to 135 °C. Spherulite growth was recorded using a video recorder coupled to a CCD camera on the microscope.

Tensile testing of injection moulded dumbbell specimens was performed at 23 °C on an Instron 1122, on two sets of specimens deformed under different conditions: i) at  $1.1 \times 10^{-3} \text{ s}^{-1}$  strain rate using a clip-on strain-gauge extensometer to measure tensile modulus at 0.5% strain, ii) at  $1.1 \times 10^{-2} \text{ s}^{-1}$  strain rate, to determine ultimate tensile properties at high strains. The different strain rates were used for experimental convenience and did not affect the measurements significantly.

Impact testing on sharp-notched Charpy specimens (notch-to-depth ratio of 0.5) was performed at room temperature using a Ceast instrumented pendulum impact tester, with a 3.46 m/s pendulum velocity.

## **Results**

### **Morphology**

The typical morphology of the PP homopolymer was spherulitic. The unfilled polymer produced large spherulites when crystallised isothermally. Fig. 1 shows an example of the spherulite size in a specimen crystallised at 115 °C in the DSC.

The addition of pigment particles caused more spherulites to be nucleated in the isothermally crystallised specimens, as shown by the much smaller spherulite size in the pigmented specimen crystallised isothermally at 115 °C (fig. 2). This effect of increasing the number of spherulites resulted in an increase in the bulk crystallisation rate, which is described in the following section.

The injection moulded bar specimens had complex skin-core morphologies. Due to the opacifying effect of the pigment, the usual technique of microtomy and optical microscopy of thin sections could not be applied to pigmented material. This, and the ability to resolve lamellar morphology and the individual pigment particles, makes the technique of permanganic etching and replication especially attractive in the study of such specimens.

In the skin layer, which is about 0.6  $\mu\text{m}$  thick and forms adjacent to the mould wall, elongational flow causes the molecules to be uncoiled and oriented. A morphology similar to the shish-kebab morphology formed by the stirring of solutions [4], is the result in the unfilled PP (fig. 3). A similar morphology, with rows of oriented lamellae, was also found in the pigmented specimens (fig. 4). Many pigment particles are extracted from the surface during replication and appear dark. Close examination of such micrographs shows that the pigment particles are distributed evenly within the crystalline morphology, and that lamellae grow in close proximity to the pigment particles, seemingly unaffected by the presence of the particles.

The central (core) zone of the injection mouldings contains spherulites as shown in fig. 5, which, significantly, are smaller than those in the isothermally crystallised unfilled specimen (compare with fig. 1). In the SEM micrograph of the core zone of the pigmented specimen (fig. 6), the pigment particles appear white. Presence of the pigment does not alter the spherulite size in the injection mouldings, and it can be seen that particles are

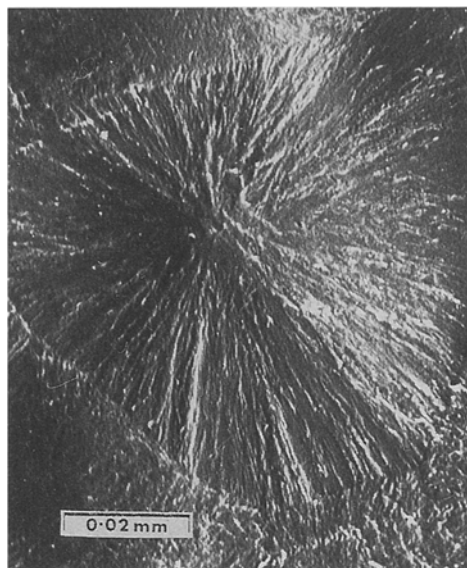


Fig. 1. Morphology of an unfilled PP specimen crystallised at 115°C in a DSC (SEM micrograph of etched cut surface).

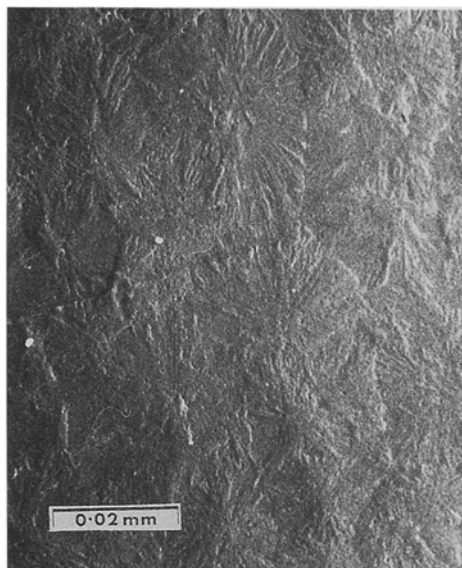


Fig. 2. Spherulites in a PP specimen containing 2.5% w/w of pigment crystallised at 115°C in a DSC (SEM micrograph of etched cut surface).

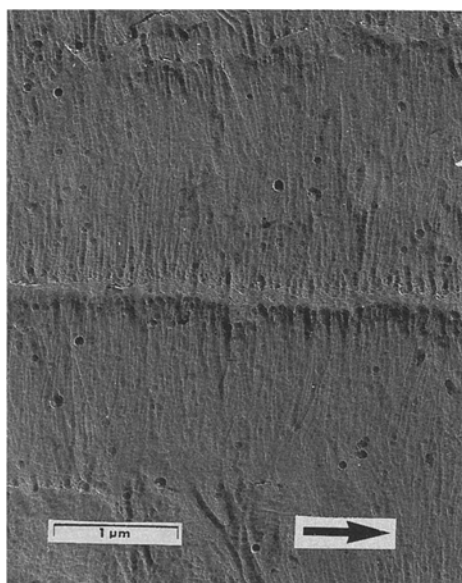


Fig. 3. Skin morphology of an unfilled PP specimen, showing material about 0.4mm from the edge of the moulding. The arrow indicates the injection direction (TEM micrograph of replica of etched cut surface).

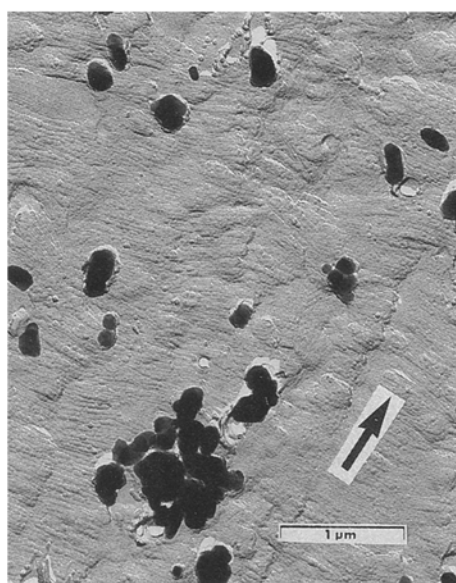


Fig. 4. Skin morphology of PP containing 40% w/w of pigment. Pigment particles extracted from the surface appear black. The arrow indicates the injection direction (TEM micrograph of replica of etched cut surface).

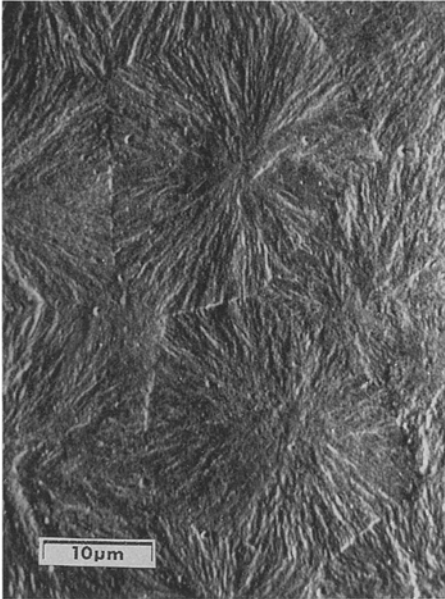


Fig. 5. Spherulites in the core zone of an unfilled PP injection moulding (SEM micrograph of etched cut surface).

Fig. 6. Spherulites in the core zone of an injection moulding of PP containing 10% w/w of pigment. Pigment particles (white) can be seen within the spherulites (SEM micrograph of etched cut surface).

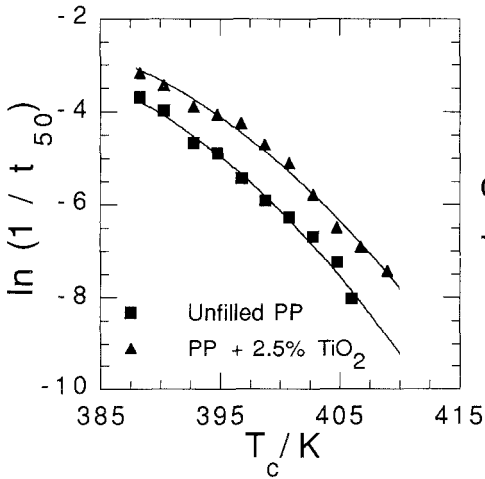


Fig. 7. Plots of  $\ln(1/t_{50})$  against  $T_c$  for PP specimens crystallised in the DSC.

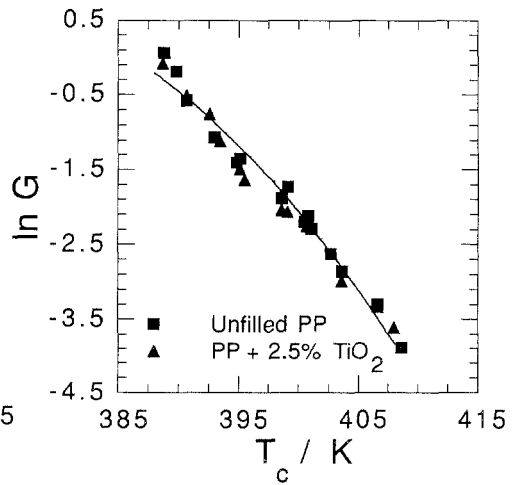


Fig. 8. Plots of  $\ln G$  against  $T_c$  for PP specimens crystallised on the hot-stage.

incorporated uniformly within the spherulites.

The pigment has little effect on the underlying lamellar morphology, and it appears that the particles are engulfed by the growth of crystalline material rather than being forced outward e.g. to spherulite boundaries, as has been reported by other workers [5].

### Crystallisation

DSC isothermal crystallisation data were analyzed to find the time ( $t_{50}$ ) at which 50% of the crystallisation had occurred. The reciprocal of this quantity,  $1/t_{50}$ , is referred to as the bulk crystallisation rate. The plots of  $\ln(1/t_{50})$  versus crystallisation temperature ( $T_c$ ) in fig. 7 show that addition of the pigment substantially increased the bulk crystallisation rate of the PP. In other words, at a particular temperature, the pigmented specimen took a shorter time to crystallise.

Over the same temperature interval, measurements of  $G$ , the radial growth rate of spherulites [6] in  $\mu\text{m s}^{-1}$  (fig. 8), show that the presence of the pigment does not significantly alter the growth rate of the spherulites.

Thus, the pigment alters the bulk crystallisation process, as measured in the DSC, but the underlying crystallisation process is not affected. The reason for the increased rate of bulk crystallisation was adumbrated in the morphologies shown in figs. 1 and 2 which show that the effect of the pigment is to nucleate additional spherulites. With more spherulites in the pigmented specimens the time until spherulite impingement occurs at a particular  $T_c$  is reduced, leading to the bulk crystallisation process being completed in a shorter time.

### Mechanical Properties

The tensile modulus of the PP was found to be  $1.53 \pm 0.05$  GPa and was increased by addition of the pigment as shown in fig. 9 where modulus values normalised with respect to the PP modulus are shown. The simplified Kerner [7,8] equation was used to analyze the tensile modulus data:

$$E_c = E_m \left[ 1 + \frac{\Phi}{1+\Phi} \left[ \frac{15(1-\nu)}{8-10\nu} \right] \right] \quad (1)$$

where  $E$  is tensile modulus  
(subscripts c and m denote composite and matrix respectively)  
 $\Phi$  is the volume fraction of pigment  
 $\nu$  is the Poisson's ratio of the matrix

It can be seen from fig. 9 that the increase in modulus is quite well fitted by eqn. (1).

The yield stress of the PP was found to be  $35.9 \pm 0.3$  MPa and was reduced by the presence of pigment as shown in fig. 10. The yield stress data were analyzed with the following equation [9]:

$$\sigma_{yc} = \sigma_{ym} (1 - C\Phi^{2/3}) \quad (2)$$

where  $\sigma_y$  is the yield stress.  $C$  is an adjustable parameter [10] and  $C=1.21$  for a lower-bound estimate of  $\sigma_{yc}$ . The reduction in yield stress was not as severe as that predicted by the lower bound of eqn. (2), which assumes that the particles are completely debonded from the matrix prior to yield. This suggests that the particles are still able to bear some of the load at the yield point.

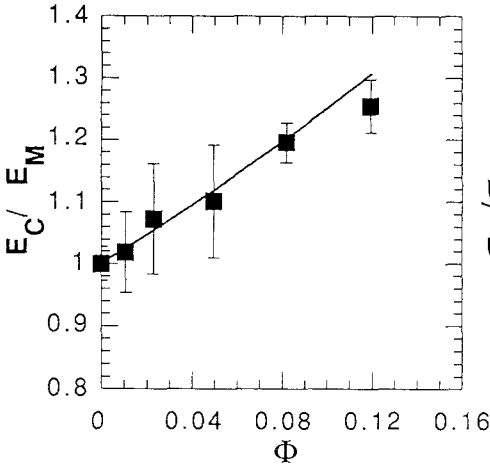


Fig. 9. Normalised tensile moduli (at 0.5% strain) of the PP composites as a function of volume fraction,  $\Phi$ , of pigment. The solid line is a plot of eqn. (1).

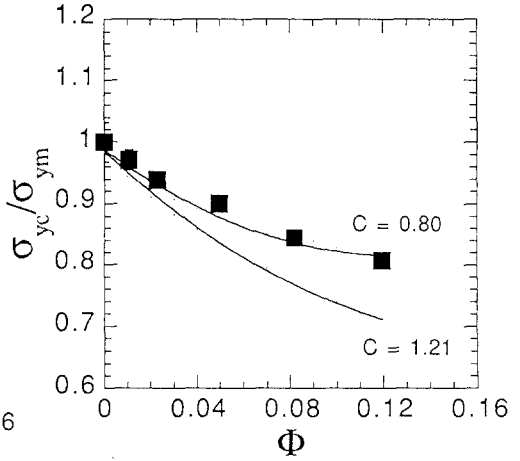


Fig. 10. Normalised yield stress values for the PP composites. The solid lines are plots of eqn. (2), with the values of the parameter  $C$  as indicated.

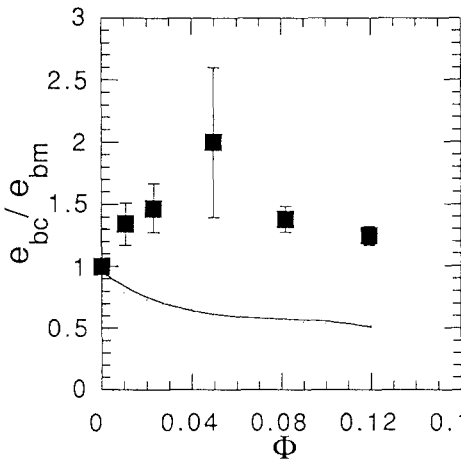


Fig. 11. Normalised elongation at break plotted against  $\Phi$ , the pigment volume fraction for the PP composites. The solid curve is a plot of eqn. (3).

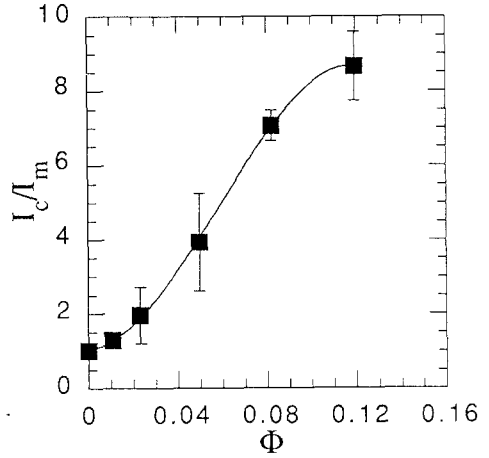


Fig. 12. Normalised impact energy,  $I$ , plotted against the pigment volume fraction  $\Phi$ , for the PP composites.

The elongation at break of the PP was  $60 \pm 15\%$  and in some cases was enhanced by the presence of the pigment as shown in fig. 11. The elongation at break was compared with the following equation, which assumes good bonding between filler and matrix [8]:

$$e_{bc} = e_{bm} (1 - \Phi^{1/3}) \quad (3)$$

Comparison of the data in fig. 11 with eqn. (3) highlights the vast difference between the experimental results and the case where adhesion to the matrix is good. Examination of the necked surfaces of tensile specimens revealed elongated voids around pigment particles, with occasional fibrils of polymer still attached to particles. Debonding of particles and fibrillation of the matrix appears to aid the necking process, making the polymer more extensible.

The impact energy ( $I$ ) of the PP was about  $2.6 \text{ kJ m}^{-2}$  and was increased markedly by addition of the pigment (fig. 12). The unfilled PP was relatively brittle under the conditions used. Once the crack had been initiated, it propagated through the specimen spontaneously, without further input of energy from the pendulum. Impact resistance increased continuously with pigment content. This fact, allied to the study of morphologies of the pigmented specimens, shows that the pigment particles increase impact resistance by altering the fracture process, rather than changing the morphology. Fracture surfaces of specimens containing 30 and 40% w/w of pigment are rough, due to voiding around particles. This alters the fracture process from brittle in the unfilled PP, to ductile in the pigmented specimens. It appears that debonding of particles ahead of the propagating crack leads to this toughening process, as suggested in a recent theoretical study [11].

### Conclusions

The use of the permanganic etching technique has led to a detailed understanding of the morphology of  $\text{TiO}_2$  filled polypropylene. It is shown that pigment particles can be incorporated within lamellar and spherulitic morphologies causing little perturbation of crystalline growth. In isothermal crystallisation, the addition of the pigment increases the number density of spherulites but not in injection moulding where the crystallisation conditions such as elongational flow and fast cooling, imposed by the moulding process, dominate over effects on subsequent morphology caused by the presence of the pigment. Isothermal crystallisation studies have shown that while the pigment increases the rate of bulk crystallisation, the fundamental crystallisation processes are unchanged. The effect of the pigment is to nucleate additional spherulites.

Mechanical testing has shown that the tensile modulus is increased at low strains, but as the strain is increased, the process of particle debonding starts to dominate the deformation behaviour leading to a decrease in yield stress. Particle debonding and voiding lead to energy dissipation in larger volumes of the matrix, which substantially increase elongation at failure and impact resistance.

### Acknowledgements

This work was supported by a research grant from Tioxide plc. RJY is grateful to the Royal Society for financial support through his Wolfson Research Professorship in Materials Science.

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Accepted January 18, 1993      C