The effect of masterbatch pigments on the crystallisation, morphology, and shrinkage behaviour of Isotactic Polypropylene

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Abstract
Variations in mould shrinkage when using organic and inorganic pigments in semicrystalline polymers is a well-known phenomenon within industry. These differences in mould shrinkage are thought to be caused by the presence of the pigments acting as nucleating agents, altering the crystallisation of semicrystalline polymers. These shrinkage variations can give rise to problems in obtaining the correct interference fit between parts and can cause issues in automated equipment such as filling lines. It has been previously reported that the onset temperature of crystallisation measured via DSC (differential scanning calorimetry) can be used to predict shrinkage when a variety of neat pigments are added to un-nucleated PP (polypropylene). However, the shrinkage and crystallisation behaviour of masterbatch pigments, which are widely used industrially is poorly understood. To better understand the influence of masterbatch pigments on crystallisation and shrinkage behaviour, injection moulded samples were prepared using variety of reds, whites, and purple commercial-masterbatch pigments with PP. The crystallisation kinetics and crystallinity were studied using DSC, LPOM (Linkam hot stage polarising optical microscopy), XRD (X-ray diffraction), and FTIR (Fourier transform infrared spectroscopy). The morphology was investigated via LPOM and SEM (scanning electron microscopy). A clear correlation was observed between the crystallisation onset temperature measured using DSC and the recorded shrinkage. A strong relationship was also observed between the percentage crystallinity measured using FTIR and shrinkage. Quinacridone and pyrrole based red and purple pigments were found to act as strong nucleating agents, with the pyrrole based red pigment also acting as β nucleator in PP. The white pigments were found to have less influence on the nucleation behaviour. For the pigments which induced the largest variation in shrinkage, a higher rate of nucleation and proportionally smaller spherulitic diameter was observed by DSC, SEM, and LPOM.

Keywords Shrinkage · Crystallisation · Pigments · Nucleation · Morphology

Introduction
Injection moulding is one of the predominant polymer production processes and has been used industrially for many years [1]. Injection moulded parts can be manufactured using both amorphous and semicrystalline polymers. Pigments are widely used in a diverse range of polymer applications from packaging to medical devices. The pigments must meet several requirements including a high colouring power, heat stability, chemical insensitivity and insolubility in the polymer carrier [2]. Pigments can be either organic or inorganic in nature and are frequently used in the form of masterbatches. Commercially available masterbatch pigments are typically a premix of organic and inorganic pigments in a suitable polymer carrier such as LDPE (low density polyethylene). When compared to neat colour powders or liquids,
masterbatch pigments offer benefits in product quality and ease of use such as: higher colour strength, reduced cleaning time, and better dispersion behaviour [3]. In addition, specialist feeding, and mixing equipment would be required if pigments were to be added to the polymer granules in liquid or powder form and the use of fine powders raises health and safety concerns.

Although pigments are added solely to achieve the desired colour in a polymer, the presence of even a small amount of pigment can cause serious dimensional issues through shrinkage and warpage of the product. Therefore, understanding the influence of pigment addition on shrinkage is of great importance. The chemical composition of the pigment is a major factor in defining the final properties of the polymer product [4]. It has been reported by previous researchers that adding pigments to semicrystalline polymers can act as nucleating agents, increasing both crystallisation temperature and nucleation rate [5, 6]. Bhatia et al. also reported an increase in crystallisation temperature when using metal monoglycerolate nucleation agents in semicrystalline polymers [7]. Lee and Tanner, reported that organic pigments had a greater nucleating effect than inorganic pigments [8]. It was noted that organic pigments increase the nucleation rate, which then dominated over the growth rate. Silberman et al. showed in their 1995 study that adding even small amount of pigment to polypropylene resulted in an increased equilibrium temperature of crystallisation and crystallinity [4]. Jan Broda, concluded that quinacridone and phthalocyanine pigments act as strong nucleating agents in polypropylene, increasing the crystallisation rate [9, 10]. The strong nucleating effect of pigments can cause warpage and shrinkage in injection moulded parts. In 2004 Suzuki and Mizuguchi, reported that the various pigment types can act as either weak or strong nucleation agents. This nucleation effect is reflected as an increase in the onset temperature of crystallisation and their study reported a correlation between the onset temperature of crystallisation measured using DSC and shrinkage [11].

Shrinkage and warpage are common dimensional issues in the injection moulding industry when using semicrystalline polymers such as polypropylene and polyethylene. In addition to the nucleation effect of additives, shrinkage in injection moulded parts can also be affected by the processing conditions. Extensive research has been carried out on the influence of processing conditions on the shrinkage of injection moulded thermoplastics [12, 13]. It has been reported that the most important parameters that effect mould shrinkage are melt temperature, holding pressure, and mould temperature. A higher the melt temperature decreases the shrinkage because of better pressure transmission. Increasing the holding pressure decreases the shrinkage, while an increase in mould temperature generally increases shrinkage for semicrystalline polymers [12]. Other processing conditions such cooling time and injection pressure can also influence shrinkage with increases in cooling time and injection pressure tending to reduce shrinkage. Shrinkage in injection moulded parts has also been reported as being anisotropic, due to differences in cooling rates and molecular orientation [14].

There are limited previous studies reporting the influence of pigment addition on the crystallisation kinetics and morphological behaviour and how this affects shrinkage and warpage. Several previous researchers have studied the impact of pigments on the crystallisation behaviour of polymers [15–17]. However, very few publications have focused on the effect of pigments on the shrinkage of injection moulded parts [11]. To the best of our knowledge, no previous work has reported the influence of masterbatch pigments on crystallinity and shrinkage. To better understand the influence of masterbatch pigments, samples were injection moulded using isotactic PP (polypropylene) with five different masterbatch pigments. The samples were characterised via, shrinkage measurements, DSC (differential scanning calorimetry), FTIR (Fourier transform infrared spectroscopy), and XRD (X-ray diffraction). The crystallisation kinetics and morphological behaviour was also studied using LPOM (Linkam hot stage polarising optical microscopy) and SEM (scanning electron microscopy). SEM and EDX analysis were also conducted on the concentrated pigments which had been separated from the masterbatches. A larger group of 14 pigments were also subjected to a more limited range of characterisation (XRD, DSC, and FTIR).

### Materials

Tables 1 and 2 show the details of the commercial unnuclide isotactic PP and masterbatch pigments used in the production of the injection moulded samples. The red masterbatch batch pigment R122 referred to as ‘R2’ pigment contains red quinacridone pigment which is organic.

| Polymer | Trade Name | Manufacturer | Type | Melt flow rate 230°C / 2.16 kg |
|---------|------------|--------------|------|-------------------------------|
| Isotactic Polypropylene (isotactic PP) | HD850MO-11 | Borealis | Unnucleated Homopolymer | 8 g / 10 min |

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*Table 1* Details of Isotactic Polypropylene used in injection moulding
The purple masterbatch P40639 referred to as pigment ‘P’ also contains organic red quinacridone (R122) along with two inorganic pigments, ultramarine blue (Blue 29) and TiO$_2$ (White 6). The other red pigment R32671 referred to as pigment ‘R1’ consists of red diketopyrrolopyrrole (R254) as an organic ingredient and inorganic TiO$_2$ (White 6). The two white pigments W90724 and WTiO$_2$ referred to as ‘W1’ and ‘W2’ respectively, contain TiO$_2$. All the commercial masterbatch pigments may also contain other additives such as fillers and use low density polyethylene (LDPE) as a carrier. This information on the pigments used in the masterbatches was provided by the masterbatch suppliers.

In terms of the chemical structure, quinacridone has a five-ring polycyclic aromatic structure with amine and carbonyl groups attached to two of its rings. Quinacridone mainly exhibits two polymorphic forms indicated as β and γ phases [9, 18]. The diketopyrrolopyrrole also known as DPP has heterocyclic phenyl rings twisted in the same direction and has been found to exist in two polymorphic phases (α and β) [19]. The ultramarine blue exhibits a three-dimensional aluminosilicate lattice structure with sodium and sulphur ionic groups entrapped in it. The basic ultramarine structure consists of equal silicon and aluminium atoms with basic formula of Na$_6$Al$_6$Si$_6$O$_{24}$ [8]. The white pigment (TiO$_2$) exists in two crystal phases, rutile and anatase [20].

**Experimental**

Rectangular 80×10×4 mm samples were made using a Wittmann Battenfeld smart power 35 injection moulding machine. All the masterbatch pigments were added at a concentration of 2 wt.% and the injection moulding conditions are shown in Table 3.

**Shrinkage measurement**

Shrinkage measurements were taken according to standard ASTM D-955 [21]. The shrinkage was measured parallel to the machine direction known as mould direction (MD) and perpendicular to the machine direction known as the transverse direction (TD). The shrinkage was measured for five specimens of each sample type using a digital micrometre and the average values are reported. Measurements were taken 48 h after injection moulding and again after 28 days. Equation (1) was used to calculate shrinkage. The errors bars were calculated according to the mean standard error formula [22].

\[
MD = \frac{Lm - Ls}{Lm} \times 100 \quad \text{and} \quad TD = \frac{Tm - Ts}{Tm} \times 100
\]

where MD = Mould shrinkage (Flow direction), TD = Transverse shrinkage (Cross flow direction), Lm and Tm = Mould dimension in the flow direction and cross flow direction

| Reference names | Trade names | Manufacturer | Pigment formulation | Chemical structure | Size ranges from SEM (µm) |
|-----------------|-------------|--------------|---------------------|--------------------|--------------------------|
| R1              | Red R32671  | Colour Tone Masterbatch | Pigment red 254, Pigment white 6 | Red 254 (~1.03–2.01), White 6 (~0.1–0.43) |
| R2              | Red R122    | Broadway Colours | Pigment red 122 and additives | (~0.06–0.20) |
| P               | Purple P40639/ RF | Colour Tone Masterbatch | Pigment blue 29, Pigment white 6, Pigment red 122 | Blue 29 (~1.96–3.62), White 6 (~0.22–0.5), Red 122 (~0.05–0.13) |
| W1              | White WTiO$_2$ | Broadway Colours | Titanium dioxide and additives | (~0.10–0.35) |
| W2              | White W90724 | Colour Tone Masterbatch | Titanium dioxide and additives | (~0.18–0.32) |

| Polymer | Temperature (ºC) | Pressure (bar) | Processing time (secs) |
|---------|------------------|----------------|------------------------|
|         | Barrel | Mould | Injection | Holding | Injection | Hold on | cooling |
| iPP     | 230    | 35    | 300       | 200     | 5         | 7       | 40       |
respectively, \( L_s \) and \( T_s \) = Dimension of the moulded part in flow direction and cross flow direction respectively.

**Onset temperature of crystallisation and DSC based percentage crystallinity**

DSC was carried out using a TA Instrument DSC 250 machine under a flowing nitrogen atmosphere. The ~6 mg specimens were heated at a rate of 10 °C/min to a temperature of 200 °C and left at 200 °C for 5 min to remove the thermal history. The specimens were then cooled down at the same rate to 50 °C.

Two specimens were tested for each sample type from the 4 mm thick injection moulded samples. A cross-section was first removed from the centre of the injection moulded sample as shown in Fig. 1a. The first specimen was then taken from the outer layer (the area from top surface to ~0.5 mm depth) of this part and the second one was taken from the centre layer (the middle ~2 mm central area), Fig. 1b, and the average values are reported. The initiation point of crystallisation on the cooling side of the first DSC scan gives the onset temperature of crystallisation.

The DSC based crystallinity percentage \( (X_{Dsc}) \) was evaluated as the ratio of measured enthalpy of crystallisation \( (\Delta H_c) \) of first heat/cool scan and enthalpy of 100% crystalline PP according to Eq. (2) [23].

\[
X_{Dsc} = \frac{\Delta H_c}{\Delta H_f^0} \times 100 \tag{2}
\]

The enthalpy for 100% crystalline PP \( (\Delta H_f^0) \) was taken as 201 J/g [24].

The isothermal crystallisation kinetics were also studied using DSC. The samples were isothermally crystallised at temperature of 140 °C for 1 h. The melting curves were then measured by heating the samples to 200 °C at a rate of 10 °C/min.

**FTIR**

FTIR was carried out on the top surface of an ~8 mm length specimen cut from middle of the rectangular injection moulded sample as shown in Fig. 1a. The FTIR was performed in the ATR mode using a BIORAD FTS 3000MX fitted with a single reflection diamond crystal. Spectra for all the samples were collected from wavenumber 700 to 4000 cm\(^{-1}\) with 50 scans at a resolution of 8 cm\(^{-1}\). The percentage crystallinity based on FTIR was calculated according to reference [25].

The spectrum of polypropylene consists of five peaks located at wavenumbers of 809, 841, 899, 974, and 998 cm\(^{-1}\). Curve fitting, via gaussian fitting using origin software, was carried out in the range of 1025–775 cm\(^{-1}\) for the five peaks in the FTIR spectrum of the PP samples [26]. The curve fitting was performed in two stages which included base line subtraction in the first stage and peak fitting in the second stage. An example of curve fitting for an injection moulded PP sample is presented in supplementary Sect. 2 (Figure S2.1). The height intensity of the five peaks was used to calculate the percentage crystallinity according to Eq. (3).

\[
X_{IR} = \frac{\sum A_{crystalline}}{\sum A_{amorphous}} \times 100
\]

where \( \sum A_{crystalline} = A_{809} + A_{841} + A_{899} + A_{998} \) and \( \sum A_{amorphous} = A_{974} \).

**XRD**

XRD was performed on a Malvern Panalytical Empyrean 3 X-ray diffractometer using the CuK\(\alpha\) X-ray emission at a wavelength 0.15406 nm, at 45 kV and 40 mA. The XRD data was recorded over a 2\(\theta\) range of 2 ° to 40 ° with a step size of 0.0525 and time per step of 400 secs. Specimens of approximately 8 mm length were cut from the top surface of the injection moulded rectangular samples as shown in Fig. 1a. The specimens were mounted on an odd shape sample holder and were held in place using plasticine. Sample spinning was enabled at 4 secs per revolution. A primary mask of 14 mm and secondary mask of 6 mm were used.

The percentage crystallinity was determined using the integral intensities of the crystalline and amorphous peaks.
using Eq. (4) [27]. The amorphous region and crystalline peaks were deconvoluted using a gaussian fitting technique in origin software. Figure S2.2 in supplementary Sect. 2 shows an example of the deconvolution of the XRD diffraction peaks of an injection moulded PP sample. The three main peaks and two overlapping peaks in the 2θ range of 14° to 22° in the XRD diffraction were considered for deconvolution and integral intensity measurements.

\[
X_{\text{Xrd}} = \frac{I_{\text{cry}}}{I_{\text{cry}} + I_{\text{am}}} \times 100
\]

where \(I_{\text{cry}}\) = Integral intensities of crystalline phase and \(I_{\text{am}}\) = Integral intensity of amorphous phase.

**Linkam hot stage polarising optical microscopy (LPOM)**

An Olympus BX53 optical microscope (× 50 magnification) equipped with a Linkam hot stage was used to observe the crystalline structure during isothermal crystallisation. The samples were held at a temperature of 200 °C for 5 min to erase the previous thermal history and supercooled to 140 °C at a rate of 30 °C /min. The samples were then isothermally crystallised at 140 °C for 1 h. The space between the top and bottom plates of the hot stage was held at 5 µm. Digital micrographs were taken every minute during the isothermal crystallisation using a digital camera attached to the system.

**Scanning electron microscopy (SEM) and EDX**

A Hitachi FE-SEM SU5000 field emission high resolution SEM was used to observe the microstructure of masterbatch pigment particles at 15 kV and ×5000. In order to remove most of the LDPE carrier from the masterbatches, the masterbatch samples were first dissolved in heated toluene at 80 °C. The solutions were then allowed to settle for 10 min before a glass pipette was used to remove the settled pigment from the bottom of the beaker. This washing process was repeated three times to remove the bulk of the LDPE carrier. Finally, the concentrated pigments were placed on a glass slide and gold coated prior to SEM analysis. The size of pigment particles was measured via SEM by taking the average of 50 measurements for each sample type. The Hitachi FE-SEM SU5000 equipped with an Oxford Instruments Ultim Max EDS100 was used to carry out EDX (energy dispersive X-ray spectrometry) analysis of the concentrated pigments.

The same SEM equipment (at 15 kV and ×3000) was also used to observe the crystalline structure of the samples prepared using LPOM. The isothermally crystallised samples were held at 140 °C for 1 h with a 20 µm space between upper and lower plate. After the samples were taken from the LPOM, they were etched with 3% of KMnO₄ in a concentrated acidic solution (2:1 of H₂SO₄:H₂P0₄) for 7 h to reveal the crystalline structure [28]. The SEM analysis was also performed on etched cross sections of the injection moulded samples cut perpendicular to the flow direction.

**Results and discussion**

**Scanning electron microscopy (SEM) of pigments**

Figure 2 shows the SEM micrographs of the pigments and the associated EDX (available in supplementary Sect. 1) which was used to identify the particle types present in the masterbatches. Spherical shaped particles with a size range of ~0.1–0.43 µm and irregular structure particles of size range ~1.03–2.0 µm were observed in the R1 pigment. EDX analysis confirmed that the round and irregular particles correspond to the white 6 and red DPP pigments respectively. R2, W1, and W2 contain spherical particles with a size range of ~0.06–0.2 µm, ~0.1–0.35 µm, and ~0.18–0.32 µm respectively. Pigment P was found to contain both spherical and irregularly shaped particles. The irregular particles exhibit a size range of ~0.96–3.62 µm and EDX analysis confirmed these as blue 29 pigment. The spherical particles in pigment P of sizes ~0.22–0.5 µm and ~0.05–0.13 µm correspond to pigment white 6 and pigment R122 respectively.

EDX of R1 and P also revealed the presence of ~1.5–4 µm CaCO₃ particles along with the pigments. W1 and W2 also contained ~1.5–9 µm CaCO₃ particles along with the TiO₂ particles.

**DSC analysis**

The DSC heating and cooling curves for PP containing the five masterbatches studied are presented in Fig. 3a, b respectively and the numerical data is shown in Table 4. The DSC traces of the samples show only a single peak for both the melting and crystallisation curves, except for the sample containing R1. The DSC curve of the PP+R1 sample shows a second small shoulder at around 154 °C in addition to the main peak at ~166 °C. We propose that this small second shoulder relates to the presence of β-crystallites, which are present in addition to the α form. Mubarak et al. also observed peaks in the range of 148 °C–155 °C for isothermally crystallised isotactic PP which were attributed to the β-crystallite form [5]. Generally, β-crystallite has a melt temperature range of 150 °C–154 °C [29]. It is also worth noting that this shoulder disappeared in the second and subsequent heating curves.

It was observed from the cooling curves that the two red pigmented samples (PP+R1 and PP+R2) caused large upshifts in the onset crystallisation temperature compared...
to pure PP. The purple pigmented sample (PP + P) also shifted the onset temperature to higher value than pure PP. This observed increase in the onset temperature of crystallisation, is an indication of the magnitude of the nucleation effects of the pigments [5, 8]. We propose that the presence of quinacridone red pigment as an ingredient in the red (R2) and the purple (P) masterbatch pigments is responsible for the large nucleation effects observed. It has been previously reported that both the β and γ form of the red quinacridone pigment act as strong nucleation agents in isotactic PP, while the γ quinacridone has been found to act as a β-nucleator in isotactic PP [5, 18]. The R1 pigment also acted as strong nucleating agent due to the presence of the organic DPP. The white samples (PP + W1 and PP + W2) were observed to have little influence on the onset temperature of crystallisation compared to pure PP. Previous researchers have also shown that inorganic white pigment has little influence on nucleation of isotactic PP [5, 11].

Figure 4a shows the melting curves for all the samples isothermally crystallised at 140 °C. The pure PP and the
white samples (PP+W1, PP+W2) show a main peak around 166 °C and a second shoulder around 171 °C. Mubarak et al. also reported two peaks (first at 163 °C and second at 171 °C) in isotactic PP isothermally crystallised at 140 °C, which were attributed to α-crystallite form. It is interesting to note that the second shoulder was not observed in the reds (PP+R1, PP+R2) and purple (PP+P) samples. This shows that these masterbatches containing organic pigments are mainly inducing one form of α-crystallites. All the samples crystallised at temperatures of 135 °C and below showed a single melting peak at 163 °C-165 °C. Figure 4b shows the isothermal crystallisation behaviour at 140 °C. Isothermal crystallisation is a sensitive method for investigating crystallisation kinetics, and it can be seen that the PP+R1 sample shows the fastest initiation and completion of crystallisation. The PP+R2 and PP+P samples also show much more rapid crystallisation compared to pure PP while the white ones (PP+W1, PP+W2) show crystallisation behaviour very similar to neat PP.

**XRD and FTIR analysis**

XRD was performed to study the morphology of the samples and to investigate the presence of any β-crystallite regions. Figure 5 shows the XRD patterns for both pure PP and the samples containing the 5 masterbatches studied. The XRD patterns of all the samples show three strong peaks at 2θ angles of around 14 ° (110), 16.8 ° (040), 18.4 ° (130) and two overlapping peaks at 20 angles of 21 ° (111) and 21.8 ° (041) [30–32]. The small peak at a 2θ angle of ~25.3 ° (150, 060) which corresponds to the α-crystallite phase is also observed in all the samples [31]. An additional peak at a 2θ angle of ~16 ° is only observed in the PP+R1 sample which contains DPP pigment as an ingredient. This is characteristic peak of β-crystallite phase with miller indices of (300) [30]. We postulate that the DPP contained in the R1 masterbatch acts as both a β and α nucleating agent in PP leading to the presence of both crystal types. The presence of the β phase was also previously confirmed via DSC (Fig. 3a). The XRD pattern of the red sample (PP+R1) also shows evidence of a small peak at ~6.4 °, which may correspond to the presence of DPP [33]. The XRD pattern of the other red pigmented sample (PP+R2) shows a small peak at ~5.67 ° which is likely due to the presence quinacridone [33].

**Table 4** Onset temperature of crystallisation and crystallinity measured using DSC, XRD, and FTIR

| Samples | Onset temperature of crystallisation (°C) | Crystallinity (%) | $X_{\text{DSC}}$ | $X_{\text{IR}}$ | $X_{\text{XRD}}$ |
|---------|----------------------------------------|-------------------|-----------------|-----------------|-----------------|
| PP      | 127.26                                 | 49.42             | 69.11           | 46.56           |
| PP+R1   | 130.77                                 | 50.16             | 73.20           | 51.97           |
| PP+R2   | 129.3                                  | 49.56             | 72.00           | 49.04           |
| PP+P    | 127.98                                 | 49.34             | 70.71           | 46.47           |
| PP+W1   | 127.28                                 | 49.20             | 69.23           | 45.12           |
| PP+W2   | 127.41                                 | 49.20             | 69.10           | 43.35           |

Fig. 4 (a) DSC melting scans of isothermally crystallised samples at 140 °C and (b) crystallisation rate of the isothermally crystallised samples
The XRD patterns for the white samples (PP + W1 and PP + W2) show an additional peak at a 2θ angle of ~27.54 ° which is characteristic of TiO₂ [32]. Another small peak at 2θ angle of ~29.29 ° is also observed in the white and red samples (PP + W1, PP + W2, and PP + R1). Similar peaks were also previously observed in the XRD patterns of titanium dioxide [34].

The FTIR spectra of the various sample types are presented in Fig. 6. It was observed that the spectra obtained for the pigmented and pure samples are similar, and are in good agreement with published literature [17, 25]. In pure PP, the peaks in the range of 2950–2850 cm⁻¹ correspond to CH₃ and CH₂ symmetrical and unsymmetrical stretching vibrations [25]. The purple sample (PP + P) also showed additional peaks in the range of 1600–1450 cm⁻¹ which are related to N = N and aromatic breathing vibrations [17, 35].

**Linkam hot stage polarising optical microscopy (LPOM)**

The nucleation and crystallisation behaviour were also studied via isothermally crystallising the samples at 140 °C in LPOM. Figure 7 shows the LPOM micrographs of all the sample types, showing the crystal structure at the start (0 min) and after 6, 12, and 50 min. The figures illustrate a clear difference in size, number, and formation time of the crystals between the sample types. The image of pure PP clearly shows the initiation (with self-nuclei formation) and growth of spherulites until they impinge upon each other. A clear difference was observed between the size and number of nuclei in the reds (PP + R1 and PP + R2) and purple (PP + P) samples compared to pure PP. The PP + R1 sample showed the largest nucleation rate with the PP + R2 and PP + P samples as the second and third highest respectively. It was observed that these three sample types had a notably higher nucleation rate than that seen in pure PP. This supports the findings from the DSC data (Fig. 3b). The presence of the opaque white pigments made it difficult to observe the crystal structure in the white samples (PP + W1 and PP + W2) however, some changes appeared in the images at 12 min which can be assumed as nuclei formation. This supports the isothermal DSC data which found that the white pigments had only a limited influence on the nucleation and crystallisation behaviour (Fig. 4b).
The effect of masterbatch addition on crystallinity, can be explained by the pigments providing extra nucleation sites. It can be concluded that the nucleating activity of the organic pigments results in nucleation dominating over the growth phase, resulting in proportionally smaller spherulitic diameters compared to pure PP. Jan Broda also observed similar behaviour with organic pigments in isotactic PP [9].

**Scanning electron microscopy (SEM) of etched samples**

To further investigate the effect of pigments on the final morphology, SEM was carried out on the surface of etched isothermally crystallised samples. The SEM micrographs of all the etched samples are presented in Fig. 8. A typical spherulitic morphology was observed in the pure PP. Both SEM and LPOM study of the pure PP revealed that the spherulites grew radially until they impinge upon each other, distorting the spherulitic shape into a polygonal shape or quadrites. Park et al. also observed a polygonal shape in isothermally crystallised isotactic PP [28]. A similar distorted spherical morphology (polygon) was also observed in the two white samples (PP + W1 and PP + W2). The crystal morphology of the purple sample (PP + P) was also observed to be somewhat polygonal, while the two red samples (PP + R1 and PP + R2) showed highly distorted shapes which are generally referred to as axialite morphology. It’s noteworthy that no evidence of β-crystallite was observed in the isothermally crystallised PP + R1 sample. This is in agreement with the observations of the isothermal DSC results, that DPP only induces α-crystallites at higher crystallisation temperatures. Isotactic PP spherulites are classified into four types (type 1-1 V) by Padden and Keith, depending on temperature of crystallisation [36]. Type 1 spherulites appear at temperature below 134 ºC, while type 11 spherulites develop above 138 ºC. Both types (1 and 11) are classified as α-spherulites and can coexist with each other. Type 111 spherulites are produced at temperature below 122 ºC, while type 1 V are formed in temperature range of 126 ºC-132 ºC and are classified as hexagonal β-structure [37]. We observed only α-spherulites in the etched isothermally crystallised samples.

SEM was also carried out on the etched injection moulded samples cut perpendicular to the flow direction. Figure 9 shows the SEM cross section micrographs of the PP and PP + R1 samples. A typical spherulitic morphology with no clear division between the grains was observed in the samples. Evidence of β-crystallites (radial lamellar morphology) was only observed in the PP + R1 sample which also displayed a characteristic β-peak in the XRD results as shown in Fig. 5. Ding et al. observed similar structures with β-nucleated PP [38]. This shows that the DPP pigment (an ingredient of R1) can nucleate β-crystallite in isotactic PP in addition to the α crystalline form. It is noteworthy that we did not observe the β-crystallite form in the same sample (PP + R1) isothermally crystallised at 140 ºC as discussed earlier. The presence of only α crystalline form in
| T=0mins | T=6mins | T=12mins | T=50mins |
|--------|--------|---------|---------|
| PP     | 50μm  | 50μm    | 50μm    | 50μm    |
| PP+R1  | 50μm  | 50μm    | 50μm    | 50μm    |
| PP+R2  | 50μm  | 50μm    | 50μm    | 50μm    |
| PP+P   | 50μm  | 50μm    | 50μm    | 50μm    |
| PP+W1  | 50μm  | 50μm    | 50μm    | 50μm    |
| PP+W2  | 50μm  | 50μm    | 50μm    | 50μm    |

Fig. 7 Linkam hot stage polarising optical micrographs of pure and pigmented samples isothermally crystallised at 140 °C for 1 h; PP, PP+R1, PP+R2, PP+P, PP+W1, and PP+W2
the isothermally crystallised sample of PP + R1 is in agreement with the results of Padden and Keith [36]. It has been reported that the formation of \( \beta \) spherulites above the characteristic temperature recognised as the upper limit is impossible. Varga found this temperature to be 140 °C to 141 °C [39]. Fillon et al. and his co-workers also reported this upper critical temperature at about 140 °C [40, 41]. Sterzyznki et al. also found no evidence of \( \beta \) spherulites at 145 °C in nucleated iPP [42]. However, they observed the presence of \( \beta \) along with \( \alpha \) crystalline form at a crystallisation temperature of 125 °C. The presence of the \( \beta \) crystallite form along with \( \alpha \) in the injection moulded sample of PP + R1 is also in agreement with the findings of Nakamura et al. [43]. They reported the presence of a central \( \beta \) form surrounded by \( \alpha \) form at a crystallisation temperature of 90 °C.

**Correlation between shrinkage and onset crystallisation temperature**

Figure 10 shows the correlation between the mould direction shrinkage and the onset crystallisation temperature as measured from the DSC cooling curves. The figure illustrates a strong correlation between the onset crystallisation temperature and the mould direction shrinkage, with an observed \( R^2 \) of 0.85. Even though the cooling rate used during the DSC testing is much lower than that experienced during injection moulding, it can be seen that the crystallisation onset temperature from DSC can be used to predict the shrinkage of moulded parts. Suzuki and Mizuguchi, 2004 previously reported a correlation between the onset crystallisation temperature and mould shrinkage. They reported a difference (between pure polymer and pigmented samples) in shrinkage of up to 0.4% between pigmented and unpigmented PP [11]. Referring to Fig. 10 we report a maximum increase in shrinkage between the pure and pigmented samples of up to 0.14% for PP system. Therefore, we report somewhat lower increases in shrinkage with the use of masterbatch pigments to that previously observed for pure pigments [11]. We also observed a similar correlation between onset crystallisation temperature and MD shrinkage when testing a larger set of 14 masterbatches.
In Fig. 10, it can be seen that the pure PP displayed the lowest values of shrinkage. The red pigmented sample (PP + R1) which exhibited the strongest nucleation behaviour measured using DSC and LPOM also displayed the largest shrinkage. The second red sample (PP + R2) and the purple sample (PP + P) also caused sizeable shifts in shrinkage. These samples had greater levels of nucleation compared to pure PP as demonstrated in the DSC and LPOM results. The white samples (PP + W1 and PP + W2) displayed little variation in shrinkage compared to pure PP [8]. The samples were remeasured after one month, and a similar trend between onset temperature of crystallisation and shrinkage was observed. A slight increase in shrinkage was recorded after one month with for example, a shrinkage of 1.61% being recorded after one month compared to 1.53% after 48 h, for the highest shrinkage sample (PP + R1). A similar slight increase in shrinkage between 48 h and 28 days was observed for the other sample types. Graphs were also drawn between the onset temperature of crystallisation and transverse mould direction shrinkage, with no statistically
significant relationship being observed for the PP system. It has previously been reported that additives in semicrystalline polymers can effect shrinkage differently in the flow and crossflow direction [14, 44, 45]. Pulkerd et al. reported that the outer skin layer of the injection moulded parts containing nucleating agents show orientation of crystals along the flow direction (MD) [46]. This may be the reason that the nucleation effect is more pronounced in the MD.

**Correlation between shrinkage and percentage crystallinity**

Figure 11 represents the correlation between the percentage crystallinity obtained from FTIR and the DSC based onset temperature of crystallisation. We observed a strong correlation between crystallinity percentage measured by FTIR and DSC based onset temperature with $R^2 = 0.96$. In Fig. 11, the pure PP demonstrates lower values of both crystallinity percentage and onset temperature of crystallisation. In agreement with the previously discussed DSC data, the red pigmented samples (PP + R1 and PP + R2) display higher values of percentage crystallinity and onset temperature of crystallisation. The white masterbatches induce only slight changes in percentage crystallinity compared to pure PP.

Figure 12 shows the strong correlation that we observed between FTIR based percentage crystallinity and mould direction shrinkage ($R^2 = 0.92$). We also found a strong correlation between the FTIR based crystallinity and mould shrinkage ($R^2 = 0.76$) for a larger set of 14 masterbatch pigments (presented in supplementary Sect. 2 (Table S2.1; Figure S2.3)). To the authors knowledge this correlation between crystallinity measured using FTIR and shrinkage when using pigments has not been previously reported. This discovery that FTIR can be used as an effective method to predict the likely effect of a pigment on shrinkage, will be useful when developing new pigments or other additives and will assist polymer processors in the selection of pigments and masterbatches. DSC is by necessity a slow characterisation method and the heating and cooling cycle necessary to measure crystallisation onset temperature typically takes 1–2 h per sample. FTIR on the other hand can be completed in several minutes.

The percentage crystallinity of the samples measured via DSC, FTIR, and XRD is reported in Table 4. Figure 13 displays the correlation between FTIR and XRD based crystallinity [47]. A strong correlation of $R^2 = 0.86$ was observed. This is in agreement with a previous study by Lanyi et al. who reported a strong correlation between FTIR and XRD based crystallinity measurements of PP [47]. The authors also noted that unlike XRD and DSC based measurements of crystallinity, FTIR can be easily used to make localised and through thickness measurements. In another study, Lanyi et al. was also able to demonstrate a strong correlation between DSC, FTIR, and XRD measurements of crystallinity ($R^2 = 0.87–0.89$) in thin pressed PP specimens [48]. Several authors have noted differences in the crystal structure between the skin and core layer of both injection moulded and melt blown samples. The higher shear stress and cooling rates experienced by the material in contact with the mould can give rise to a thin skin layer with a smaller, more oriented crystal structure [49, 50]. We also observed a somewhat weaker correlation of $R^2 = 0.68$ between the crystallinity measured via XRD and MD shrinkage.

![Graph of FTIR based crystallinity percentage versus mould direction shrinkage of pure and pigmented samples](image-url)
Conclusion

The addition of commercial masterbatch pigments had a significant effect on the measured shrinkage for injection moulded PP. Shrinkage values of 1.4% to 1.53% were recorded for the pigmented PP compared to 1.39% for pure PP. In agreement with a previous study of pure pigments, it was found that adding masterbatch pigments to PP causes an increase in crystallisation onset temperature measured by DSC. This shift in crystallisation onset temperature was correlated with machine direction shrinkage. It was also found that the percentage crystallinity measured using FTIR was strongly correlated to the recorded MD shrinkage. Morphological analysis carried out via XRD, LPOM, and SEM demonstrated that the PP samples exhibit mainly α-crystallite form with the β-crystallite also being observed in the PP + R1 sample containing red DPP pigment. The LPOM and SEM results revealed that pigment addition induces heterogenous nucleation resulting in proportionally smaller spherulitic diameters. The information presented in this paper will be useful to compounders developing new masterbatch pigments and to processors selecting pigments.

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Authors’ contributions Jawad Ullah: Experimental design, carried out all experimentation, and write up. Eileen Harkin-Jones: Proof reading and lead applicant on the project funding. Alistair McIlhagger: Proof reading and project principal. Ciaran Magee: Industrial collaborator and provided materials for experimentation. David Tormey: Proof reading. Foram Dave: Assisted in initial XRD experimentation. Richard Sherlock: Proof reading. Dorian Dixon: Proof reading and supervision of the project.

Declarations

Ethics approval Not applicable.

Consent to participate The authors give their consent to participate in publication of this article.

Consent for publication The authors give their consent to for publication of this article.

Fig. 13 Graph of FTIR versus XRD based crystallinity percentages of pure and pigmented PP samples
Conflict of interest  The authors declare that there is no conflict of interest regarding the publication of this article.

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