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The effect of pigmentation on the mechanical properties and the crystallisation behaviour of polymer blends (Xenoy®)

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Abstract

Several techniques have been used to study the effect of C.I. Pigment Blue 15:4 and C.I. Pigment Red 122 on the properties of a pigmented Xenoy® blend. The pigments were incorporated into the blend during extrusion. Both pigments acted as nucleating agents, increasing the crystallinity of the pigmented Xenoy® compared to that of the unpigmented blend. Of the two pigments studied, C.I. Pigment Red 122 has a greater effect on the properties than occurs with C.I. Pigment Blue 15:4.

Keywords: Pigmentation; Polymer blends; Nucleating agents; Processing properties

1. Introduction

The effect that a pigment has on a polymer depends upon the level of interaction that occurs between the polymer matrix and the pigment. Factors influencing the final physical properties and mechanical properties of the polymer include the chemical composition and surface energy of the pigment, together with its particle size and particle size distribution. The inclusion of the butyl sequence in poly(butylene terephthalate) (PBT) significantly influences the flexibility of the chain, and the ability of the carbonyl group to undergo interaction with the pigment surface. Hence, PBT has a greater ability to interact chemically with the surface of an additive [1].

It is well known that phthalocyanine pigments and quinacridone pigments are capable of acting as nucleating agents, affecting the rate of crystallisation and inducing crystallisation at temperatures that are higher than would otherwise be expected. This effect is in addition to influencing the dimensional stability of moulded parts by causing shrinkage and warpage.

Turturro and co-workers investigated the effect of organic pigments on the crystallisation behaviour of linear poly(ethylene) [2]. The authors concluded that organic pigments affect the kinetics, and not the thermodynamics of the crystallisation process by acting as nucleation seeds. When particularly active nucleating pigments are used, such as the copper phthalocyanines, the spherulitic structure of the bulk polymer is modified. These active pigments can induce the development of fibrils that do not organise themselves into a spherulitic structure. This phenomenon is referred to as trans-crystallisation and is thought to occur when a large number of nuclei are present on a plane surface.

Silberman and co-workers examined the effect of C.I. Pigment Red 122, a quinacridone, and C.I. Pigment Green 7, a halogenated copper phthalocyanine, on the properties of isotactic poly(propylene) [3]. Strong

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nucleation was observed with the quinacridone giving the polymer a very high degree of crystallinity. It was concluded that chemical adsorption occurs with low pigment concentrations, and physical adsorption at high concentrations. For the phthalocyanine pigment, the symmetry of the nitrogen atoms resulted in physical adsorption of the poly(propylene) on the pigment surface.

Van de Velde and co-workers observed that C.I. Pigment Blue 15:1 acted as a nucleating agent for spin-dyed poly(propylene) [4]. The crystallisation temperature and enthalpy of the blue yarns were increased relative to those of the uncoloured yarn, both of which are indicative of nucleation. In addition, smaller crystallites were observed in the blue yarns compared to those in the uncoloured yarn.

Nagy and White carried out an experimental study regarding the effect of colourants on the properties of rotomolded poly(ethylene) [5]. The pigments concentrated in the zones between the polymer particles. Even small amounts of pigment reduced mechanical properties, particularly the low temperature impact resistance.

Broda and Wlochowicz investigated the structure of natural poly(propylene) fibres and coloured poly(propylene) fibres [6]. In the presence of a phthalocyanine, well-formed α-crystallites were formed. In the presence of a quinacridone, a structure with a large content of β-crystallites was formed. At higher take-up velocities, the nucleating action of the pigments became smaller. The structures of the fibres were observed to be more perfect for the coloured fibres compared to the structures of the uncoloured fibres.

Marks and co-workers observed that isotactic poly(propylene) films that were pigmented with copper phthalocyanine had higher values of tensile modulus and crystallinity than did the unpigmented poly(propylene) film [7]. The spherulite sizes for the pigmented films were significantly smaller than those of the unpigmented film.

Pei-ren studied the flow properties, the morphological structures and the drawing behaviour of poly(propylene) matrices that contained different pigments [8]. Inorganic pigments were evaluated, as were copper phthalocyanine and a red and an orange organic pigment (both of which were unspecified). The viscosity of the poly(propylene) increased for the samples that contained the inorganic pigments and that which contained the copper phthalocyanine. Different reasons were proposed for this. The agglomerated inorganic pigment particles were much larger than the macromolecules in the system. The author concluded that the presence of these rigid particles increased the stiffness of the polymer chains. The phthalocyanine pigment was thought to increase the viscosity through the effect of having many small particles available, to influence the flow of the macromolecules. This suggestion was based on the theory that the addition of finely divided solid particles increases the viscosity of a polymer [9]. The viscosities of the samples that contained the other organic pigments decreased. The reason that was proposed for this was the occurrence of a decomposition event that resulted in some internal lubrication of the polymer chains. Each of the pigments studied gave a different crystalline morphology to the poly(propylene). This observation was related to the different draw strengths that were recorded for each of the samples. Such differences were thought to be due to the pigments acting as nucleating agents for the different poly(propylene) crystalline structures.

2. Experimental

2.1. Materials

The pigments studied were C.I. Pigment Blue 15:4 (supplied by BASF, Germany) and C.I. Pigment Red 122 (supplied by Bayer, The Netherlands). These pigments contained the surface treatment provided by the manufacturers. Manufacturers of such commodities are reluctant to disclose the specific nature of their treatments because of the need for product protection. For this reason, an inverse gas chromatographic (IGC) evaluation of the pigments was undertaken to establish the Lewis acidity–Lewis basicity of the two pigment types, as supplied by the manufacturers [10]. These pigments were used as supplied. The IGC study showed the commercial sample of C.I pigments Blue 15:4 to act primarily through apolar forces, thus being likely to have limited interaction with species of a Lewis acidic nature or of a Lewis basic nature (as displayed by the PC–PBT combination). The commercial sample of C.I Pigment Red 122 was clearly shown to be amphoteric in character and dominantly Lewis basic in its responses. Thus, the pigment has the ability to interact with species of a Lewis acidic nature and with species that are of a Lewis basic nature. Both of these characteristics are displayed by the PC–PBT blend.

The components of the Xenoy® blend were supplied by GE Plastics (Bergen op Zoom, The Netherlands). The major components consisted of bisphenol A polycarbonate, poly(butylene terephthalate) and a core-shell type of impact modifier.

2.2. Sample formulation

2.2.1. Extrusion

A standard Xenoy® blend formulation was used for the test samples. In this formulation the ratio of PC to PBT was approximately equal. The formulation also contained a number of additives to protect the blend both during compounding and post-processing. These

additives included a transesterification stabiliser, and antioxidants. The various pigment loadings that were used were the same for both pigments: 0.005, 0.050, 0.100, 0.150, 0.250, 0.350 and 0.500% (w/w). The blends were prepared using a Werner and Pfleiderer Supercompounder generation ZSK-30 twin-screw extruder. The settings and the screw temperature profile were those optimised for the compounding of Xenoy®.

2.2.2. Injection moulding

The Xenoy® pellets that were obtained from the extrusion process were injection moulded into test specimens (impact bars, tensile bars and circular plaques). Prior to injection moulding, the pellets were dried for 2 h at 110 °C. An ENGEL injection moulder was used, with standard pre-programmed Xenoy® settings.

2.2.3. Cryoscopic grinding

In order to be able to carry out certain types of analysis on the pigmented polymeric systems, it was necessary to obtain a different form of the pigmented polymers. Hence, a sample from each of the batches was ground down to form a "fluffy" powder. Cryoscopic grinding was carried out using an electric rock grinder (model Retsch ZM100). Before the polymer pellets were added, liquid nitrogen was poured through the funnel to cool the system. Once cooled, the speed was set to 14,000 rpm and the pellets were added through the top funnel. Additional liquid nitrogen was poured into the system at intervals, to ensure that the system remained cold throughout the grinding operation (to prevent the motor overheating from the work being done and the polymer from melting due to the heat being generated). The particle size of the powder produced was determined to be approximately 40 μm, as determined by the "grating" wheel.

2.3. Izod notched impact testing of moulded samples

Izod notched impact test specimens were prepared and tested according to the standard ISO 180. Twenty injection moulded impact bars were selected from each batch of samples. A v-shaped notch was then machined into the centre of these impact bars using a notch cutter. The dimensions relating to the notch were: remaining width of sample = 8.0 ± 0.2 mm, angle = 45° and notch tip radius = 0.25 ± 0.05 mm. One set of five bars from each batch was conditioned before testing at temperatures of 0 °C, −10 °C and −20 °C. Sample conditioning was carried out to eliminate the effects of the pre-treatments (notching and injection moulding) and the storage environment on the impact measurements. The remaining five bars from each batch were reserved for testing at room temperature, 23 °C. A Zwick pendulum impact tester equipped with a pendulum rated at 5 J was used for the analyses. This gave an impact velocity of 3.5 m/s.

2.4. Tensile testing of moulded samples

Tensile testing was carried out according to the standard IS0 527. Ten (or in some isolated cases five) moulded tensile bars were selected from each batch of samples. For each set of five bars, the width and thickness of each specimen was measured in the centre of the bar using a micrometer, and average values obtained in order to calculate a cross-sectional area for the bar. Specimens were carefully loaded into a Zwick ZO10 tensile tester, which was equipped with a robot to enable automated testing. Testing was then carried out at room temperature (23 °C) and at a tensile strain rate of 50 mm/min.

2.5. Dynamic mechanical thermal analysis (DMTA): evaluation of moulded samples

A Polymer Labs. PL-DMTA Mk II instrument was used for DMTA studies. A moulded tensile bar was selected from each sample batch under study, and a specimen cut from it. The specimen dimensions were approximately $32 \times 4 \times 2$ mm. Each specimen was clamped in single cantilever bending mode. A strain of 64 μm and a frequency of 5 Hz were used. Some samples were studied in the temperature range −150 °C to 180 °C, with liquid nitrogen used as a coolant. For these samples, each run was carried out in two stages: −150 °C to 10 °C, then 10 °C–180 °C. This was necessary because the cooling stage resulted in the sample becoming partly detached in the holder upon reaching positive temperatures. Hence, the specimens were reclamped after the first stage. Additional samples were studied in the range 25 °C–180 °C. A heating rate of 2 °C/min was used for all samples.

2.6. Evaluation of the Vicat softening point (VSP)

Two moulded impact bars were selected from each batch of samples for Vicat testing according to standard procedure. An automated Koesfeld Oeko instrument was used, with a load of 5 kg and a heating rate of 120 °C/h.

2.7. Thermal analysis: crystallisation studies

Ground pellet samples were used for analysis in a Perkin Elmer Pyris Diamond DSC, equipped with an AS 6 Autosampler accessory. Runs on samples were carried out in air, in a four-step regime. The samples were first heated from 40 °C to 260 °C at a rate of 20 °C/min, and held at 260 °C for 2 min to remove previous thermal history and to release any internal

stresses. The samples were then cooled to 40 °C at 20 °C/min to give slow crystallisation data. The samples were held at 40 °C for 2 min before again being heated to 260 °C at a rate of 20 °C/min. The melt transition was evaluated during this step. Finally, the samples were held at 260 °C for 2 min before being cooled to 40 °C at a rate of 200 °C/min. This step supplied fast crystallisation data, a more accurate representation of cooling of the polymer blend from the melt during injection moulding.

3. Results and discussion

3.1. Izod notched impact evaluations of moulded samples

Izod notched impact strength investigations were undertaken to determine the effect of the pigments on the ductility of the PC/PBT blends. In Fig. 1 each point represents an average value determined from the five bars tested, and the associated value of the standard deviation is included with each point.

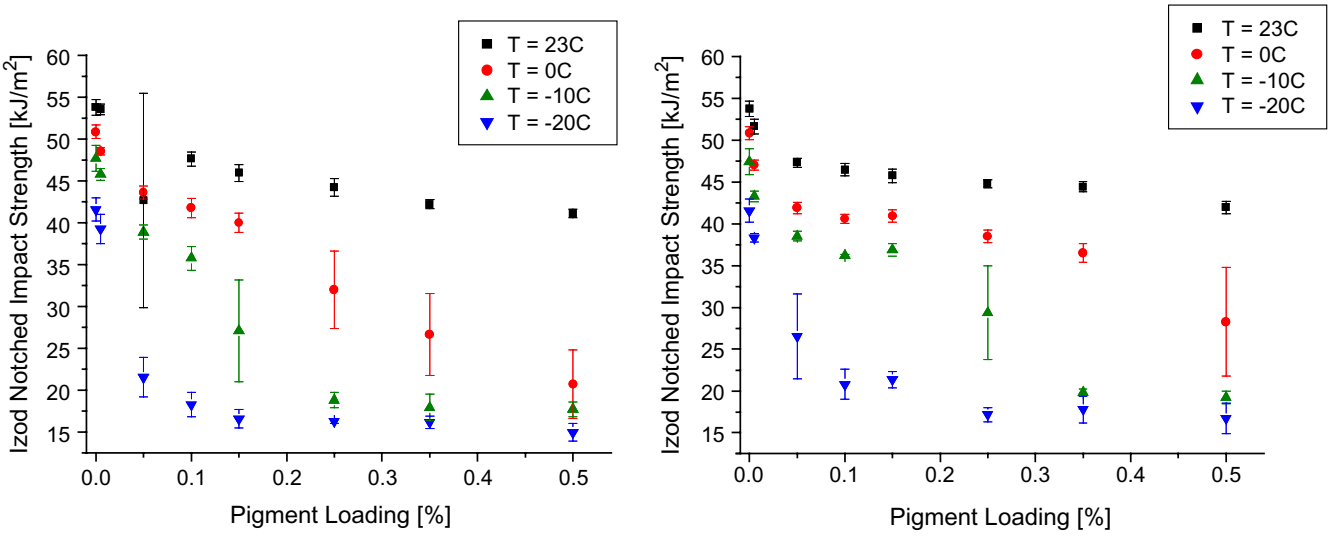
By considering the unpigmented Xenoy® blend alone, the effect of the test temperature on the polymer matrix may be determined. The data in Fig. 1 (0% pigment loading) show that the impact strength decreases as the test temperature decreases. However, even at −20 °C the sample still exhibited ductile behaviour.

The relationship between the Izod notched impact strength and the pigment loading for the samples is shown in Fig. 1, for C.I. Pigment Blue 15:4 pigmented blends (a) and for C.I. Pigment Red 122 (b) pigmented blends.

The overall trends are similar for those samples that were pigmented with C.I. Pigment Red 122 and the samples that were pigmented with C.I. Pigment Blue 15:4. At each test temperature, a small addition of pigment (0.005%) leads to a small decrease in the impact strength. Pigment loadings of 0.050% result in a more significant decrease in the impact strength. Beyond a pigment loading of 0.050%, the impact strength decreases as the pigment loading increases. Thus, the effect of the pigment is to increase the brittleness of the blends (i.e. to reduce the ductility) and to cause the blends to fail at higher temperatures. The trends that occur at each of the test temperatures will now be described separately.

At room temperature (23 °C) the same basic trend is observed for both pigments. This trend is seen as a sharp decrease in impact strength between pigment loadings of 0% and 0.050%, followed by a more gradual decrease as the pigment loading increases. There are small standard deviations associated with these results. This implies that each of the bars demonstrates a "standard" behaviour. At this test temperature, at a pigment loading of 0.500%, the Xenoy® blend lost approximately 20% of its impact strength compared to the unpigmented blend.

At 0 °C, the basic trend of a decrease in the impact strength as the pigment loading increases is evident for both pigments. However, the most significant difference between the two plots is observed at this test temperature. When the pigment loading is above a value of 0.250%, the impact strength decreases rapidly for the samples that contained C.I. Pigment Blue15:4, while the decrease is much less severe for the impact strength of



(a) C.I. Pigment Blue 15:4

(b) C.I. Pigment Red 122

Fig. 1. Impact test results for samples.

the samples that contained C.I. Pigment Red 122. The associated standard deviations are also more significant at this temperature, particularly for the samples that contained C.I. Pigment Blue 15:4. This observation will be discussed in more detail later.

At −10 °C, the samples that contained C.I. Pigment Blue 15:4 exhibit a similar trend to that observed at 0 °C, although the standard deviations are reduced. For the samples that contained C.I. Pigment Red 122 a significant decrease in impact strength was observed when the pigment loading was above 0.150%. If an impact strength value of 20 kJ/m^2 is considered to be the onset of brittle behaviour (A. Grimm, Personal Communication. GE Plastics, Bergen-op-Zoom, The Netherlands), samples that were pigmented with C.I. Pigment Red 122 reach this value when the pigment loading is above 0.350%. However, for blends that were pigmented with C.I. Pigment Blue 15:4, samples became brittle when the level of pigment addition is greater than 0.250%.

At −20 °C, the trends are again similar for the samples containing the different pigments. A pigment loading of 0.005% causes a small decrease in the value of the impact strength compared to the value for the unpigmented blend. A pigment loading of 0.050% results in a very significant decrease in the value of the impact strength. This decrease is so significant that the samples pass from exhibiting ductile behaviour to exhibiting brittle behaviour, within that pigment loading range. As the pigment loading increases further, the impact strength decreases more gradually. In general, the values of the standard deviation for these samples are relatively small.

The decreases in the impact strength that were observed and described as being significant (at 0 °C and at −10 °C), coupled with the associated standard deviations, are indicative of the occurrence of a ductile-to-brittle transition. This transition occurs when the samples fracture by different mechanisms (ductile or brittle) in a ratio of 2:3. This is the reason for the large standard deviation corresponding to those points. Thus, it can be suggested that the samples that contain C.I. Pigment Blue 15:4 undergo a ductile-to-brittle transition at a higher temperature than applies to the samples that contain C.I. Pigment Red 122.

3.2. Tensile testing of moulded samples

3.2.1. Tensile modulus

The relationship between the tensile modulus and the pigment loading is shown in Fig. 2.

The same trend is evident for samples that contained each of the two pigments. As the pigment loading increases the modulus increases gradually. This occurs up to a pigment loading of 0.350%, after which the values of the modulus decrease slightly. The values of the modulus for the samples that contain C.I. Pigment Red 122 are consistently higher than the values for the samples that contain C.I. Pigment Blue 15:4. The values of the modulus for each of the pigmented samples are higher than that of the unpigmented blend. These results suggest that incorporation of pigment into the Xenoy® blend increases the stiffness of the blend, particularly so for the samples that are formulated with C.I. Pigment Red 122.

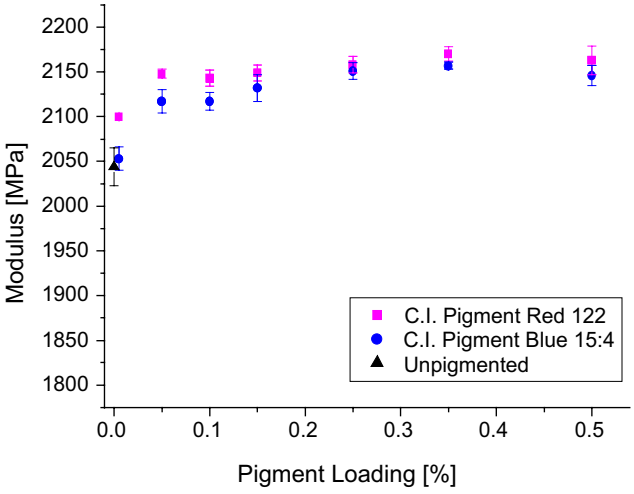


Fig. 2. The influence on the modulus of pigment loading.

3.2.2. Yield stress

The influence of the pigment loading on the yield stress is shown in Fig. 3. A similar trend is seen as was described for the modulus. As the pigment loading increases, the stress at yield increases up to a pigment loading of 0.250%. Beyond this loading, the stress remains constant for the samples that contained C.I. Pigment Red 122 and decreases for the samples that contained C.I. Pigment Blue 15:4. Again, the values of

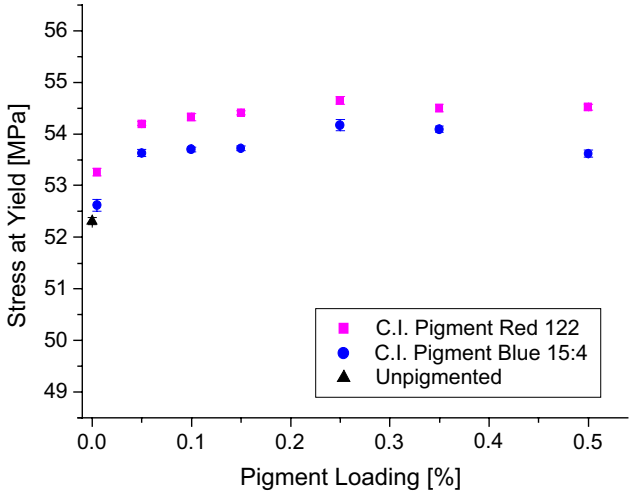


Fig. 3. The influence on the yield stress of pigment loading.

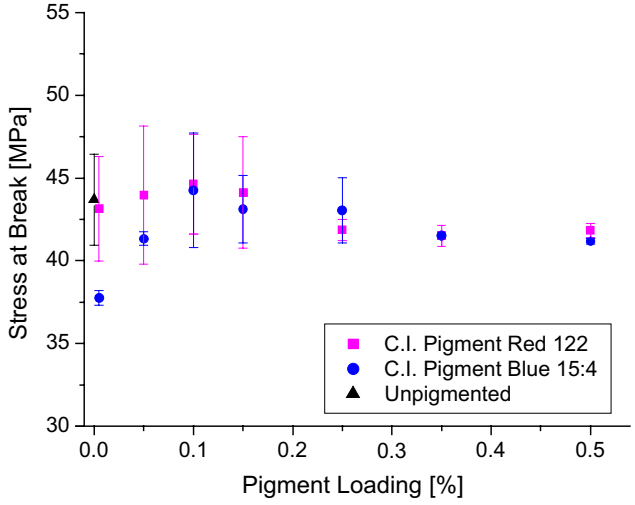


Fig. 4. The influence on the stress at break of pigment loading.

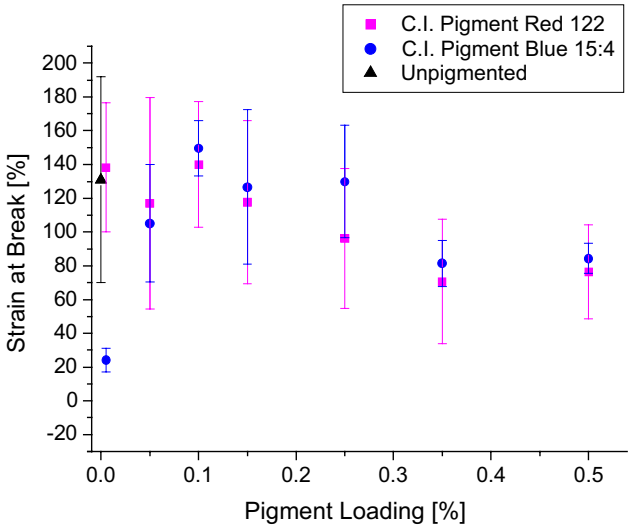


Fig. 5. The influence on the strain at break of pigment loading.

stress for the pigmented samples are higher than that of the unpigmented sample.

3.2.3. Stress at break

The relationship between the stress at break and the pigment loading is illustrated in Fig. 4.

There are slightly different trends exhibited for the two pigment types. For the samples that contain C.I. Pigment Red 122, the values of the stress at break are consistent up to a pigment loading of 0.150%. The large standard deviations of these results mean that it is not possible to describe a definite trend for these samples. Beyond a pigment loading of 0.150%, the decrease in values remains consistent as the pigment loading increases further. However, for these points the standard deviation values are relatively small. For the samples that contain C.I. Pigment Blue 15:4, the value of the stress at break increases as the pigment loading increases from 0.005% to 0.050%. Above this pigment loading, the values of stress decrease as the pigment loading increases. The unpigmented blend sample has a value of stress at break with a relatively large spread of the results. The values of the stress at break for the pigmented samples are similar to, or lower than, the value for the unpigmented blend.

3.2.4. Strain at break (elongation)

The influence of the pigment loading on the strain at break is shown in Fig. 5. For the majority of the points, the two pigments exhibit similar trends. Again, the spreads of the values are large and therefore trends cannot be described and interpreted with confidence. As the pigment loading increases (beginning at a loading of 0.050%), the value of the strain at break initially increases before decreasing. In the pigment loading range from 0.100% to 0.500%, the values for the samples that contained C.I. Pigment Blue 15:4 are higher than those for the samples that contained C.I. Pigment Red 122. At the lowest pigment loadings, the reverse of this observation is seen. The most significant difference between the two pigments occurs at a pigment loading of 0.005%. At this loading, the strain at break for the pink sample is similar to that for the unpigmented sample. For the blue sample, the value of strain is much lower than for all of the other samples in this set. As the pigment loading increases, the values of the strain at break for the pigmented samples decrease relative to that of the unpigmented blend.

3.3. Dynamic mechanical thermal analysis (DMTA) evaluations of moulded samples

DMTA evaluations were carried out to assess the effect of the pigments on the structure of the Xenoy® blend. Samples were evaluated via their dynamic characteristics of stiffness (modulus) and energy dissipation.

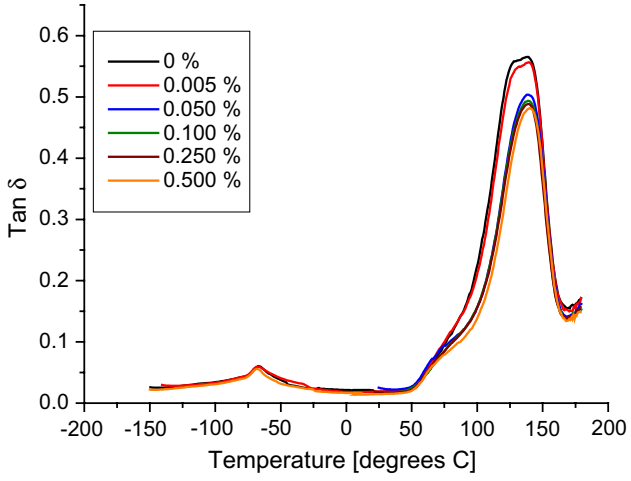


Fig. 6. Tan δ plots for samples containing C.I. Pigment Blue 15:4.

Fig. 6 shows the tan δ plots for the samples that contained C.I. Pigment Blue 15:4.

The plot for each of the pigmented samples has the same basic shape, with a more defined shoulder at around 70 °C compared to that of the unpigmented sample (0%). There is only a small decrease in the tan δ peak when moving from the 0% sample to the 0.005% sample. There is then a much larger decrease, and the peak decreases further as the pigment loading increases.

Fig. 7 shows the tan δ plots for the samples that contained C.I. Pigment Red 122. Again, the plot for each of the pigmented samples is similar with the more defined shoulder at around 70 °C. Here, there is a significant decrease in the tan δ peak moving from the 0% sample to the 0.005% sample. The peak decreases with the increasing pigment loading. The peaks for the 0.050% and 0.100% samples are similar, as are the peaks for the 0.250% and 0.500% samples.

The same features are evident in both figures. The position of the tan δ peak corresponds to the T_g of the PC, and the shoulder corresponds to that of the PBT. There does not appear to be a significant difference in the position of either peak, and hence, the difference in the values of T_g.

The height of the tan δ peak is related to the crystallinity of the sample. This implies that increasing the pigment loading increases the crystallinity of the Xenoy® blend. Values of the tan δ peak are lower for the samples that contained C.I. Pigment Red 122 compared to the values of the tan δ peak for the samples that contained C.I. Pigment Blue 15:4. This suggests that the samples containing the pigment C.I. Pigment Red 122 are more crystalline than are the samples that contained C.I. Pigment Blue 15:4. The peak at −76 °C is related to the T_g of the impact modifier. There is no change in the profile of this peak that arises as a result of the variances in the pigment loading or pigment type.

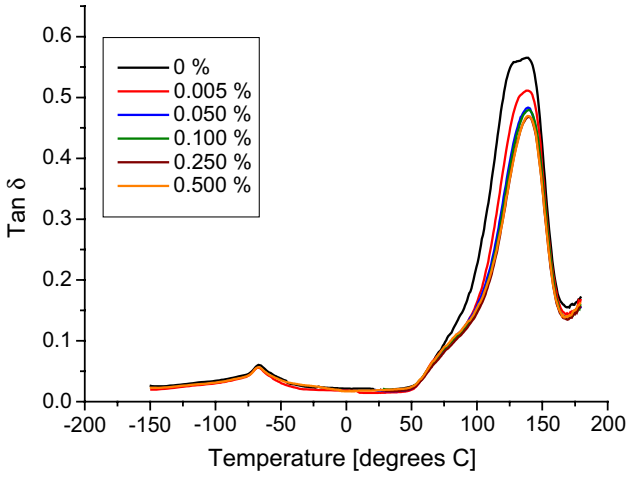


Fig. 7. Tan δ plots for samples containing C.I. Pigment Red 122.

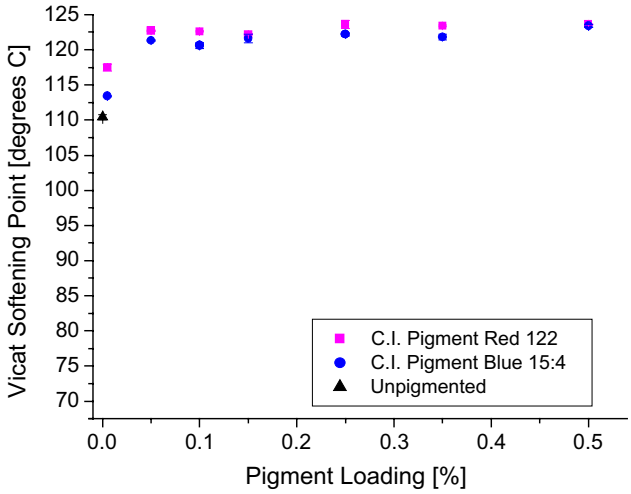


Fig. 8. The influence of pigment loading on the VSP.

3.4. Vicat softening point evaluations of moulded samples

The Vicat Softening temperature of a material gives a measure of the temperature at which the material loses its solid phase properties. Evaluations were undertaken to compare the effect of the pigments on this aspect of the deformation behaviour of the Xenoy® blend. Two specimens from each sample batch were tested. An average value was obtained with a corresponding standard deviation. The standard deviation values are included in the relevant plots, although in the majority of the cases it is too small to be observed.

The results of the Vicat studies for the samples that were evaluated are shown in Fig. 8.

Fig. 8 shows that the incorporation of either pigment into the blend system, up to a loading of 0.050% pigment, increases the Vicat temperature compared to the value for the unpigmented blend. Beyond a loading of 0.005% pigment, the Vicat temperature remains approximately constant. The values for samples containing C. I. Pigment Red 122 are consistently higher than the values for the samples containing C. I. Pigment Blue 15:4.

3.5. Thermal analysis: crystallisation evaluations of powder samples

Studies were undertaken to determine the effects of the pigments on the crystallisation characteristics of the Xenoy® blend.

3.5.1. Slow crystallisation evaluations

A rate of 40 °C/min was used for the study of crystallisation with a slow cooling rate. The crystallisation temperatures and enthalpies are shown in Fig. 9.

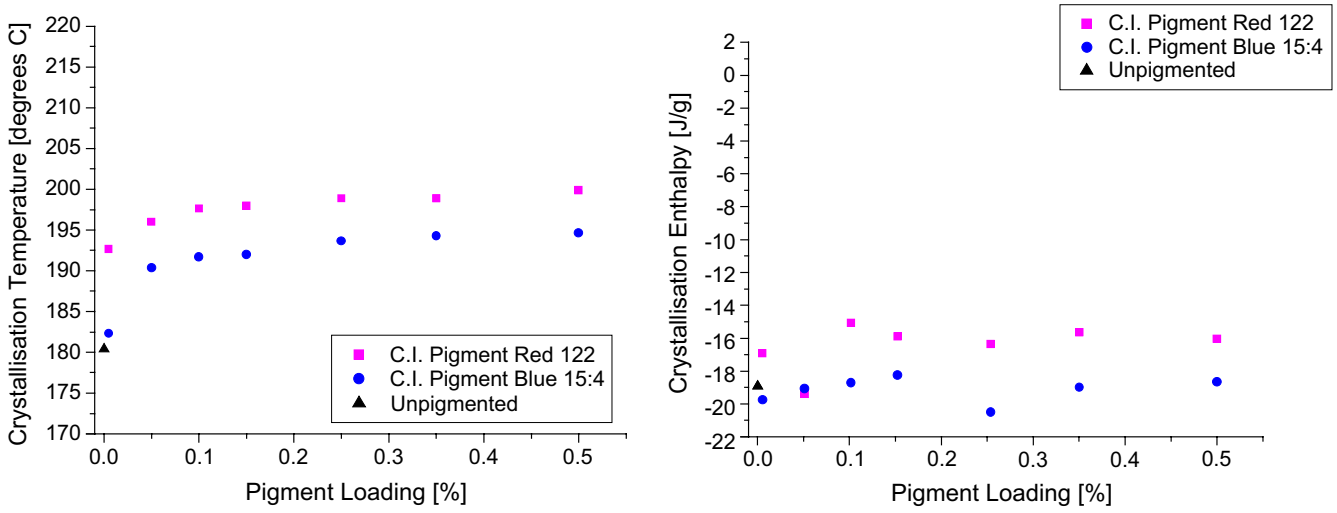


Fig. 9. Temperature and enthalpy values of slow crystallisation.

Both pigments result in an increase in T_c compared to the value for the unpigmented blend. The trend that was observed with increasing pigment loading was the same for both pigments. T_c increased the most when the pigment loading increased from 0.005% to 0.100%. Above a pigment loading of 0.100%, T_c increased much more gradually with increasing pigment loading. Values of T_c were consistently higher for the samples that contained C.I. Pigment Red 122 than for the samples that contained C.I. Pigment Blue 15:4. The greatest difference between the two sets was observed at a pigment loading of 0.005%.

Fig. 9 shows the trends in the enthalpy of crystallisation with increasing pigment loading. Different trends were observed for the two pigment types. Considering the samples that contained C.I. Pigment Red 122, the majority had an enthalpy value that was smaller than that of the unpigmented blend. The sample with a pigment loading of 0.050% had an enthalpy value that was marginally larger than that of the unpigmented blend. For the samples that contained C.I. Pigment Blue 15:4, the enthalpy value initially decreases, then increases or remains similar relative to the value for the unpigmented blend, depending on the pigment loading. The enthalpy decreases as the pigment loading increases, up to a pigment loading of 0.250%, before again decreasing as the pigment loading increases further.

3.5.2. Fast crystallisation evaluations

A rate of 200 °C/min was used for the study of crystallisation that took place using a fast cooling rate. The aim of this study was to mimic the crystallisation behaviour of the samples cooling in the injection moulding operation. The crystallisation temperatures and enthalpies are shown in Fig. 10.

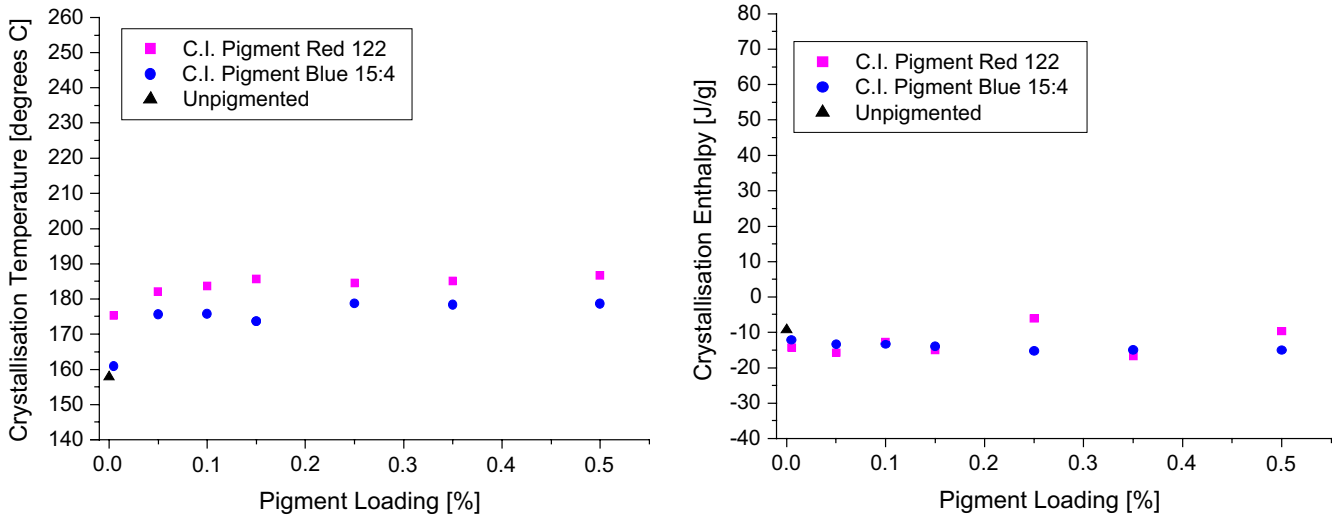


Fig. 10. Temperature and enthalpy values of fast crystallisation.

Similar trends in the results obtained from the slow crystallisation study are seen. For both pigment types, the values of T_c initially increase before reaching a consistent value for pigment loadings greater than 0.250%. Again, all of the pigmented samples had higher values of T_c than that of the unpigmented sample, and the values were higher for the samples that contained C.I. Pigment Red 122 than those that contained C.I. Pigment Blue 15:4. Compared to the results for the slow crystallisation study, all of the values of T_c are less in the fast crystallisation process. This is because the samples had less time to order themselves and were therefore less crystalline.

The corresponding values of enthalpy for the fast crystallisation process are shown in Fig. 10. Little variation is shown in the values in Fig. 10. The enthalpy values for the samples that contained C.I. Pigment Blue 15:4 appear to remain consistent at a value of approximately −12 J/g, as the pigment loading increases. There is more scatter in the values for the samples that contained C.I. Pigment Red 122, particularly for the samples with a pigment loading greater than 0.250%. However, these values fluctuate about a value of approximately −15 J/g.

3.5.3. Evaluation of the intermediary melt transition phenomena

A melt transition was studied for each of the blends between the studies of the two crystallisation processes. The melt temperature, T_m, that was recorded for each sample is shown in Fig. 11, together with the values of the associated enthalpy.

There are only small variations in T_m with pigment type and loading. Pigmentation of the Xenoy® blend with C.I. Pigment Red 122 increases T_m by 1–2 °C, in a reasonably consistent manner. Pigmentation with C.I. Pigment Blue 15:4 leads to much greater scatter in the T_m data, although the values are still quite close to those for the unpigmented blend.

The corresponding values of enthalpy for the melt transition are shown in Fig. 11. Samples that contained C.I. Pigment Red 122 gave values that were smaller than that of the unpigmented blend. The enthalpy decreased gradually with increasing pigment loading, up to a loading of 0.150%. The value then increased before remaining consistent as the pigment loading increased further. No trend is apparent for the samples that contained C.I. Pigment Blue 15:4. However, at all pigment loadings, the values of enthalpy are higher than those of the equivalent samples that contained C.I. Pigment Red 122.

3.5.4. The multiple melting phenomenon of PBT

In the plot (Fig. 12), for the melt process two peaks were evident: a minor peak at a lower temperature (peak I) and a major peak at a higher temperature (peak II). This phenomenon of multiple melting of PBT has been described in the literature [11,12]. To investigate this point further, the relative heights of the peaks were measured for each sample. Fig. 12 illustrates the two peaks, identified as I and II respectively, in the upper portion of the DSC trace.

These results are presented in Tables 1 and 2. The data for the unpigmented sample provided a "standard", so that the effects of the pigments could be determined.

The data for the samples that contained C.I. Pigment Blue 15:4 are shown in Table 1. At the lowest pigment loading, there is little difference in the peak heights compared to those for the unpigmented sample. However, as the pigment loading increases, peak I

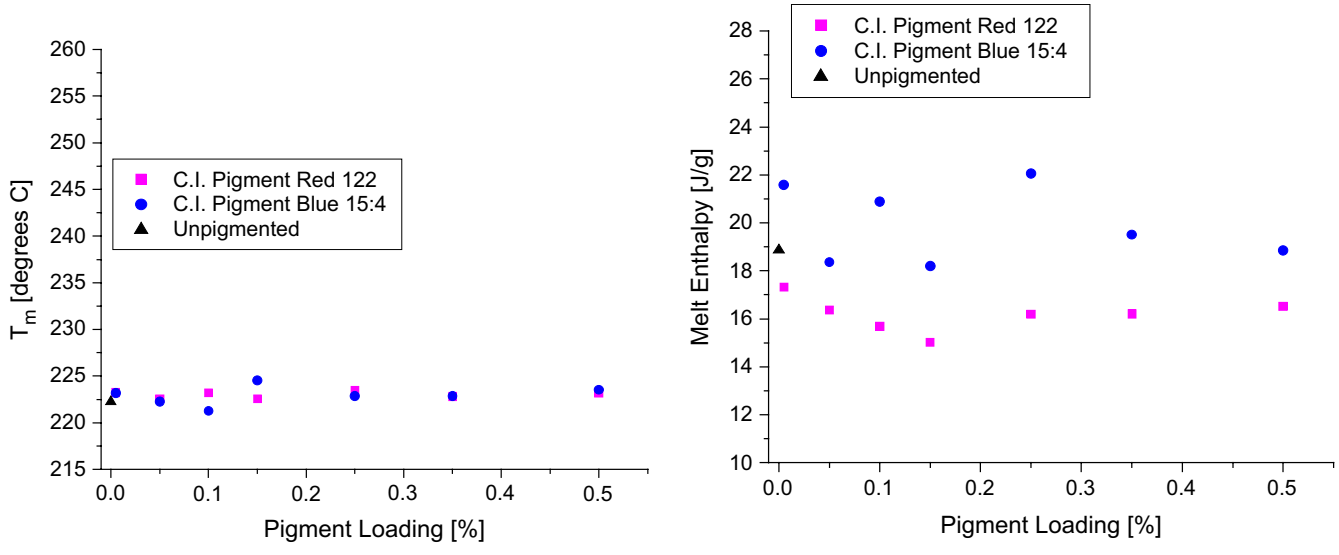


Fig. 11. Temperature and enthalpy values of the melt process.

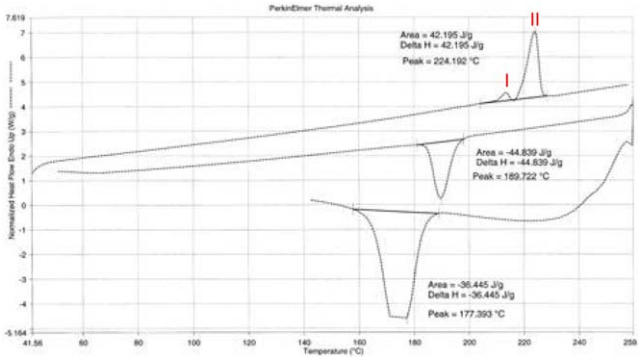


Fig. 12. DSC trace to illustrate the peaks and troughs obtained for each sample during crystallisation studies.

becomes larger and peak II becomes slightly smaller. These observations are in contrast to those made for the samples that contained C.I. Pigment Red 122 (Table 2).

Table 2 shows that, at the lowest pigment loading for the samples that contained C.I. Pigment Red 122, there is a significant difference between the peaks observed for that sample and for the unpigmented sample. Peak I is much larger for the pigmented sample, and peak II is slightly smaller. As the pigment loading increases, peak I continues to increase while peak II decreases further.

Suggestions may be made in terms of the effects of the pigments for both the samples that contained C.I. Pigment Blue 15:4 and those that contained C.I. Pigment Red 122. The lower temperature peak (I) is indicative of the formation of crystals with a higher degree of perfection than the crystals indicated by the higher temperature peak (II). As the pigment loading increases, the formation of more perfect and, thus, more stable crystals is encouraged. In the case of C.I. Pigment Red 122, this formation takes place even at the lowest pigment loading.

3.5.5. *Additional crystallisation data processing*

In the literature, Arrhenius type equations that have been applied to isothermal crystallisation processes are described [3,13]. Although the studies undertaken in this work were conducted under non-isothermal conditions,

Table 1
Melt peak data relating to samples that contained C.I. Pigment Blue 15:4

Pigment loading [%]	Height of peak I [W/g]	Height of peak II [W/g]
0.000	0.1	1.0
0.005	0.1	1.1
0.050	0.4	1.1
0.100	0.4	1.1
0.150	0.4	0.9
0.250	0.5	1.0
0.350	0.5	1.0
0.500	0.6	0.9

Table 2
Melt peak data relating to samples that contained C.I. Pigment Red 122

Pigment loading [%]	Height of peak I [W/g]	Height of peak II [W/g]
0.000	0.1	1.0
0.005	0.4	0.9
0.050	0.5	0.8
0.100	0.6	0.8
0.150	0.5	0.8
0.250	0.5	0.7
0.350	0.6	0.7
0.500	0.6	0.8

the question was posed as to whether or not it was possible to represent the crystallisation temperature data in terms that can be related to the kinetics of the process. The Arrhenius equation was used as the basis of the investigation. The general Arrhenius equation has the form:

$$\ln k = \ln A - E_a/RT$$

Here, k is the rate constant, A is the collision frequency factor, E_a the activation energy ($J\,mol^{-1}$), R the universal gas constant ($8.31\,J\,K^{-1}\,mol^{-1}$) and T is the temperature (K).

Thus, if

$$\text{Rate} \propto [\text{concentration of reactant A}]$$

$$\text{Rate} = k[\text{concentration of reactant A}].$$

As the "concentration" of the pigment in the sample is known, the equation can be rearranged so that

$$[\text{Pigment}] = \text{Rate}/k$$

Hence, the Arrhenius equation becomes:

$$\ln [\text{Pigment}] = \ln A - E_a/RT_c.$$

Here, T_c is the crystallisation temperature.

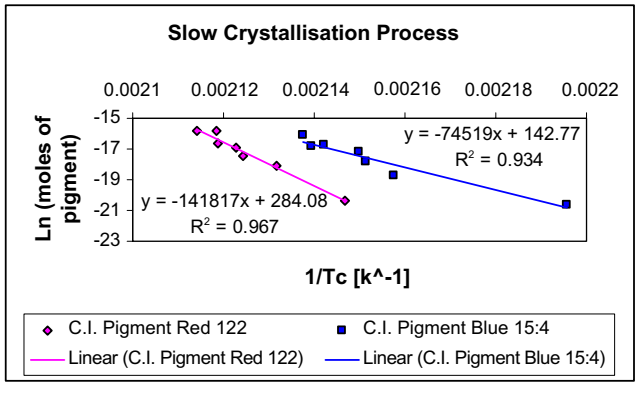


Fig. 13. Arrhenius-type data treatment for the slow crystallisation process.

Fig. 13 shows the Arrhenius type plot for the slow crystallisation data.

The number of moles of pigment was calculated for the mass of pigment in the sample being analysed (determined by weight percentage). The data appear to follow the Arrhenius model of behaviour:

$$\ln[\text{moles of pigment}] = \ln A - E_a/RT_c.$$

The values taken from the plots in Fig. 13 are given in Table 3.

The absolute numerical values calculated here are not strictly appropriate, being far too high. Instead, it is the difference between the two sets of data that is important, any errors that have occurred in calculation being the same for both sets. The difference that is observed is important, implying that crystallisation is a more difficult process for the blends containing C.I. Pigment Red 122 to crystallise, compared to those that contain C.I. Pigment Blue 15:4. If ln [moles of pigment] is calculated for the complete batch of sample (i.e. calculated from the mass of pigment added to the blend during processing), and plotted against $1/T_c$, an even better correlation coefficient is achieved for both sample sets.

Fig. 14 shows the treatment of the crystallisation data for the fast crystallisation process. While the plots appear to be similar to those given in Fig. 13, the correlation coefficients are poorer.

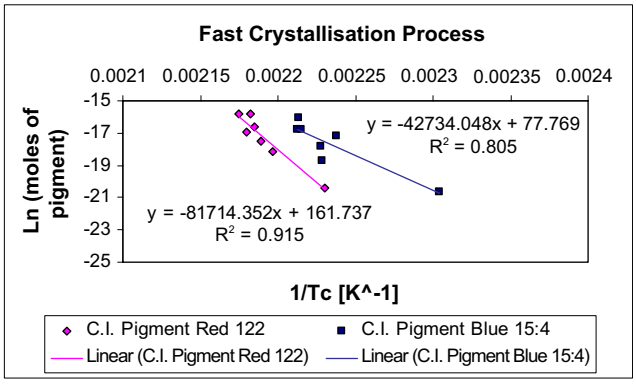


Fig. 14. Arrhenius-type data treatment for the fast crystallisation process.

4. Conclusions

C.I. Pigment Blue 15:4 and C.I. Pigment Red 122, when included in a Xenoy® blend formulation, cause changes in a number of the important properties of the blend.

Results from a number of the techniques have indicated that the pigments have a significant influence on the crystallisation properties of the Xenoy® blend. The crystallisation temperature of the blend, as observed by cooling DSC studies, was increased when either pigment was included in the formulation. C.I. Pigment Red 122 resulted in a greater increase than that provided by C.I. Pigment Blue 15:4. This suggests that the pigment particles act as "crystallisation" sites so that crystallisation of the polymer blend is completed sooner/easier. It must be recalled that the speed of crystallisation itself is not affected, but that crystallisation is stopped when the spherulites that are formed impinge upon one another. This is typical behaviour of a nucleating agent.

Table 3
Data resulting from the linear regression fits for the crystallisation data

C.I. pigment	Slope	Intercept	E_a [kJ/mol]
Red 122	141,817	284.08	1178
Blue 15:4	74,519	142.77	619

It may also be recalled that there are two types of crystallisation: primary (conversion of the bulk material) and secondary (perfection of the formed crystallites and additional crystallisation of the material trapped between them). The DSC studies indicated that the pigments are able to influence both processes, with the secondary crystallisation increasing in importance as the pigment loading is increased.

Indications that C.I. Pigment Red 122 resulted in a more crystalline polymer system than that arising with C.I. Pigment Blue 15:4 were also seen in the results for the Vicat evaluations and in the DMTA evaluations. The Vicat softening temperature may be correlated with the speed of crystallisation in that a higher crystallisation temperature correlates with a higher Vicat temperature. However, for both pigments the Vicat temperature stabilised beyond a pigment loading of 0.050%. This suggests that above a particular pigment content, little further improvement is obtained.

The increased crystallinity of the sample that was pigmented with C.I. Pigment Red 122 is apparent from some of the mechanical test evaluations. Increased crystallinity means that the material is stiffer (an increased value of Young's modulus) as more of the chains form ordered arrangements. Evidence of increased brittleness, or loss of toughness, was observed in the decreased impact strength values and in the decreased elongation (tensile strain at break) values. An increase in the number of macromolecules that are forming spherulites means that the number of chains that are capable of undergoing local chain dynamics decreases. This restriction in mobility decreases the impact strength of the sample. However, the values of yield stress increase as the stress is transferred more efficiently through the more uniform blend. These trends are also seen for the majority of the samples that contained C.I. Pigment Blue 15:4, but to a lesser extent.

If there is an increased number of "tie" molecules connecting the spherulites in the samples containing C.I. Pigment Red 122, compared to the number in the

samples containing C.I. Pigment Blue 15:4, this could account for the higher values of impact strength and tensile stress of the former samples compared to the latter samples. This is because the tie molecules improve the stress transfer within the sample. A greater number of spherulites may have more associated "tie" molecules. This is a situation that may be envisioned for the two-pigmented systems. However, connected to this is the degree of "perfection" of the spherulites. If the pigments result in the formation of spherulites of different levels of crystallisation (i.e. one pigment enhances the amount of secondary crystallisation taking place) this could also have an effect on the stress transfer processes. At this time, there is not sufficient information regarding the nature of the spherulitic structures to comment on which type of structure development may be taking place in this polymer system, if indeed differences exist.

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