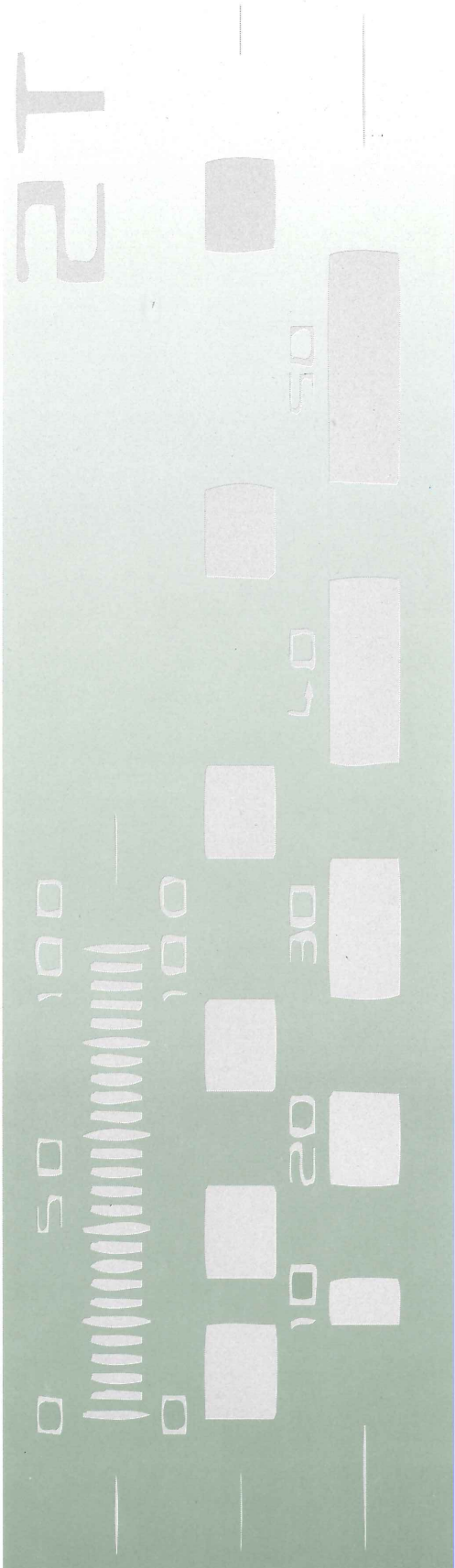
REPORT

The Influence of Nucleating Agents on the Dimensional Stability of Pigmented Mouldings

P E Tomlins, I Smith and P Bartlett

September 2001



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The Influence of Nucleating Agents on the Dimensional Stability of Pigmented Mouldings

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SUMMARY

Certain organic pigments are known to cause dimensional instability problems, particularly in semi-crystalline polymers such as polypropylene and high density polyethylene. This may be attributable to the polymers crystallizing at higher temperatures than normal as a result of nucleation by the pigments causing shrinkage stresses that are different to those observed in virgin polymer. Adding a second more effective nucleating agent to both pigmented and virgin feedstocks to control crystallization and hence the shrinkage behaviour of mouldings may provide a solution to this problem.

Whilst adding either sodium benzoate or palmerol in one of two concentrations does have an affect on the dimensional stability of mouldings, the changes that occur depend on the type of pigment present. It is possible to tailor the shrinkage and/or warpage of differently pigmented mouldings for a particular application by identifying particularly active or benign pigments or by adding an additional nucleating agent.

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1 INTRODUCTION

It is well known that certain organic pigments such as phthallocyanine blue can induce unacceptable levels of shrinkage and warpage in some polymers, principally polypropylene and polyethylene[1]. This is a particular issue for the packaging industry which is often required to manufacture a product in a range of different colours, some of which may contain 'dimensionally active' pigments. In recent studies [2,3] we have shown that phthallocyanine blue behaves as a nucleating agent by raising the crystallization temperature of both polyethylene and polypropylene. The presence of 0.1% phthallocyanine blue increases the crystallization temperature of high density polyethylene[4] by approximately 3°C and that of polypropylene by around 18°C. Phthallocyanine blue also has a pronounced effect on reducing the size of the crystalline spherulites in both materials, although the overall level of crystallinity remains unchanged. These differences in crystallization behaviour and crystal morphology are thought to be responsible for causing differences in the shrinkage behaviour of mouldings containing this pigment compared to those manufactured from virgin material.

Past experiments[2,3,5] using a simple plate geometry have shown that phthallocyanine blue increases the shrinkage in a direction perpendicular to that of the flow compared to that of virgin material, i.e. the shrinkage is anisotropic. This suggests that it is difficult to compensate for pigment induced shrinkage by changing the processing conditions. A potential solution to this problem is to deliberately dope virgin and other 'benign' pigments with a nucleating agent with a view to mimicking the effect of phthallocyanine blue and other 'active' pigments. The mould can then be designed to compensate for asymmetric shrinkage so that mouldings regardless of colour will be dimensionally very similar. This approach to solving pigment induced shrinkage and warpage is the topic of this paper.

2 MOULDING TRIALS

The moulding trials have been designed in two stages:
Stage 1: Compares the dimensional stability of mouldings produced from different pigments in the absence of a nucleating agent.
Stage 2: Compares the dimensional stability of differently coloured mouldings that contain one of two nucleating agents at one of two different concentrations.

The purpose of Stage 1 is to characterise the ten base pigments selected for the investigation in terms of their shrinkage and/or warpage behaviour compared to that of non-pigmented virgin material. A constant concentration of each pigment was used throughout the trial. Two different nucleating agents were used for stage 2 at two different concentrations to assess which nucleating agent had the most influence on dimensional instability and how this was affected by its concentration.

The moulding conditions were kept constant for both stages of the trial. These conditions were chosen on the basis of producing a commercially acceptable moulding from non-nucleated virgin feedstock.

3 EXPERIMENTAL

3.1 MOULDING GEOMETRY

The simple edge-gated plate moulding shown in Figure 1 has been specially designed to be uniformly filled by the advancing flow front. This is achieved by ensuring that the path lengths of the melt as it flows into the spreader are equivalent so that the flow front reaches all points along the weir gate simultaneously. This is the role of the domed region. The performance of the cavity and its cooling circuit has been described elsewhere[5]. The mould cavity and cooling circuit are contained within a block of P20 steel of dimensions 296 mm x 496 mm x 168 mm. The dimensions of the square plate cavity are 150 mm x 150 mm x 4 mm.

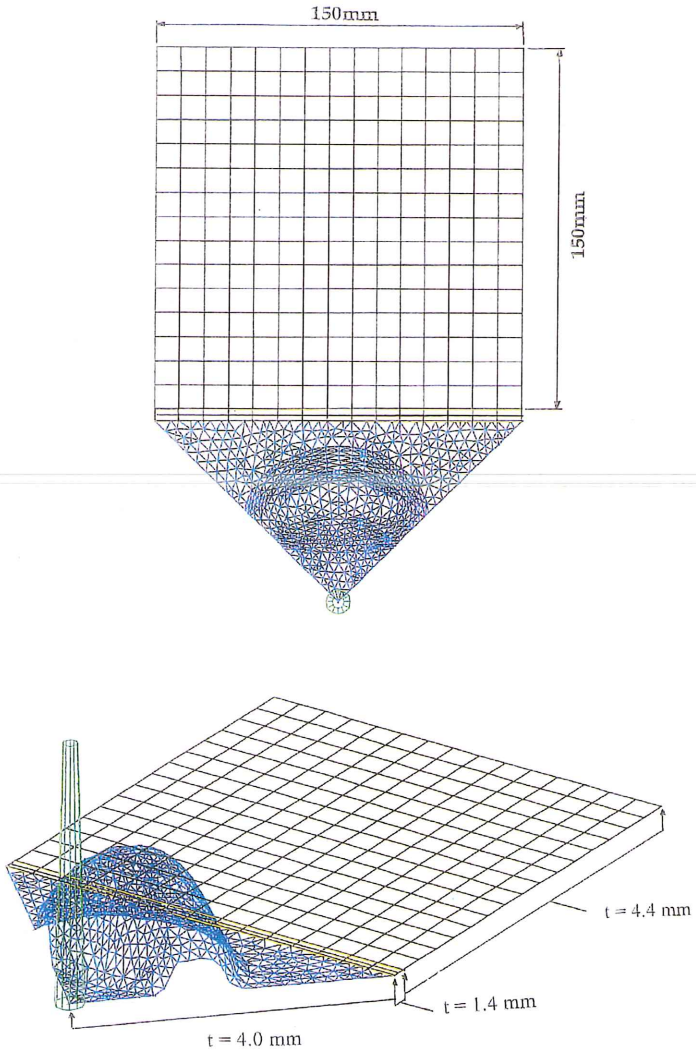


Figure 1: The dimensions of the cavity

3.2 MATERIALS AND SAMPLE PREPARATION

Pelletised masterbatches were used containing the following pigments:

- Chromophtal Red 2030 (Ciba)
- Chromophtal Orange GP (Ciba)
- PVFast Yellow H3R (Clariant)
- Chromophtal Yellow GR (Ciba)
- PA Fast Yellow HG (Clariant)
- Paliotol Yellow K0961 HD (BASF)
- Heuco Green 600703K (Heubach)
- Langdocyl Blue 341 (SLMC)
- Langdocyl Blue 341 1 Part (SLMC) + Titanium Dioxide RCL188 10 Parts (Millenium)
- PV Fast Pink E (Clariant)

In addition these contained PE wax (0.05%) and zinc stearate (0.05%) to facilitate wetting and dispersion of the pigment particles respectively. The masterbatch samples were supplied by Victors International Plastics Ltd and tumble mixed with pellets of polypropylene (SM6 130, MFI = 12) before moulding the 4 mm thick square plates for Stage 1 of the investigation. Non-pigmented virgin feedstock acted as a control. The pigment concentration in the final article was 0.2%. 0.1% and 0.15% concentrations of palmerole and sodium benzoate were used as the nucleating agents for Stage 2.

All the plate mouldings were produced using the following moulding conditions:

- Injection time 2.9 s
- Holding pressure 9.0 s
- Holding time 40 bar
- Injection speed slow (Exact figures are not available)
- Melt temperature 225 °C
- Mould temperature 14 °C

Virgin feedstock was used to purge all traces of each colour or nucleating agent as the trial progressed. Having established stable conditions for each pigment/nucleating agent combination 15 plates were collected of which 3 were used for measurement and analysis.

3.3 CALORIMETRY

One of the effects of a nucleating agent in semicrystalline polymers is to raise the temperature at which crystallization occurs on cooling of a melt. This can be monitored by differential scanning calorimetry. Small samples (~10-15mg) of moulded material are placed into sealed aluminium containers and heated at a controlled rate (20°C min^{-1}) to a temperature above the melting point of the polypropylene crystals (180°C). The sample is then held at this temperature for a short period of time (4 minutes) to ensure that all the crystals melt and then cooled at a rate of 10°C min^{-1} to 80°C. The onset of crystallization in the sample during cooling is accompanied by the evolution of heat (the latent heat of crystallization) which can be detected by the calorimeter.

3.4 MEASURING AND ASSESSING SHRINKAGE AND WARPAGE

After manufacture the plates were allowed to cool in air at room temperature and subsequently stored in an upright position for a period of approximately six weeks. The plates were then weighed after removing the sprue.

A three dimensional map of the surface of each plate was obtained using shadow Moire interferometry as described elsewhere[3]. A three dimensional surface fitted to the plate surface co-ordinates allowed the out-of-plane deformations (RW_z) to be determined together with true shrinkages in directions both parallel and perpendicular to that of the flow - $S_{\parallel}$ and $S_{\perp}$ respectively. In-plane warpages ($W_{\parallel}$ and $W_{\perp}$) and the cosine of the angle formed by the intersection of the diagonals (θ) were also used as measures of dimensional instability. Mathematical descriptions of each of these quantities have been described in previous publications[3,5] and are hence only briefly discussed in Appendix 1. Figure 2 depicts the measures of shrinkage and warpage.

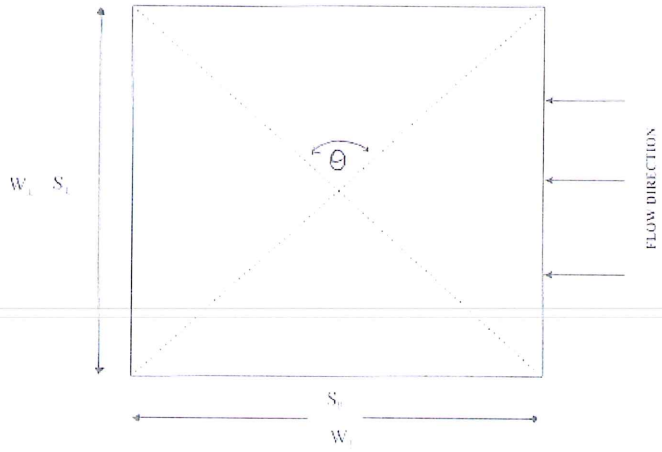


Figure 2: A schematic representation of the measures used to assess dimensional instability.

In-plane shrinkage and warpage are characterised by scores that represent averaged data and the variability or range of values that exist within it. The mathematical relationships between each score and measured data can be found in Appendix 1. Averaging the data is a convenient way of reducing a large number of values to a single number to facilitate comparisons. However this procedure 'desensitizes' data which can mask or dilute trends i.e. smooth out shrinkage data determined at different distances away from the gate. To some extent this information can be preserved by considering a range value that is a measure of the spread of the data about the mean. (Note that we have only considered the range of out-of-plane warpages as averaging was shown to profoundly desensitize these data.)

3.5 DATA INTERPRETATION

Clearly measurements of in- and out-of-plane warpage, in-plane shrinkage and sample weight for each of the ten pigments containing one of two different nucleating agents at one of two concentrations and control data for each of three replicates generates a large amount of

information. These data can be reduced by using the scoring system described above (and in Appendix 1) to generate six measures (two shrinkage, three warpage and one angular distortion) for each of the 165 samples examined, together with weight measurements. We have used the analysis of means method to assess the influence that different pigments, nucleating agents and concentrations of a particular nucleating agent have on each of these scores and to look for trends in the data. This technique compares the medians (i.e. middle values) of replicate data sets. (Using the median rather than the mean removes any bias that can exist in small data sets due to outlying points.) The replicate data sets can be grouped together in a number of different ways i.e. according to colour, the presence of one or other nucleating agent or with respect to different concentrations of a particular nucleating agent. Plots of the medians of each group reveal the variability between different data sets as shown, for example, in Figure 3.

Whilst the analysis of means approach provides an easily understood illustration of trends in the sample data set, it does not assume that the trends exist in the general population. In order to make this step, the data must be analysed using statistical methods that rely on the sample test data being representative of the results that would be obtained from a much larger number of tests. Prior to carrying out the statistical tests the data sets have to be checked mathematically to ensure that the tests can be applied. At least five replicates are usually required to ensure that the mathematical check has sufficient information to provide a valid response. In this investigation only three replicates have been measured hence we have encountered some statistical problems. The results described here are therefore, in principle, confined to the data presented here.

4 RESULTS AND DISCUSSION

The results have been analysed with respect to the influence that the different pigments and nucleating agents have on:

- the weight of the mouldings
- both in- and out-of-plane plate warpage
- plate shrinkage
- angular distortion
- the crystallization behaviour of the base polypropylene.

(Note that shrinkage and warpage scores are related to actual plate dimensions.)

4.1 VARIATIONS IN THE WEIGHT OF THE MOULDINGS

Figure 3 shows how the median weights of the moulded plates vary with both the type of nucleating agent and pigment present. The weights of the mouldings clearly fall into two distinct groups, although the reasons for this are not clear. Adding either one of the nucleating agents to the base polymer/pigment mixture tends to increase the median weight, albeit by a small amount. This effect is more apparent in Figure 4 which also shows that changing the concentration of either nucleating agent has a minor effect on the weight of the plates.

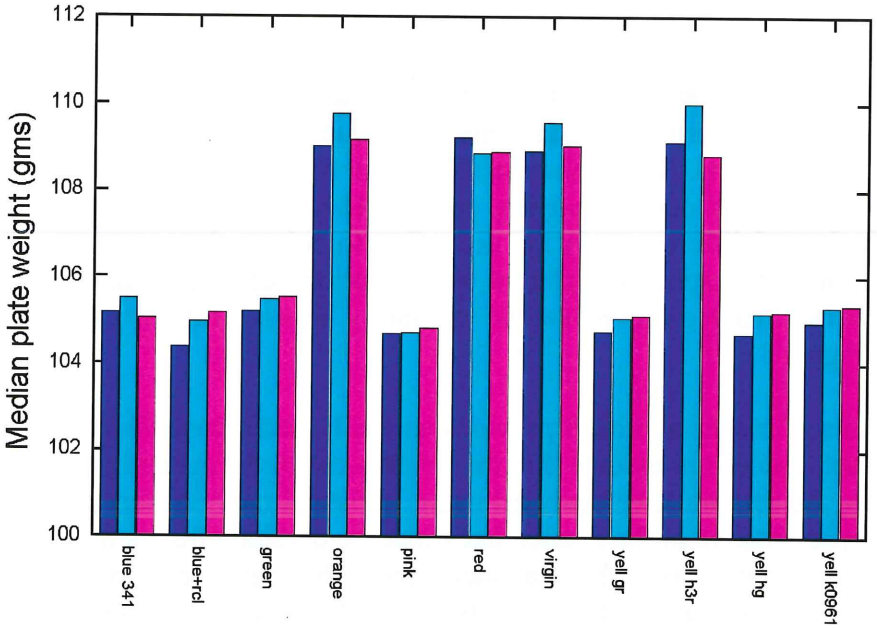


Figure 3: A comparison of the median plate weights of differently pigmented polypropylene feedstocks with virgin material.

■ = non-nucleated, ■ = Palmerol, ■ = Sodium benzoate

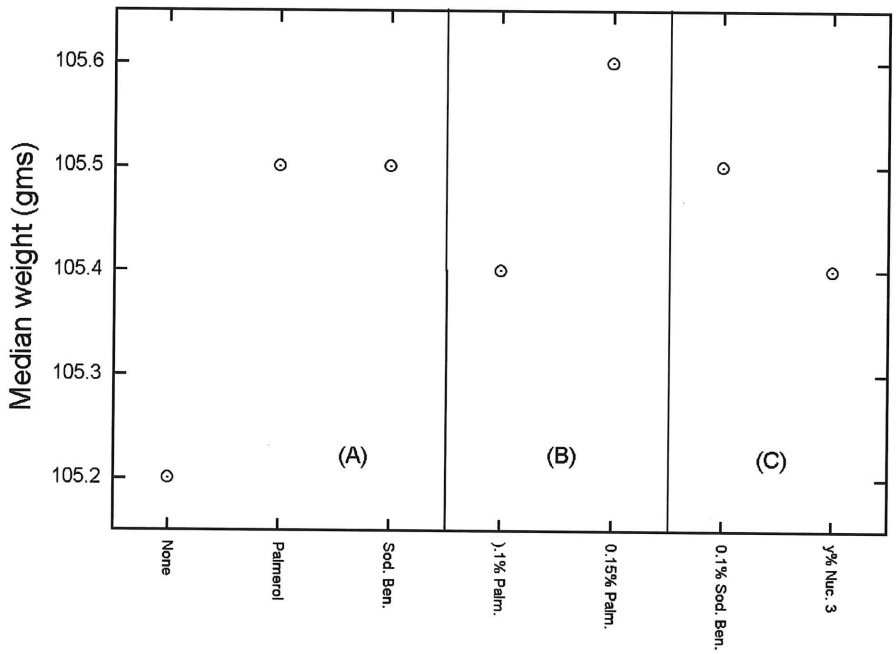


Figure 4: (A). Adding a nucleating agent to polypropylene slightly increases the median weight of the plate mouldings regardless of which pigment is present. (B) and (C) show how the median plate weight depends on the concentration of the nucleating agents.

4.2 MOULDING WARPAGE

4.2.1 Out-of-plane warpage

Figure 5 shows how the out-of-plane warpage score, RW_z, depends on both the type of pigment and nucleating agent present. These differences do not appear to be correlated with the weight of the plates (shown in Figure 3) as some of the 'heavy plates', e.g. yellow H3R, are similar to some 'light plates', e.g. yellow K0961, in terms of their out-of-plane warpage behaviour.

- Plates containing blue 341, heuco green or chromopthal orange are significantly flatter than those manufactured from polypropylene containing other pigments or virgin material.
- The out-of-plane plate warpage (RW_z) is strongly dependent on the type of pigment present in the polypropylene feedstock and less sensitive to the presence of nucleating agents.
- The effect of adding nucleating agent to the feedstock is different for different pigments.

For example, adding a nucleating agent to chromopthal orange causes it to become more warped, whilst others are essentially unaffected, e.g. virgin or yellow Hg.

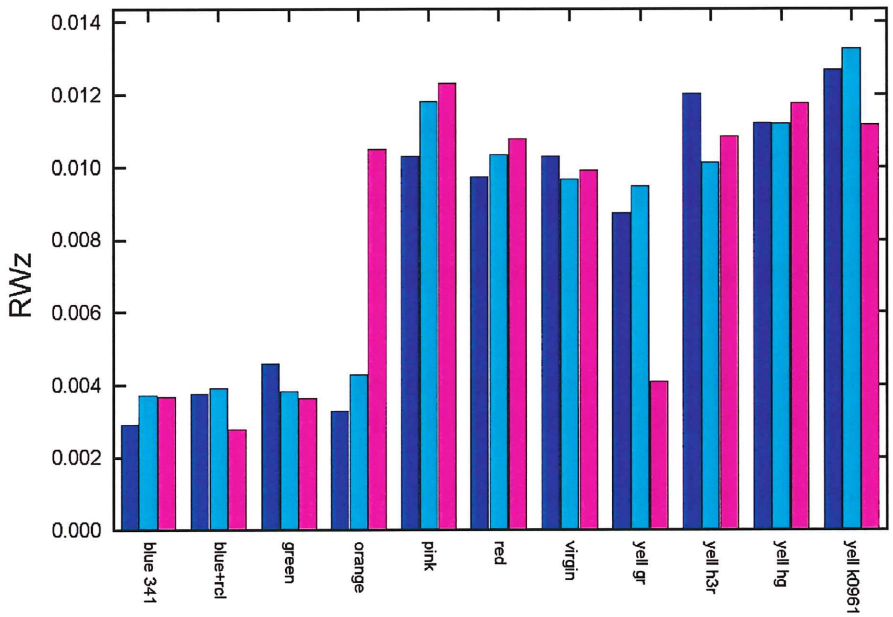


Figure 5: Out-of-plane plate warpage (RW_z) depends strongly on the type of pigment present in the polypropylene feedstock is less sensitive to the presence of nucleating agents.

■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

Table 1 shows the pigments categorized according to their out-of-plane warpage behaviour with respect to non-nucleated virgin.

Table 1
Classification of pigments into low and high out-of-plane distortion.
(The pigments are unranked within each classification)

Low out-of-plane warpage pigments	**High out-of-plane warpage pigments**
Blue 341	Chromopthal orange (containing sodium benzoate)
Blue 341 + rcl 188	Fast pink
Heuco green	Chromopthal red
Chromopthal orange (non-nucleated and containing palmerol)	Virgin
Chromopthal yellow GR (containing sodium benzoate)	Chromopthal yellow GR (non-nucleated and containing palmerol)
	Fast yellow H3R
	Fast yellow HG
	Paliotol yellow K0961

4.2.2 In-plane warpage

Figures 6 and 7 show how the calculated in-plane warpage varies with the flow direction. The in-plane warpage that occurs in a direction perpendicular to that in which the melt fills the cavity (wxscore) varies according to the type of pigment present.

- Adding a nucleating agent to pigmented polypropylene can significantly reduce in-plane warpage.

The magnitude of the reduction depends on the pigment present e.g. compare plates containing heuco green with those containing yellow GR.

- Sodium benzoate appears to be more effective at reducing in-plane distortion than palmerol.

This difference between the nucleating agents is apparent for feedstocks containing yellow Hg, fast pink or blue 341.

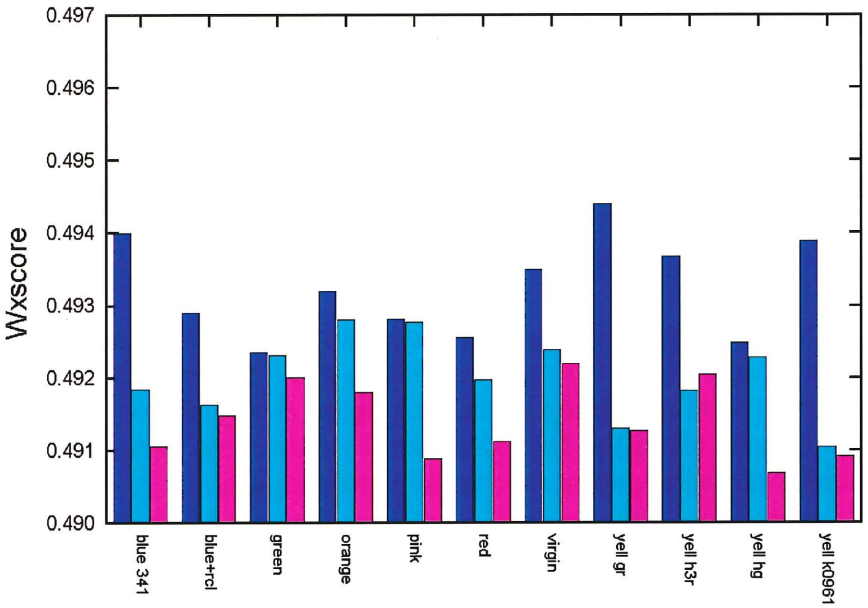


Figure 6: Adding nucleating agents to differently pigmented polypropylene feedstocks decreases the in-plane warpage that occurs in a direction perpendicular to that in which the cavity fills (wxscore). The magnitude of this effect depends on the pigment present.

■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

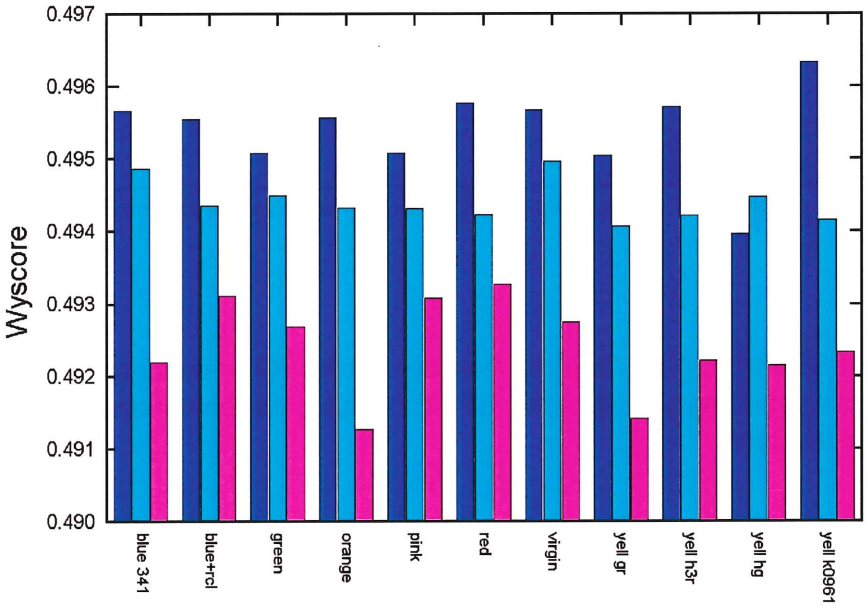


Figure 7: The in-plane warpage that occurs in a direction parallel to that in which the flow front flows (wyscore) is significantly reduced by adding a nucleating agent.

■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

Figure 7 shows how the in-plane warpage that occurs parallel to the flow fill direction (wyscore) is affected by pigmentation and nucleation. The scores are higher than those shown in Figure 6.

- More in-plane warpage occurs parallel to the flow direction than perpendicular to it.
- Adding palmerol substantially reduces the amount of in-plane warpage compared to that observed for all the pigmented feedstocks (except yellow Hg).
- Adding sodium benzoate further reduces in-plane warpage.

This behaviour mirrors that shown in Figure 6 and could be used to balance in-plane parallel and perpendicular warpage. Figure 8 shows how the in-plane warpage scores are affected by the concentration and type of nucleating agent. The figure clearly shows the difference in in-plane warpage across and along the flow direction (wxscore and wyscore). Increasing the concentration of either nucleating agent reduces in-plane warpage.

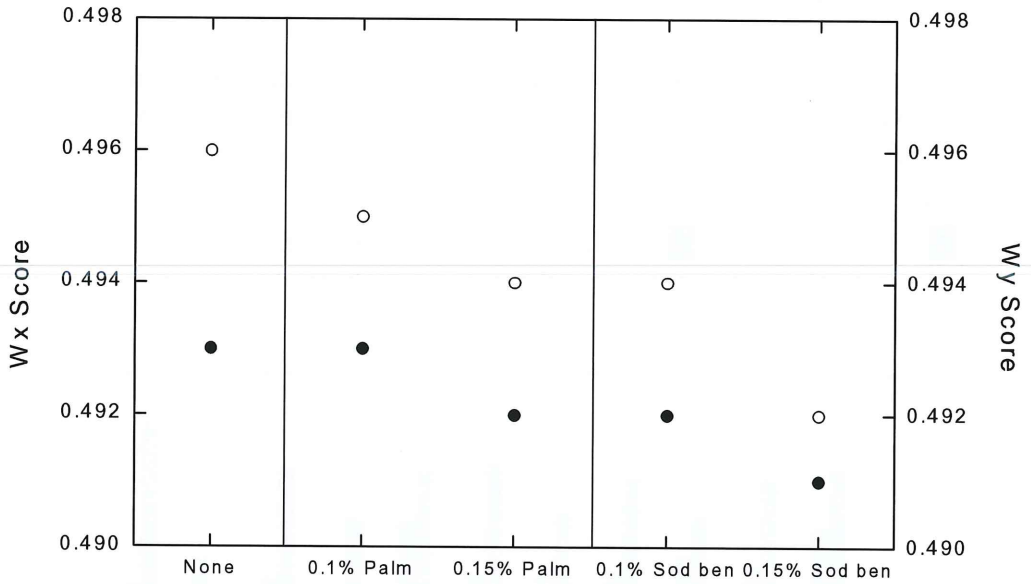


Figure 8: The dependence of the in-plane warpage scores (O = wxscore, ● = wyscore) for all plate mouldings, irrespective of their colour, on the concentration and type of nucleating agent.

4.3 SHRINKAGE

The shrinkage scores determined in directions parallel (syscore) and perpendicular (sxscore) to the flow direction are shown in Figures 9 and 10. Less shrinkage occurs parallel to the flow direction than perpendicular to it.

The shrinkage scores parallel to the flow direction are similar with the exception of yellow H3R which appears to be a low shrinkage material and relatively unaffected by nucleating agents.

Shrinkage scores perpendicular to the flow direction are greater than those measured parallel to it and show more variability. Figure 10 shows that perpendicular shrinkage is greater than that of the virgin material for most pigments with the exception of chromopthal orange, yellow GR and yellow HG. Adding palmerol to feedstocks significantly increases the shrinkage score particularly for chromopthal orange, fast pink and yellow H3R. Sodium benzoate has less impact on the shrinkage scores measured perpendicular to the flow direction, although they are still larger than for virgin non-nucleated materials. The data from figures 9 and 10 have been re-presented in Figure 11 to show how shrinkage scores are affected by different types and concentrations of nucleating agent.

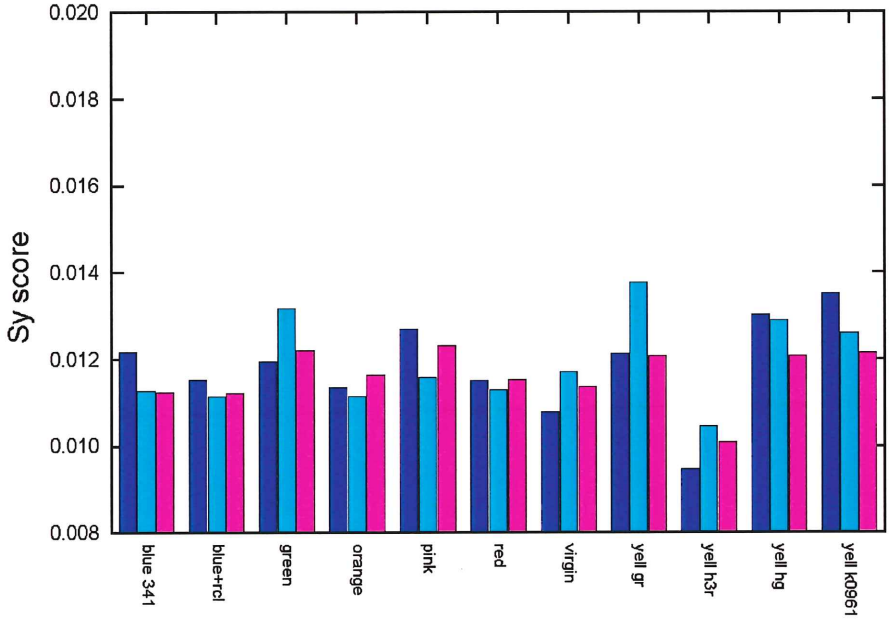


Figure 9: Shrinkage parallel to the flow direction shows minor variations with different pigments with the exception of yellow H3R

= non-nucleated, = Palmerol, = Sodium Benzoate.

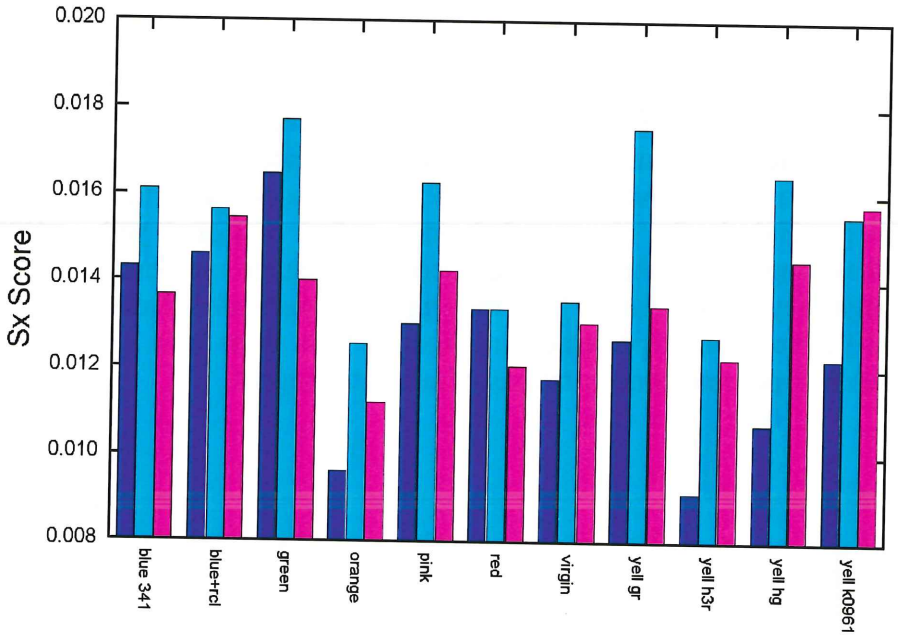


Figure 10: The variation in shrinkage that occurs across the plate (i.e. perpendicular to the flow direction) shows a significant dependence on pigment type and generally increases in the presence of nucleating agents.
■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

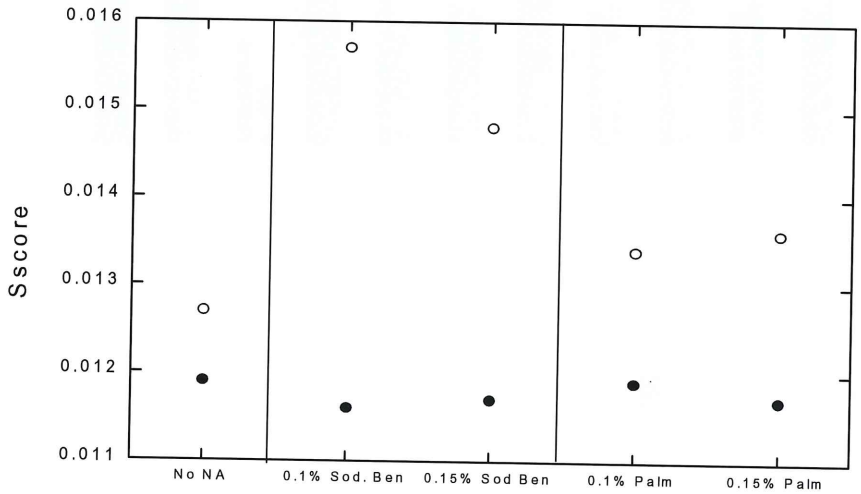


Figure 11: The dependence of Sxscore (●) and Syscore (○) for all the plate mouldings (irrespective of colour) on different concentrations of palmerol and sodium benzoate.

Tables 2 and 3 show the pigments categorized according to their shrinkage behaviour with respect to non-nucleated virgin measured perpendicular and parallel to the flow respectively.

Table 2

Compared to virgin non-nucleated polypropylene pigments can be classed as 'high' or 'low' shrinkage materials. (The pigments are unranked within each classification and the data refer to shrinkage measured **perpendicular** to the flow direction).

Low shrinkage pigments	**High shrinkage pigments (non-nucleated)**	**High shrinkage pigments (containing palmerol)**	**High shrinkage pigments (containing sodium benzoate)**
Orange Gp (non- and nucleated materials particularly containing sodium benzoate)	Blue 341	Blue 341	Blue 341
Yellow H3R	Blue 341 + rcl	Blue 341 + rcl	Blue 341 + rcl
Yellow HG	Heuco green	Heuco green	Heuco green
	Fast pink	Chromopthal orange (weak)	Fast pink
	Red 2030	Fast pink	Red 2030 (weak)
	Yellow GR	Red 2030	
	Paliotol yellow K0961 (weak)	Yellow GR	Yellow GR
		virgin	virgin
		Yellow H3R (weak)	Yellow H3R (weak)
		Yellow HG	Yellow HG
		Yellow K0961	Yellow K0961

Differences in the values of the shrinkage scores across and along the plate i.e. perpendicular and parallel to the flow direction will affect the ratio of the shrinkage scores (Sx/Sy) and the angle score (Figures 12 and 14). These two measures reflect any imbalance in the shrinkage behaviour of the plates, higher scores indicating bigger differences. For the majority of pigments high values of (Sx/Sy) can be traced to the changes in perpendicular shrinkage (sxscore) caused by adding a nucleating agent.

- Palmerol has more influence on the shrinkage ratio than sodium benzoate, (which in some cases has a negligible effect on it when compared to the virgin material i.e. blue 341.)

Table 3

Compared to virgin non-nucleated polypropylene pigments can be classed as 'high' or 'low' shrinkage materials. (The pigments are unranked within each classification and the data refer to shrinkage measured **parallel** to the flow direction).

Low shrinkage pigments (parallel to flow direction)	**'High' shrinkage pigments (non-nucleated)**	**'High' shrinkage pigments (containing palmerol)**	**'High' shrinkage pigments (containing sodium benzoate)**
Yellow H3R (non- and nucleated materials)	Blue 341	Blue 341 (weak)	Blue 341 (weak)
	Blue 341 + rcl	Blue 341 + rcl (weak)	Blue 341 + rcl (weak)
	Heuco green	Heuco green	Heuco green
	Chromopthal orange	Chromopthal orange (weak)	Chromopthal orange (weak)
	Fast pink	Fast pink(weak)	Fast pink
	Red 2030	Red 2030 (weak)	Red 2030
	Yellow GR	virgin	Virgin
	Yellow HG	Yellow GR	Yellow GR
	Paliotol yellow K0961	Yellow HG	Yellow HG
		Paliotol yellow K0961	Paliotol yellow K0961

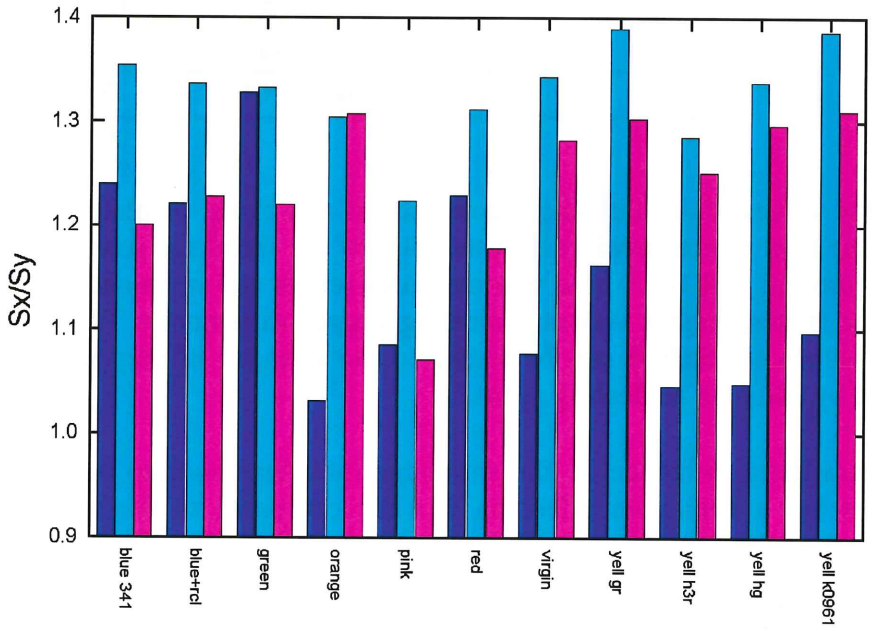


Figure 12: The ratio Sx/Sy| varies with different pigment types and increases in the presence of nucleating agents.
■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

Figure 12 shows that differences in the shrinkage ratio between different pigments can be 'smoothed out' by adding small amounts of an appropriate nucleating agent. The dependence of the shrinkage ratio on different types and concentrations of nucleating agent shown in Figure 13 mirrors the behaviour of the perpendicular shrinkage (figure 9).

- The shrinkage ratio is much more sensitive to the type of nucleating agent present rather than its concentration.

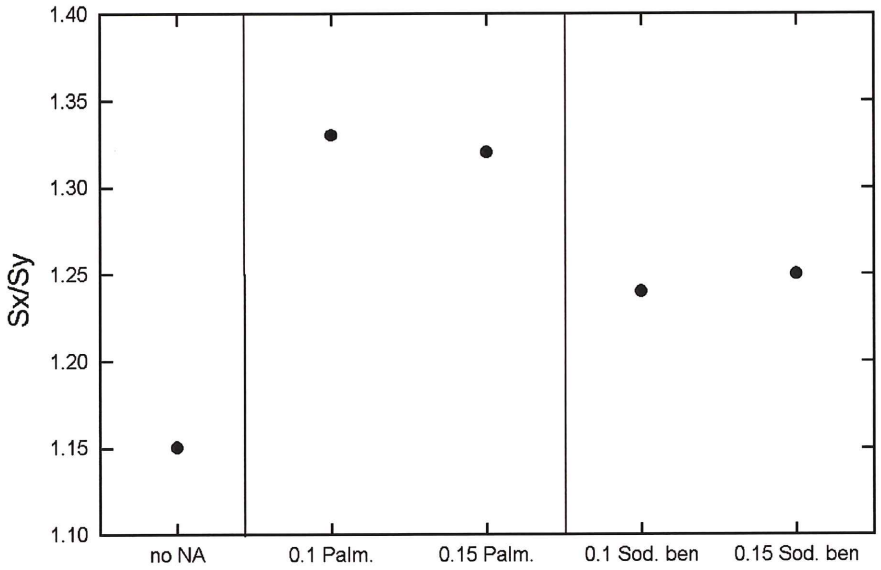


Figure 13: The addition of nucleating agents significantly increases the ratio of the shrinkage scores of the polypropylene plates irrespective of their colour.

The angle scores shown in Figure 14 show that polypropylene plate mouldings containing chromopthal orange or yellow H3r are almost square. These low angle scores reflect similar shrinkages obtained parallel and perpendicular to the flow direction.

- Adding palmerol substantially increases the angle scores of all the pigmented feedstocks including the virgin material i.e. the plate becomes less square.

This effect is due to the increased perpendicular shrinkage that occurs in nucleated feedstocks (Figure 10).

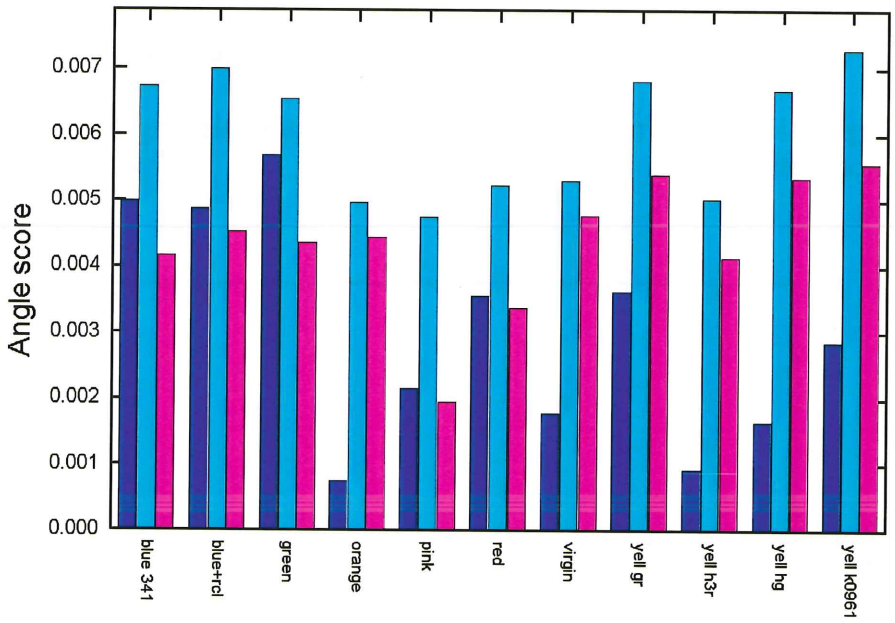


Figure 14: Angular distortion depends on the type of pigment present and significantly increases in the presence of nucleating agent 1.
■ = non-nucleated, ■ = Palmerol, ■ = Sodium Benzoate

4.4 CALORIMETRY

Figure 15 shows how the crystallization behaviour of polypropylene containing 0.1wt% red 2030 is affected by both palmerol and sodium benzoate at different concentrations. Red 2030 increases the crystallization temperature of polypropylene by approximately 10°C but is unaffected by adding sodium benzoate at concentrations of up to 0.15 wt%. Adding palmerol to polypropylene containing red 2030 results in an upward shift of the crystallization temperature of approximately 6°C that is also insensitive to the amount of palmerol present. These results suggest that red 2030 is acting as a nucleating agent but that palmerol is more effective at inducing crystallization. Similar patterns of behaviour can be seen in Figure 16 for virgin polypropylene and polypropylene containing blue 341.

The influence of different pigments on the crystallization behaviour of polypropylene can be seen in Figure 17.

- The addition of any pigment to the base material increases the crystallization temperature by 2 to 18 °C.

- Adding titanium dioxide to polypropylene containing blue 341 (blue 341 + rcl) has no effect on the crystallization temperature of the mixture.

Variations in crystallization behaviour do not appear to be related to any of the measures used to assess dimensional instability either due to different pigments or nucleating agents.

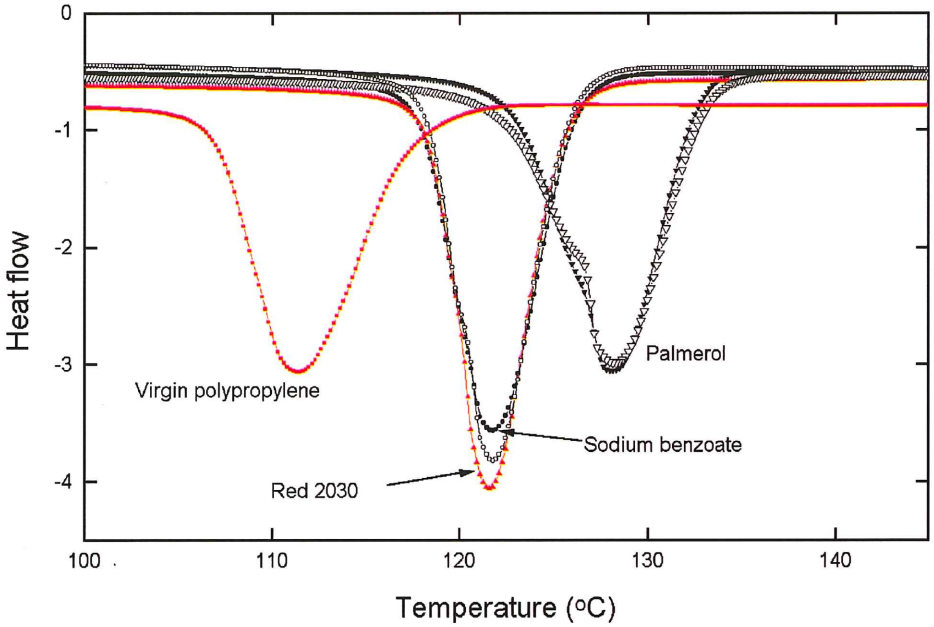


Figure 15: Polypropylene containing red 2030 crystallizes some 10°C higher than virgin material but in unaffected by the presence of sodium benzoate (❍ = 0.1 wt%, ● = 0.15 wt%). Adding palmerol increases the crystallization temperature which is insensitive to its concentration (▽ = 0.1 wt%, ▼ = 0.15% wt%).

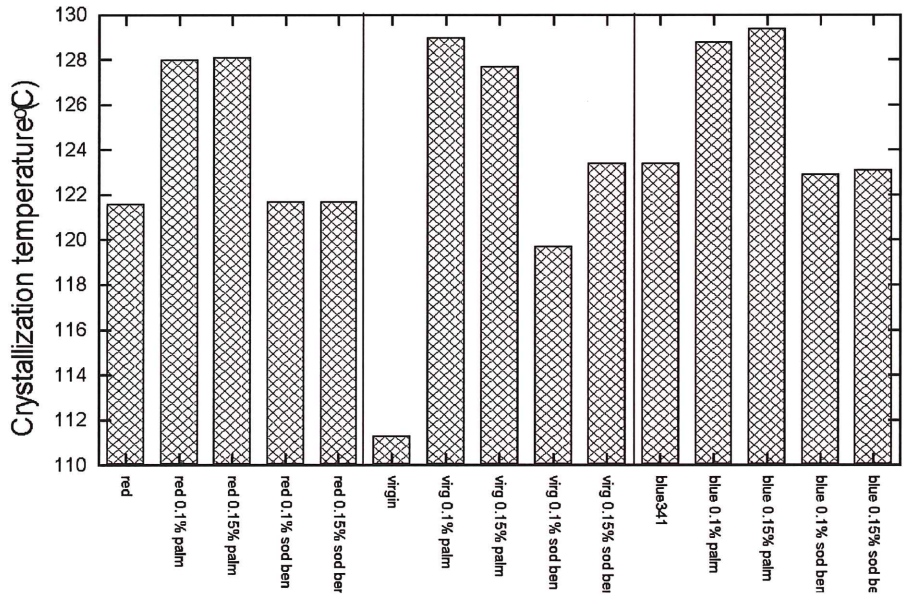


Figure 16: The crystallization temperature of polypropylene is sensitive to the type of pigment and nucleating agent present. It is independent of the concentration of nucleating agent.

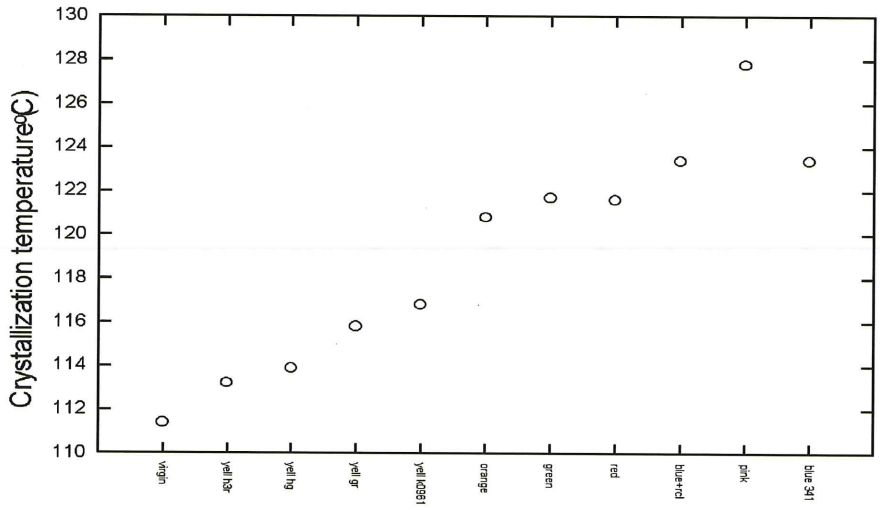


Figure 17: The addition of any of the ten pigments considered in this investigation increases the crystallization temperature of virgin polypropylene.

5 CONCLUSIONS

The dimensional stability of injection moulded polypropylene plates coloured with different pigments can be assessed via measurements of shrinkage, in- or out-of-plane warpage and weight. The results show a complex relationship between different pigments and these measures, for example, pigments that minimise out-of-plane distortion can induce high levels of in-plane distortion compared with non-pigmented feedstock. These variations in dimensional stability appear to be unrelated to the nucleating capabilities of the pigments ranked according to crystallization temperature.

The effect of adding nucleating agents to differently coloured polypropylene feedstocks can have a significant influence on dimensional stability of mouldings. The magnitude of the effect depends on the type of nucleating agent, its concentration, the type of pigment and which aspect of dimensional instability is being considered. There is no obvious link between any of the measures of dimensional instability and the crystallization behaviour of pigmented mixtures doped with nucleating agents with the possible exception of perpendicular shrinkage.

Despite these complications this investigation has shown that it is possible to alter the dimensional stability of differently pigmented feedstocks by adding appropriate nucleating agents. This offers the possibility of controlling the distortion of coloured mouldings so that the resultant products are within a customers specification without compromising cycle times.

- The out-of-plane plate warpage (RW_z) is strongly dependent on the type of pigment present in the polypropylene feedstock and less sensitive to the presence of nucleating agents.
- The effect on the dimensional stability of a plate moulding of adding a nucleating agent to the feedstock is different for different pigments.
- Adding a nucleating agent to pigmented polypropylene can significantly reduce in-plane warpage.

- Sodium benzoate appears to be more effective at reducing in-plane distortion than palmerol.
- More in-plane warpage occurs parallel to the flow direction than perpendicular to it.
- Parallel in-plane warpage is relatively independent of pigment type.
- Adding nucleating agents can substantially reduce the amount of in-plane warpage compared to that non-nucleated mixtures and can be used to balance in-plane parallel and perpendicular warpage of differently coloured feedstocks.
- Differences in the shrinkage ratio that exists between pigments can be significantly reduced by adding small amounts of an appropriate nucleating agent.
- The shrinkage ratio is much more sensitive to the type of nucleating agent present than its concentration.
- Adding palmerol substantially increases the angle scores of all the pigmented feedstocks including the virgin material i.e. the plate becomes less square.
- The addition of any pigment to the base material increases the crystallization temperature over the range of approximately 2 to 18°C.
- Adding titanium dioxide to polypropylene containing blue 341 (blue 341 + rcl) has no effect on the crystallization temperature of the mixture.
- Variations in crystallization behaviour do not appear to be related to any of the measures used to assess dimensional instability either due to different pigments or nucleating agents.

A graphical summary of the relationships between different pigments and measures of dimensional instability can be found in Appendix 2.

6 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Dr Colin Forno for Moire interferometry measurements of the plates and Mr Crispin Allen for carrying out calorimetry measurements. We would also like to thank Mr S Daniels of Victor International Plastics Ltd for providing the masterbatch samples and Ultratools for modifying the mould tool. The scoring system for assessing dimensional instability was originally derived by Dr Bernard Butler and Dr Gabriel Lord.

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7 REFERENCES

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APPENDIX 1: MEASURING AND ASSESSING SHRINKAGE AND WARPAGE

The amount of shrinkage that occurs in the square plate moulding can be easily assessed by comparing the measured lengths and breadths with those of the mould cavity itself. The amount of shrinkage that occurs along the length or breadth of the plate varies with position. Averaging the data to compare the shrinkage behaviour of a number of different plates can, by smoothing out these variations, very effectively mask any differences that might exist. This issue can be overcome by using a scoring system that not only considers average values but also the spread of data. This approach is summarized briefly below, a more detailed description can be found in reference 3.

In-plane shrinkage may be accompanied by in-plane warpage which distorts the shape of the plate without affecting its dimensions. The effects of in-plane warpage can again be calculated from measurements of the length and breadth of each plate.

Out-of-plane warpage requires 3-dimensional coordinates for each plate. These data can be obtained relatively quickly by using shadow Moire interferometry. In the technique a shadow from a grating (with a 2mm pitch) is projected on to the surface of a plate. Interference between the reflected shadow and the grid itself produces a pattern that can be captured using a camera and stored on a computer. A thin layer of matt finish white paint was sprayed on to the surface of each plate to increase its opacity and hence the intensity of the interference pattern. The 3-dimensional coordinates are obtained by unwrapping the phase information contained within the pattern of interference fringes. This operation was performed by the software package Fringe Application V3.20. The dimensionless 'optical units' were converted into SI units by scaling the data to length and breadth data obtained by measuring each plate at 5 equidistantly spaced points using vernier callipers in the XY direction. He out-of-plane data was converted to SI units by calculating the distance between two adjacent fringes to be 1.8mm.

A1 DETERMINATION OF SHRINKAGE

Shrinkage is defined as the ratio between the measured distance between any two points on opposite edges of a moulding and that measured at the same point inside the mould cavity. Obviously this procedure is inappropriate for plates that are subject to significant out-of-plane deformation. To overcome this limitation we determine the arc length between points located on opposite edges of the plate.

A 3-dimensional surface is used to fit the coordinates obtained from the phase unwrapped Moire interferometry data. Using this surface the arc length, **a** can be calculated between any two points on opposite edges of a plate according to:

$$a_{\parallel}(x_k, y, z) = \int_{\tilde{e}_2}^{\tilde{e}_4} \sqrt{1 + \left(\frac{\partial f(x_k, y, z)}{\partial y}\right)^2}\, dy \qquad (1)$$

$$a_{\perp}(x, y_k, z) = \int_{\tilde{e}_1}^{\tilde{e}_3} \sqrt{1 + \left(\frac{\partial f(x, y_k, z)}{\partial x}\right)^2}\, dx \qquad (2)$$

f(x,y,z) denotes the polynomial or spline function used to fit the z (out-of-plane) co-ordinates. The subscripts // and ⊥ refer to directions parallel and perpendicular to that of the flow. This is shown schematically in Figure A1 where the edges e_1 to e_4 are defined.

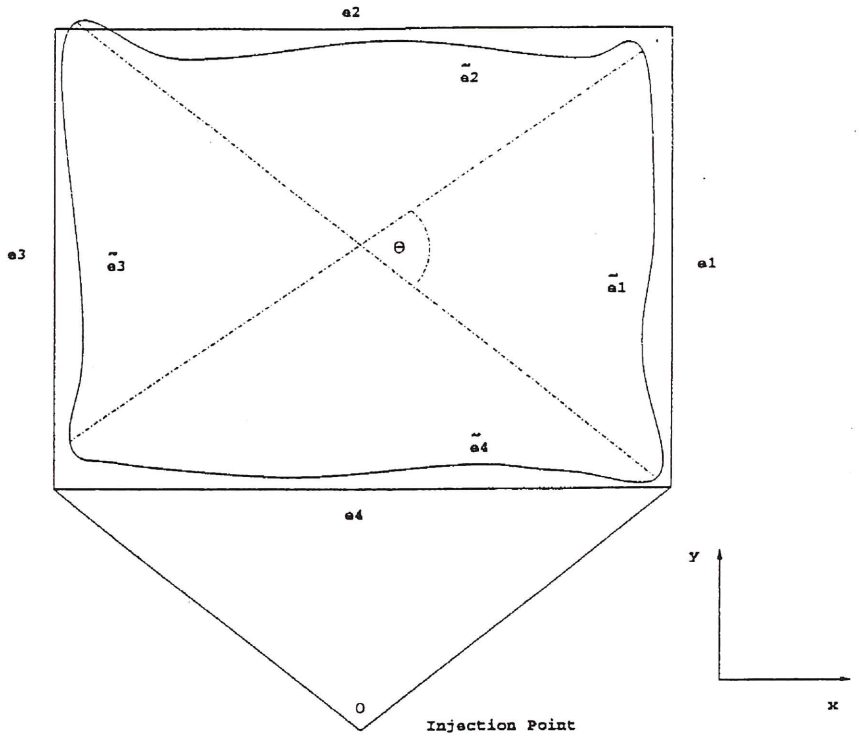


Figure A1: A comparison of the projections of the undeformed plate with edges e_1, e_2, e_3 and e_4 and a deformed plate with edges $\bullet_1$, $\bullet_2$, $\bullet_3$ and $\bullet_4$ on to the xy plane

The shrinkage at any location in x or y is then generated by substituting the arc length, for example $a_\perp$ for $|\tilde{e}_1(x,y_k,z)-\tilde{e}_3(x,y_k,z)|$, into the following equation:

$$s_{\perp,k}=\frac{|e_1(x,y_k,z)-e_3(x,y_k,z)|-|\tilde{e}_1(x,y_k,z)-\tilde{e}_3(x,y_k,z)|}{|e_1(x,y_k,z)-e_3(x,y_k,z)|} \qquad (3)$$

$e_1(x,y_k,z)$ is the k^{th} point on edge 1 of an undeformed plate and $\tilde{e}_1(x,y_k,z)$ is the corresponding point on the equivalent deformed edge. Equation (3) can also be used to calculate the plate shrinkage that occurs parallel to the flow direction by substitution of the data relating to edges 2 and 4. Unfortunately this method of evaluating shrinkage has its limitations. It is not possible to compute the true shrinkage between the physical edges of each plate for every pair of corresponding edge points because of discontinuities that can arise in the path of the integrals in equations 1 and 2 if the outermost edges bow in towards the centre. This is shown schematically for equation 2 in Figure A2. In all cases the same coordinate frame was used for deformed plates as that used to describe the mould cavity and the flow direction is parallel to 'y'.

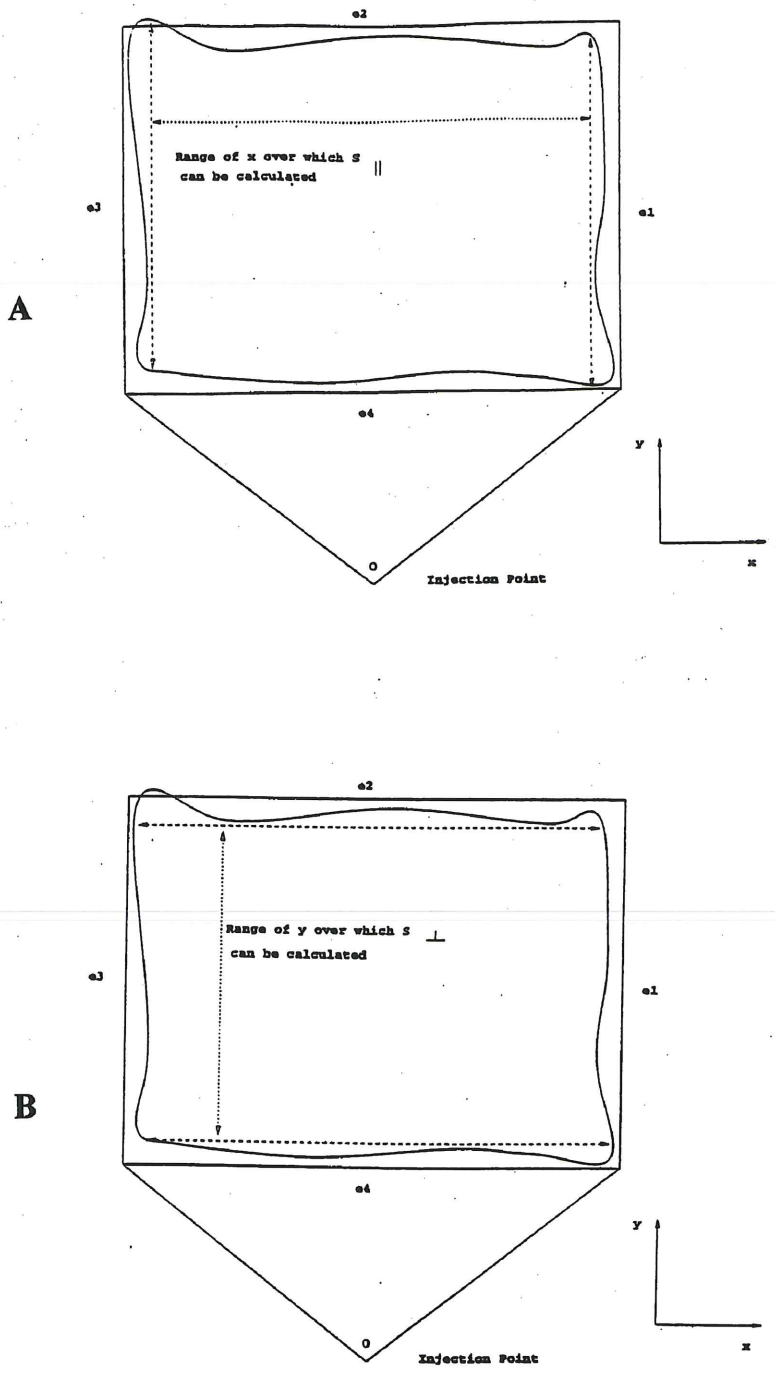


Figure A2: (A) Equation (1) can be used to compute the shrinkage parallel to the direction of flow between the dashed line boundaries.
(B) Equation (2) can be used to compute the shrinkage perpendicular to the flow direction between the dashed boundaries.

A2 SHRINKAGE SCORES

The shrinkage across the plate in either direction depends on where it is measured, for example, shrinkages perpendicular to the flow direction tends to increase with increasing distance from the gate. Because of this variation along an axis it is difficult to compare

shrinkages measured in different plates unless it is done on a point by point basis. This cumbersome approach can be avoided by defining a shrinkage score. Here the mean and range of shrinkages are calculated in directions both parallel and perpendicular to that of the flow i.e.

$$\text{Mean } S_{\perp} = \text{mean}_k(s_{\perp,k}), R_{\perp} = \text{range}_k(s_{\perp,k}) \tag{4}$$

and

$$\text{Mean } S_{\parallel} = \text{mean}_k(s_{\parallel,k}), R_{\parallel} = \text{range}_k(s_{\parallel,k}), \tag{5}$$

The shrinkage range, R is defined as the difference between the maximum and minimum shrinkage values.

An overall measure of plate shrinkage can be obtained by combining the mean and range of shrinkage following:

$$S_{\parallel} = (\text{mean}\, S_{\parallel} + R_{\parallel}) / 2 \tag{6}$$

and

$$S_{\perp} = (\text{mean}S_{\perp} + R_{\perp}) / 2 . \tag{7}$$

A3 DETERMINATION OF WARPAGE

Warpage can occur both in-plane and out-of-plane. In-plane warpage occurs when parallelism between two opposite edges is lost despite the distance between them remaining constant. In-plane warpage can occur in directions both parallel to and perpendicular to that of the flow. The in-plane warpage for edges 1 and 2 are given by;

$$W_{\perp}(e_1) = \text{mean}_k\left(\frac{\tilde{e}_1(x, y_k, z)}{|e_1|}\right), \quad R(W_{\perp}(e_1)) = \text{range}_k\left(\frac{\tilde{e}_1(x, y_k, z)}{|e_1|}\right) \tag{8}$$

and

$$W_{\parallel}(e_2) = \text{mean}_k\left(\frac{\tilde{e}_2(x_k, y, z)}{|e_2|}\right), R(W_{\parallel}(e_2)) = \text{range}_k\left(\frac{\tilde{e}_2(x_k, y, z)}{|e_2|}\right) \tag{9}$$

where '~' denotes the deformed edge and $|e_i|$ the length of the undeformed edge e_i. Functions for edges 3 and 4 are obtained by substituting e_3 for e_1 and e_4 for e_2 respectively.

The range of out-of-plane warpage is given by;

$$R(W_z) = \text{range}_k(z_k) \tag{10}$$

where $z_k = f(x_k, y_k, z_k)$ is the fitted algebraic surface at points x_k and y_k. Out-of-plane warpages, $R(W_{ei})$ for each of the plate edges were defined in a similar manner restricting f to the relevant edge data.

As significant amounts of information are lost by calculating the mean out-of-plane warpage we have chosen only to consider the range of deformation. This method is equivalent to measuring the vertical distance between any two opposite edges of a warped plate.

A4 WARPAGE SCORES

The in-plane warpage at each point along each edge can be combined to give single measure of the mean and range of in-plane warpage e.g.

$$W_{\perp} = \left\| \left[W_{\perp}(e_1) - W_{\perp}(e_3) \right] \right\| \tag{11}$$

and

$$R(W_{\perp}) = \left[R(W_{\perp}(e_1)) + R(W_{\perp}(e_3)) \right] / 2 . \tag{12}$$

This procedure can be applied to warpage data obtained in a direction parallel to that of the flow.

An overall measure of in-plane warpage can be obtained by combining the mean and range following;

$$\text{Warpage } W_{\perp} = \left(W_{\perp} + R(W_{\perp}) \right) / 2 \tag{13}$$

and

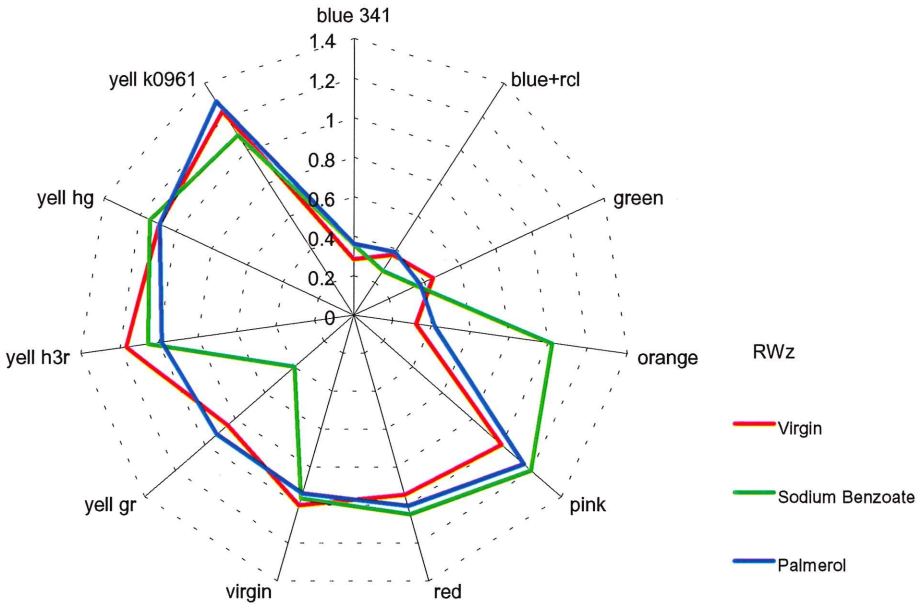
$$\text{Warpage } W_{\parallel} = (W_{\parallel} + R(W_{\parallel})) / 2 . \tag{14}$$

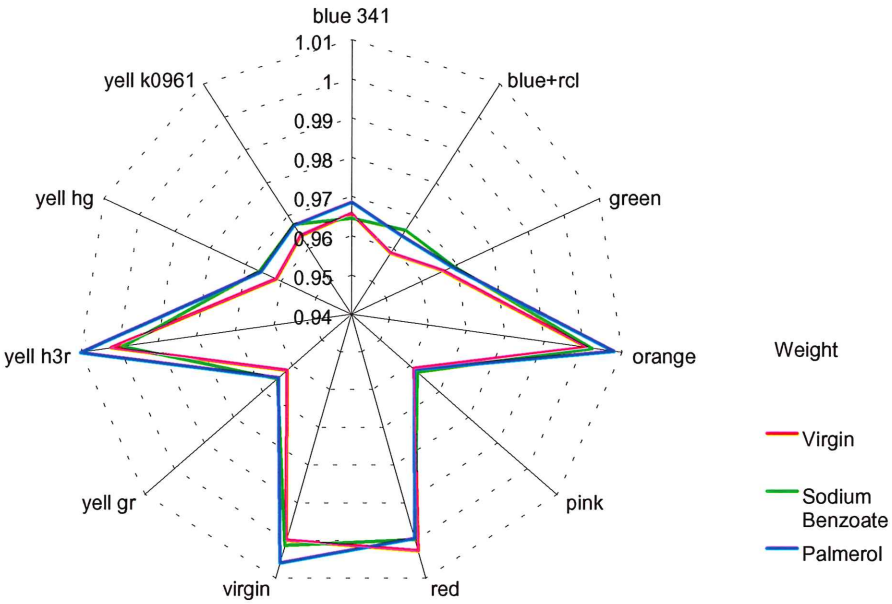
A5 ANGLE SCORES

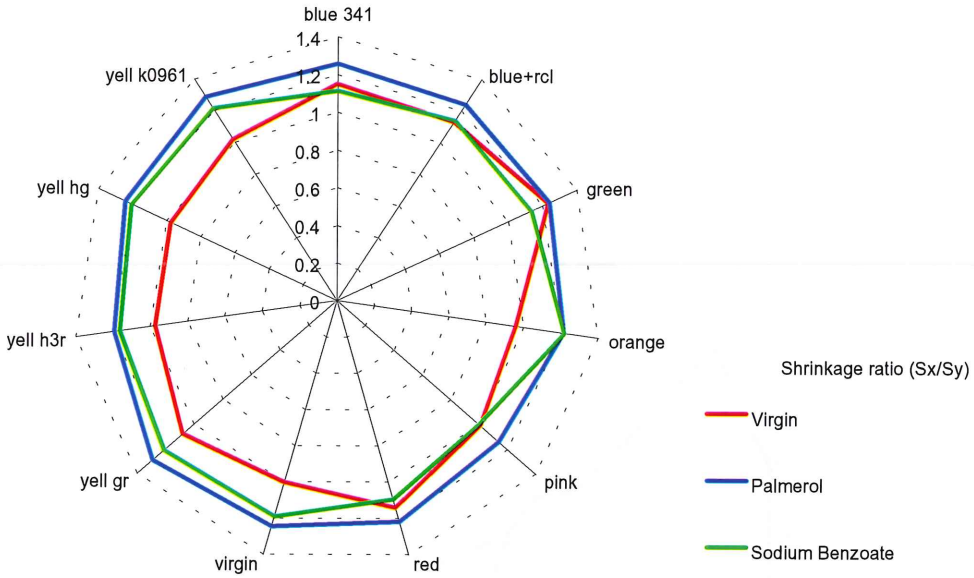
Changes in the angle formed at the intersection of the diagonals of the square plate moulding can be used as a measure of distortion. In an undeformed square plate this angle is given by $\theta(L_{\perp}, L_{\parallel})$. Since $L_{\perp} = L_{\parallel}$ then $\theta = \pi/2$ and so $\cos(\theta) = 0$. The mean x and y values for the four edges of the plate are given by $M(W_{\parallel})$ and $M(W_{\perp})$. Taking the dot product of the vectors formed by these vertices and normalizing yields the cosine of the angle θ of the deformed plate, as illustrated in Figure A2. This cosine is then taken as the angle score.

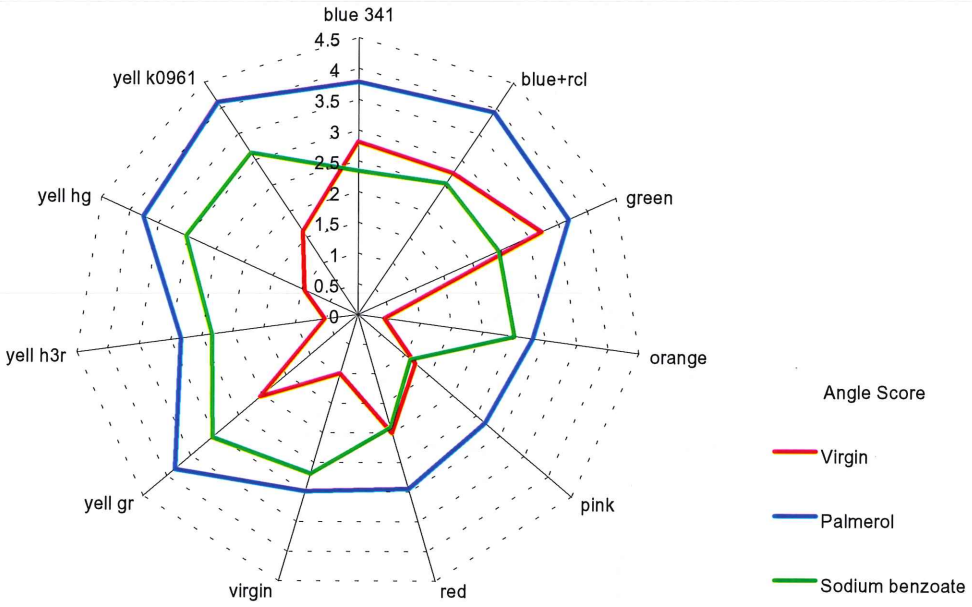
APPENDIX 2: SUMMARY OF DIMENSIONAL INSTABILITY DATA

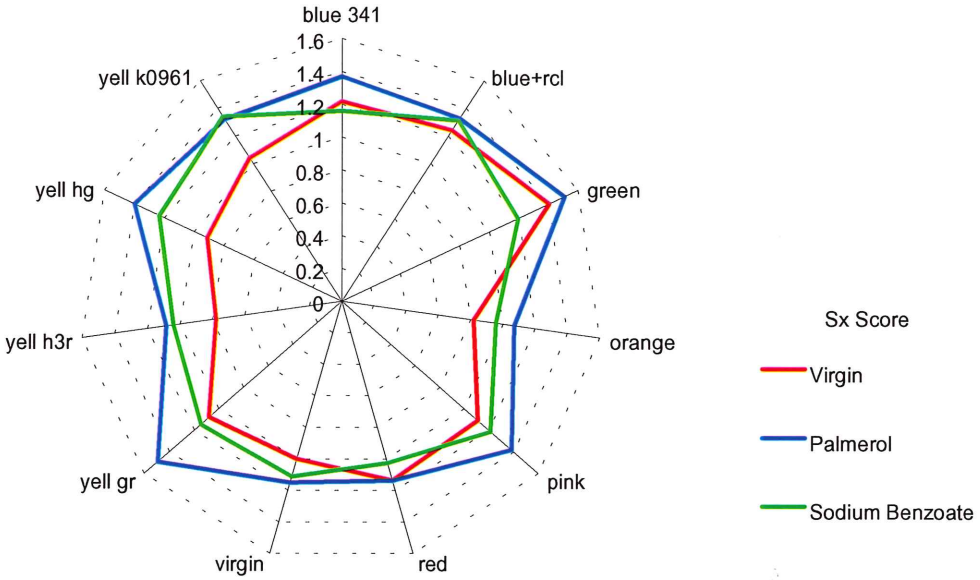
The radar plots on the following pages provide a summary of all the parameters used to assess dimensional instability. Each measure has been compared to that of non-pigmented, non-nucleated virgin feedstock.

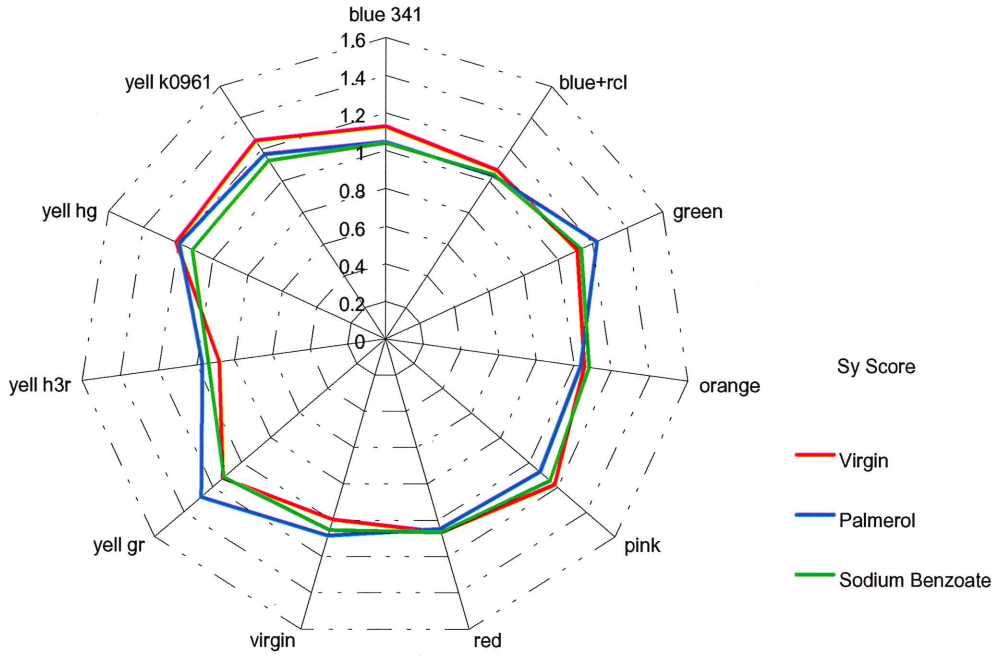


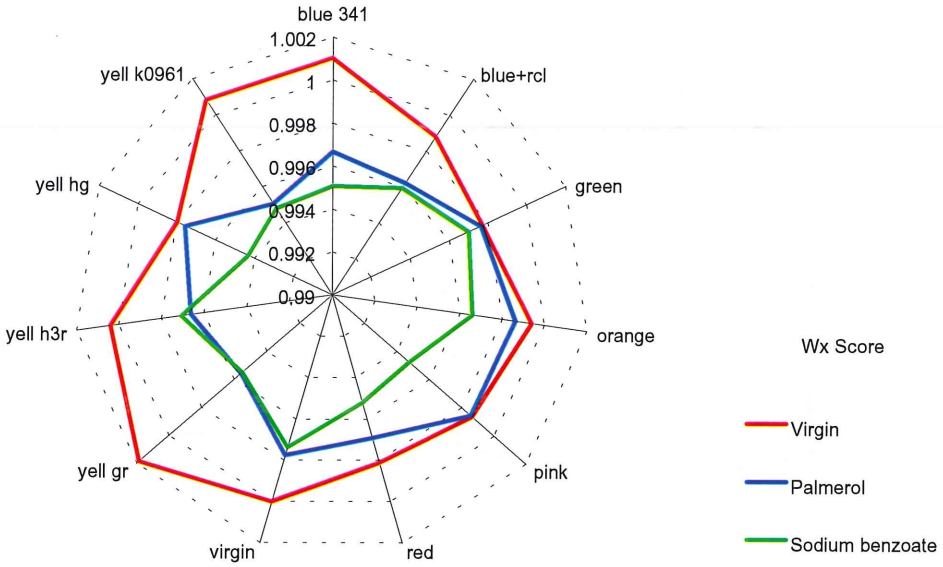


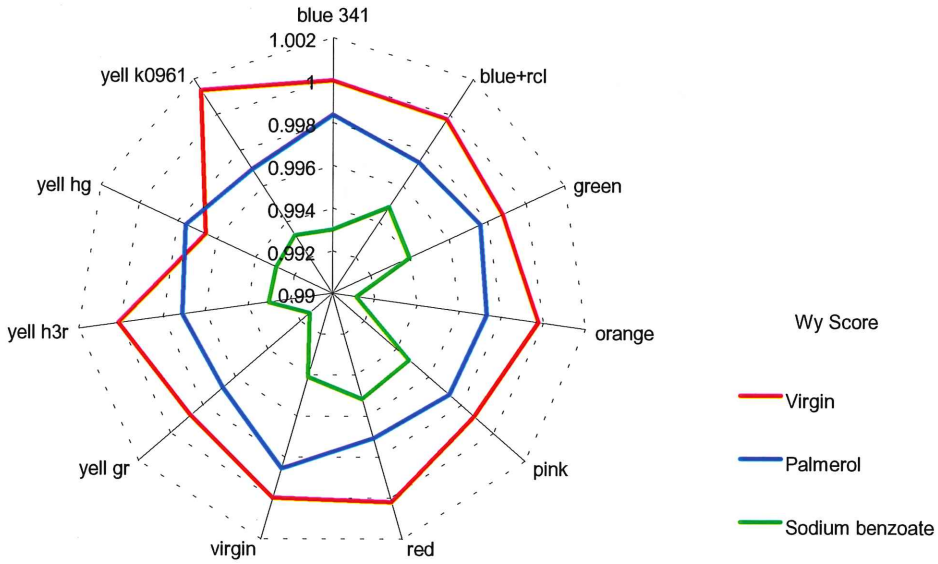

blue 341
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Shrinkage ratio (Sx/Sy)
Virgin
Palmerol
Sodium Benzoate


blue 341
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Angle Score
Virgin
Palmerol
Sodium benzoate


blue 341
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Sx Score
Virgin
Palmerol
Sodium Benzoate


blue 341
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Sy Score
Virgin
Palmerol
Sodium Benzoate


blue 341
1.002
1
0.998
0.996
0.994
0.992
0.99
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
Wx Score
Virgin
Palmerol
Sodium benzoate


blue 341
1.002
1
0.998
0.996
0.994
0.992
0.99
blue+rcl
green
orange
pink
red
virgin
yell gr
yell h3r
yell hg
yell k0961
Wy Score
Virgin
Palmerol
Sodium benzoate