

REPORT

The Influence of Shear History on the Crystallization Behaviour of Talc Filled Polypropylenes

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ABSTRACT

Unexpected problems of shrinkage and warpage can occur when organic pigments are added to feedstocks to change the colour of moulded parts. This is particularly true for polyolefins coloured with blue or green phthalocyanines. We have shown that this can, at least in part, be related to changes in the crystallization behaviour of these materials that occur because of these pigments even in the presence of a second nucleating agent - talc. As these data were obtained using quiescent samples contained within a calorimeter they may not be representative of the dynamics of crystallization that occur during the cooling phase of injection moulding. In this study we explore the influence that phthalocyanine blue has on the crystallization behaviour of unfilled and talc filled polypropylene melts. These data have been derived from measurements of the temperature dependent viscosities of melts cooled whilst being oscillated or continuously sheared in a rotational rheometer.

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1 INTRODUCTION

Copper phthalocyanine blue (C.I. blue 15:3), because of its vibrant blue colour and excellent resistance to ageing, thermal degradation, acids and alkalis, is extensively used throughout the moulding industry as a colourant¹. The relatively low cost of this material adds to its attractiveness as a pigment, although it does have a reputation for causing unacceptable levels of shrinkage and warpage in articles moulded from polyolefins^{2,3}. The reason why this particular family of pigments cause excessive warpage or shrinkage in polyolefins is unclear. Recent work has shown that the presence of the pigment in both polypropylene and high density polyethylene has a substantial influence on the morphology of these materials^{4,5,6}. Addition of small amounts of pigment, i.e. 0.1 wt% is sufficient to reduce the size of spherulites by an order of magnitude and to significantly increase their number^{5,6}. These results suggest that the pigment is behaving as a nucleating agent, a finding that has been confirmed by studies of crystallization kinetics⁶. Calorimetric measurements have shown that the onset of crystallization occurs some 16 °C higher in polypropylene containing 0.1 wt% phthalocyanine blue than for non-pigmented material during controlled cooling of a melt. In this material the overall level of crystallinity was unaffected by the presence of the pigment although the morphology of the spherulites changed from 2-D discs in the virgin material to 3-D spheres.

A significant proportion of the published literature on the use of fillers to improve the properties of thermoplastics is concerned with talc (hydrated magnesium silicate). This material, when added to materials such as polypropylene, improves Young's modulus, flexural strength and creep resistance⁷⁻¹⁰ but reduces notched impact performance¹¹. However the latter property can be restored by coating the talc particles with materials such as phosphate^{11,12}. The effect that different fillers have on the mechanical performance of the matrix material may be a reflection of their size, shape, modulus or concentration. Alternatively, changes in performance may reflect differences in the micromorphology of the matrix polymer that occur because of adding the filler. It is known that the fracture properties of filled polypropylene are affected both by spherulite size¹³ and changes in the skin - core ratio that are attributable to differences in processing¹⁴.

Whilst valuable information concerning the kinetics of crystallization can be obtained from calorimetry, it must be recognised that this situation is not representative of materials behaviour during processing. During the mould filling phase of injection moulding the melt is often subjected to shear strain rates in excess of 1000 s⁻¹. These high rates are usually encountered as the melt flows through the sprue, runner and gate system although they can occur as it flows through thinner cross-sections of the cavity. Shearing the melt induces the polymer chains to elongate. Lower levels of chain elongation can facilitate crystallization. This phenomenon is referred to as strain induced crystallization (SIC). SIC can result not only in the material crystallizing at higher temperatures than expected^{15,16,17} but can also affect the mechanical properties of mouldings^{18,19,20}.

In this paper we assess the influence that small shear strains and or shear rates have on the crystallization behaviour of both pigmented and non-pigmented talc filled polypropylene where the concentration of talc varies from 10 wt% to 40 wt%.

2 EXPERIMENTAL

2.1 MATERIALS AND SAMPLE PREPARATION

Samples of talc filled isotactic polypropylene were kindly supplied by Hellyar Plastics either as an non-pigmented pelletised extrudate or one containing 0.2 wt% phthalocyanine blue. These mixtures of polypropylene (Montell XS6500S) containing 10, 20 or 40 wt% talc (Osmanthus) were prepared by twin-screw extrusion at a set temperature of 215 °C. The phthalocyanine blue was a Ciba Speciality Chemicals product, irgalite blue 4GNP. The polypropylene was intimately mixed with the talc and pigment at the levels required without the aid of processing additives. This blend was then processed through a 19 mm twin-screw extruder and pelletised. The melt temperature was measured at 228 °C.

2.2 STEADY SHEAR AND OSCILLATORY RHEOMETRY

A cone and plate rheometer consists of a shallow angled, truncated cone that sits above the surface of a flat plate such that the virtual apex of the cone intercepts the surface of the plate as shown in Figure 1.

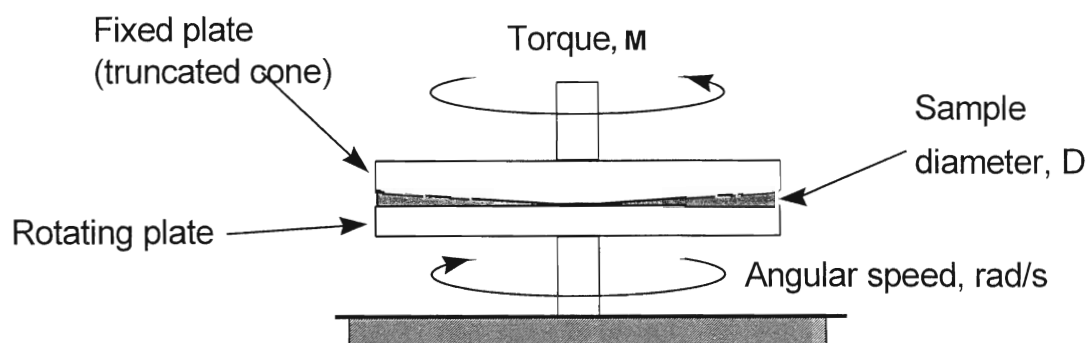


Figure 1: The sample is sandwiched between a fixed cone and a rotating plate in the cone and plate rheometer.

During operation the lower plate is continuously rotated at constant speed subjecting the sample sandwiched between the plates to a constant shear strain rate. The viscosity of the melt is derived from measurements of the torque generated on the upper cone and the angular speed of the lower plate. The advantage of using a cone and plate geometry to measure the temperature dependent viscosity is that the sample is subjected to a constant shear strain rate as it is cooled.

In this study a 25 mm diameter cone and plate geometry was used in a Bohlin VORM rheometer. The angle of the cone was 5.44°. The cone, sample and plate assembly is contained within a small furnace, the temperature of which is

controlled by forced air circulation. The temperature of the melt was assumed to be the same as that of a calibrated thermocouple mounted within the cone geometry.

Typically, the cone and plate geometry is used to obtain information relating to the time dependent viscous behaviour of viscoelastic materials. Additional information relating to the elastic component of viscoelastic materials can be obtained by measuring the properties of melts subjected to an oscillatory strain using parallel plates set 1 mm apart. The crystallization temperatures obtained from oscillatory measurements should in principal be closer to those measured by calorimetry since the net molecular orientation is effectively zero.

2.3 PRACTICAL DETAILS

Disc samples 25 mm in diameter were manufactured within the rheometer by melting granules of material placed between the cone and plate which was maintained at a temperature of 190 °C. During melting the distance between the cone and plate was reduced until the truncated virtual apex of the cone made contact with the plate. The thickness of the sample at the edge of the plate was ~ 1.2 mm. Samples were allowed to anneal at this high temperature for a period of at least five minutes prior to testing. After ensuring that all traces of any previous thermal history had been erased by the annealing period the samples were cooled at rates of either 1 °C min⁻¹ or 5 °C min⁻¹ either under continuous or oscillatory shear. Runs were terminated when the torque limit of the rheometer was reached that, depending on the shear rate, typically occurred when the viscosity exceeded 2 x 10⁶ Pa. s.

Checks were made to assess the thermal stability of the materials by monitoring the viscosity, in oscillation, at the annealing temperature for periods in excess of 90 minutes. Plots of viscosity as a function of time at constant temperature showed that the samples were thermally stable. This period of measurement, i.e. 90 minutes, is in excess of that required for data collection: all the tests were complete within a timescale of less than 60 minutes.

2.3.1 Shear rates attainable

Melts are exposed to much higher shear rates during injection moulding than are attainable using a cone and plate rheometer of the type used in this study. In practice the upper limit for continuous shear in a cone and plate rheometer is defined as that at which the melt is not expelled from between the discs. In this study this maximum is approximately 1.3 s⁻¹. To explore the influence of shear rate on crystallization behaviour a lower value of approximately 0.13 s⁻¹ was used.

The maximum strain imposed on the melt during successive oscillations using the parallel plate geometry was 0.10 %. This strain is that measured at the outer rim of the plates.

2.3.2 Determination of a crystallization temperature

Figure 1 shows a plot of log viscosity against temperature for a polypropylene melt containing 10 wt% talc cooled at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$ whilst being sheared at a rate of 0.127 s^{-1} . From this plot it is evident that there is a linear relationship between log viscosity and temperature that breaks down as the material begins to crystallize. A measure of the crystallization temperature can be obtained from the intersection of two lines drawn through regions where the material is molten and semi-solid respectively as shown in the figure.

The estimated experimental error in the crystallization temperatures based on repeat measurements is $\pm 0.4\text{ }^{\circ}\text{C}$.

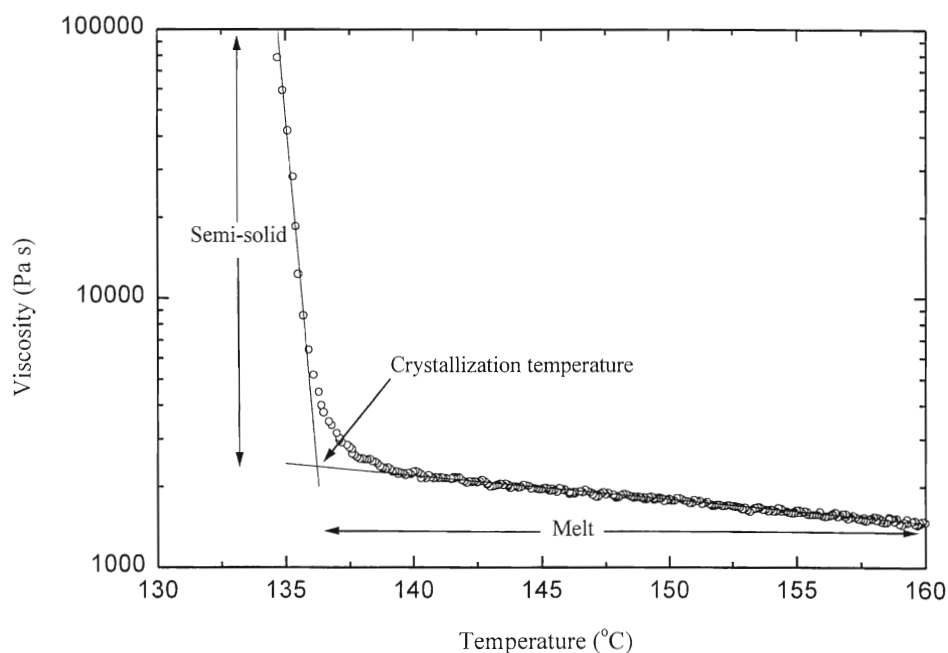


Figure 1. A measure of the crystallization temperature of a melt can be obtained from the intersection of two lines drawn through regions of the plot where the material is molten and 'semi-solid'. The example shown represents a sample containing 10 wt% talc which was continuously sheared at a rate of 0.127 s^{-1} whilst being cooled at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

3 RESULTS AND DISCUSSION

3.1 THE INFLUENCE OF SHEAR ON CRYSTALLIZATION BEHAVIOUR

3.1.1 Continuous shear

Figure 2 shows the melt viscosity of the molten material increases with increasing talc concentration, as expected. Adding talc to polypropylene increases the temperature at which the matrix material crystallizes. Whilst 10 wt% talc raises the crystallization temperature by almost 13 °C (Table 1), increasing the talc concentration to 40 wt% results in only an additional 4.5 °C rise in crystallization temperature. These results are in excellent agreement with those obtained by differential scanning calorimetry (DSC)^{21,22,23}. Such changes in crystallization temperature have been associated with differences in mechanical performance^{12,24,25}.

Figure 3 shows how the crystallization behaviour of talc filled polypropylene changes due to the presence of pigment (0.2 wt% phthalocyanine blue). The addition of 0.2 wt% pigment to a 10 wt% talc filled polypropylene raises its melt crystallization temperature by some 2 °C (Table 1) but has less effect on the behaviour of the 40 wt% filled material (~ 0.6 °C). These results broadly agree with those obtained by using calorimetry²¹. The increased insensitivity of the non-isothermal crystallization temperature to increasing amounts of talc implies that the system is reaching a limiting nucleation rate. This phenomenon has been observed previously^{26,27,28} although earlier reports²⁷ show that the saturation point is reached at talc concentrations around 5 wt%.

Nucleating particles function through their ability to orientate polymer chains on their surfaces, thus initiating the formation of crystals. Diffraction studies have shown that the preferential orientation of polypropylene on talc particles has a maximum value when doped with 10 wt% talc²⁹. The efficiency of talc as a nucleating agent decreases²⁹ as its concentration is increased from 10 wt% to 40 wt%. The results here suggest that there is some capacity for individual nucleation sites within the polypropylene matrix when the concentration of talc is less than 40 wt% that can be provided by phthalocyanine blue pigment particles.

Scanning electron microscopy observations suggest that the efficacy of talc as a nucleating agent decreases at concentrations in excess of 30 wt% because of aggregation in quiescent melts²⁹. In contrast we would expect these particulate agglomerates to rapidly disperse in melts that are continuously sheared during cooling. The similarity of the results obtained here and those reported for quiescent melts suggest that interpretations based on poor dispersal of platelets at high levels of talc may be flawed. This of course presumes that the shear stresses within the melt are sufficient to disperse the agglomerates.

Increasing the shear rate by a factor of ten to 1.27 s⁻¹ has no significant effect on the crystallization behaviour of both virgin and talc filled materials. This is illustrated in Figure 4 which shows that the crystallization temperatures are

essentially independent of the rate of shear within experimental error and the range of rates used.

There has been some debate within the literature over the amount of shear strain that is required to produce homogenous molecular orientation. The amount of molecular orientation that can be achieved in response to a particular shear strain depends on the viscosity of the melt, the degree of molecular entanglement and the sample thickness. It has been suggested that measurements that are intended to establish links between molecular orientation and a phenomenon such as crystallization should only be carried out on materials that have been intensively pre-sheared³⁰. This 'pre-shearing' should be carried out at high temperatures. Its function is to 'comb' all of the knots out of the melt i.e. disentangle molecular entanglements. However such highly oriented melts are un-representative of those encountered in practical moulding processes.

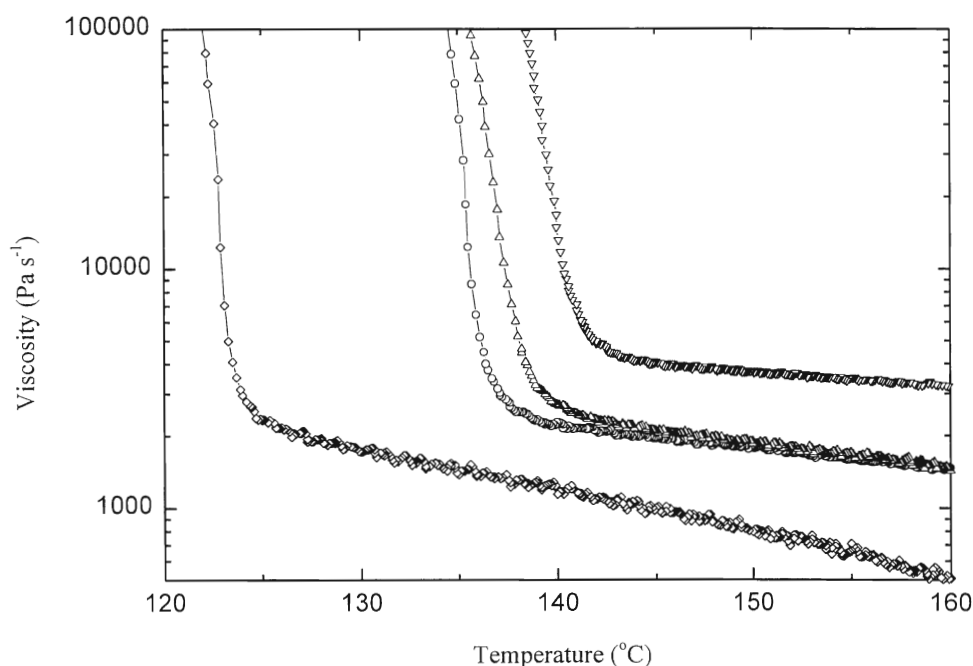


Figure 2. The effect of increasing talc concentration on the crystallization behaviour of polypropylene at the following talc concentrations: $\diamond = 0$ wt%, $\circ = 10$ wt%, $\triangle = 20$ wt%, $\nabla = 40$ wt%. These data were obtained from melts continually sheared at a rate of 0.127 s^{-1} during cooling at a rate of $5 \text{ }^{\circ}\text{C min}^{-1}$.

3.2.2 Oscillatory shear

The results obtained from cooling melts whilst subjecting them to an oscillatory strain of 0.10 are shown in Figure 5 together with those derived from continuous shear data. There is a small difference in the viscosity between the oscillated and continuously sheared melts. This is at least in part attributable to the fact that we are comparing two measures of viscosity. More importantly is the comparison of

the crystallization temperatures. These are independent within experimental error of the type of shear strain that the melt experiences. The crystallization temperatures derived from the oscillatory data are compared in Figure 4 and listed in Table 2.

Talc concentration (wt%)	Run Number	Pigment concentration (wt%)	Shear rate (s^{-1})	Cooling rate ($^{\circ}C\ min^{-1}$)	T_{cryst} ($^{\circ}C$)
0	Boh 257	-	0.127	5	123.6
10	Boh 255	-			136.3
20	Boh 253	-			138.7
40	Boh 251	-			140.9
10	Boh 256	0.2			138.5
20	Boh 254	0.2			140.4
40	Boh 252	0.2			141.5
0	Boh261	-	1.27	5	123.8
10	Boh294	-			138.3
20	Boh307	-			140.6
40	Boh302	-			143.7
10	Boh295	0.2			140.6
20	Boh308	0.2			142.3
40	Boh303	0.2			142.9
0	Boh296	-	0.127	1	128.9
10	Boh297	-			144.5
40	Boh299	-			148.0
10	Boh298	0.2			146.8
40	Boh300	0.2			147.6

Table 1: Crystallization temperatures for unpigmented and pigmented talc filled polypropylenes measured under continuous shear.

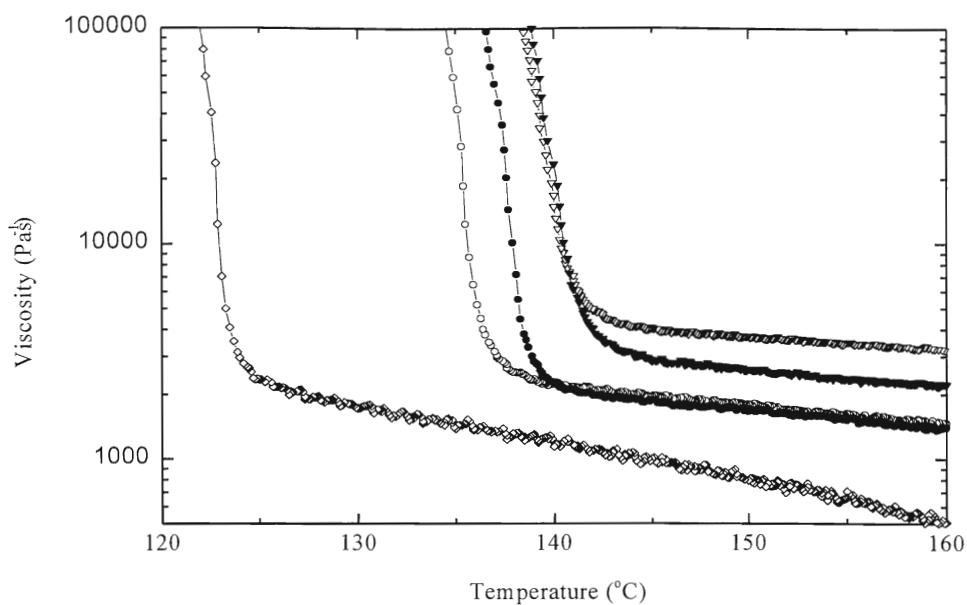


Figure.3. The effect of adding pigment on the crystallization behaviour of virgin and talc filled polypropylene: $\diamond$ = virgin, $\circ$ = 10 wt% talc, $\bullet$ = 10 wt% talc + 0.2 wt% pigment, ∇ = 40 wt% talc, $\blacktriangledown$ = 40 wt% talc + 0.2 wt% pigment. These data were obtained at a shear rate of 0.127 s^{-1} .

Talc concentration (wt%)	Run number	Pigment concentration (wt%)	$T_{\text{cryst}} (^{\circ}\text{C})$
0	Boh287	-	123.6
10	Boh292	-	136.9
20	Boh290	-	140.1
40	Boh288	-	140.7
10	Boh293	0.2	139.5
20	Boh291	0.2	141.0
40	Boh289	0.2	141.6

Table 2: Crystallization temperatures for unpigmented and pigmented talc filled polypropylenes subjected to an oscillatory strain of 0.10 wt%. All the melts were cooled at a rate of $5 ^{\circ}\text{C min}^{-1}$.

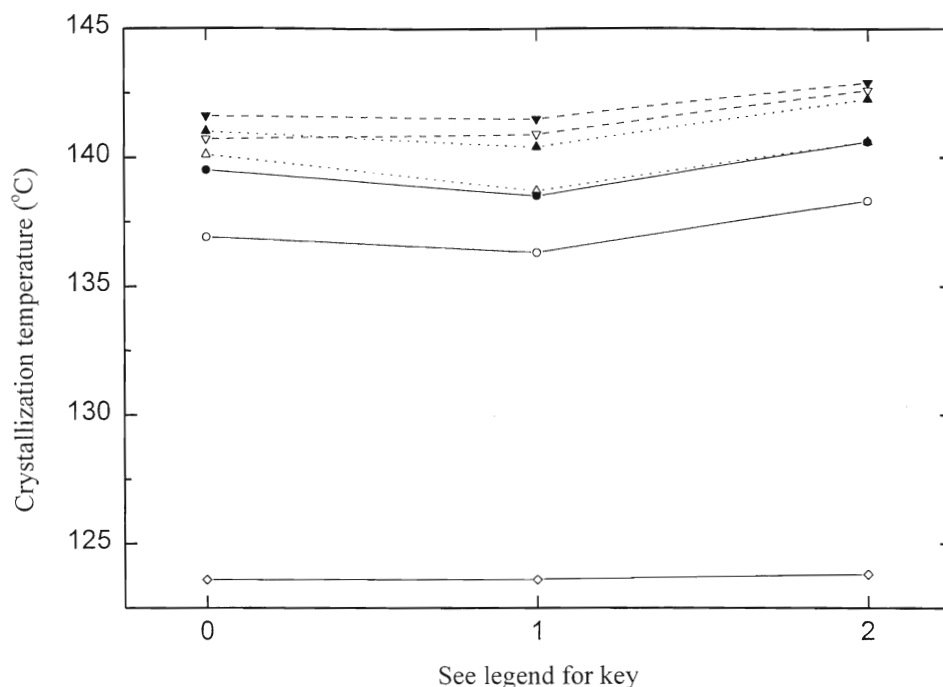


Figure 4. The influence of different shear deformations (0 = oscillatory strain of 0.10, 1 = continuous shear rate of 0.127 s^{-1} , 2 = continuous shear rate of 1.27 s^{-1}) on the crystallization behaviour of talc filled polypropylene. $\diamond$ = virgin, $\circ$ = 10 wt% talc, $\triangle$ = 20 wt% talc, ∇ = 40 wt% talc. Filled symbols refer to samples that contain pigment. All samples were cooled at a rate of $5 \text{ }^{\circ}\text{C min}^{-1}$.

3.2 THE INFLUENCE OF COOLING RATE ON CRYSTALLIZATION BEHAVIOUR

Plots of the temperature dependence of the viscosities of both unpigmented and pigmented talc filled polypropylenes are shown in Figure 6. From this figure it is apparent that lowering the cooling rate raises the temperature at which the materials crystallize. This phenomenon is due to a reduction in the amount of supercooling that occurs when a lower cooling rate is used. The effect can be seen more clearly in Figure 7 where crystallization temperatures have been plotted as a function of the amount of talc contained within the polypropylene. From this figure it is evident that the shift in crystallization temperature is slightly greater for talc filled material than for virgin polypropylene. The explanation for this is not clear.

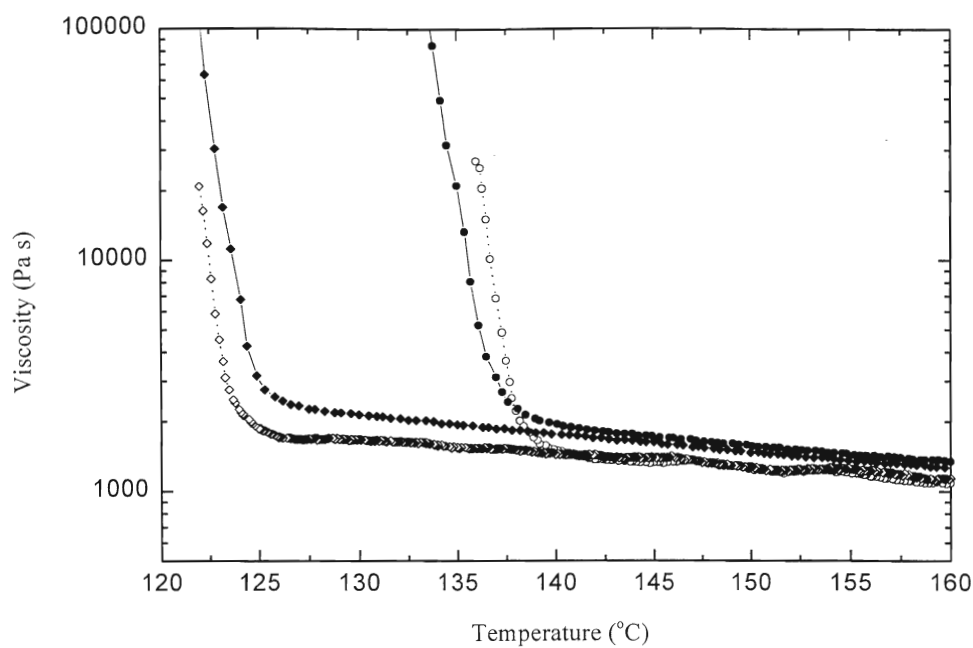


Figure 5: A comparison of data obtained under continuous shear (1.27 s^{-1}). ($\diamond$ = virgin, $\circ$ = 10 wt% talc) with that derived from oscillatory measurements (0.10 wt% strain), ($\blacklozenge$ = virgin, $\bullet$ = 10 wt% talc).

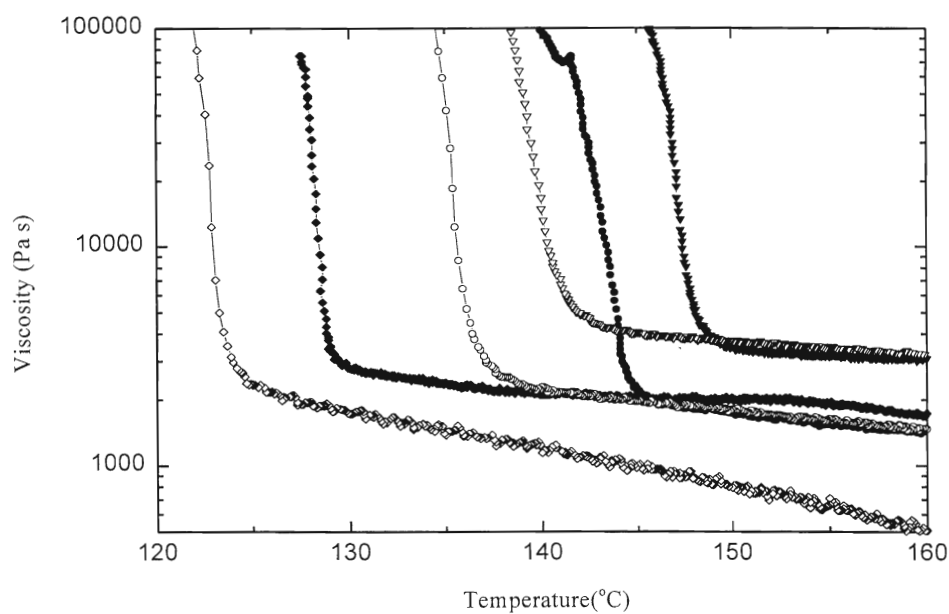


Figure 6: A comparison of data obtained under continuous shear (0.127 s^{-1}). Cooling rates of $5 \text{ }^{\circ}\text{C min}^{-1}$ and $1 \text{ }^{\circ}\text{C min}^{-1}$ are denoted by open and closed symbols respectively. $\diamond$ = virgin, $\circ$ = 10 wt% talc, ∇ = 40 wt% talc. The corresponding filled symbols are for talc filled samples containing 0.2 wt% phthalocyanine blue.

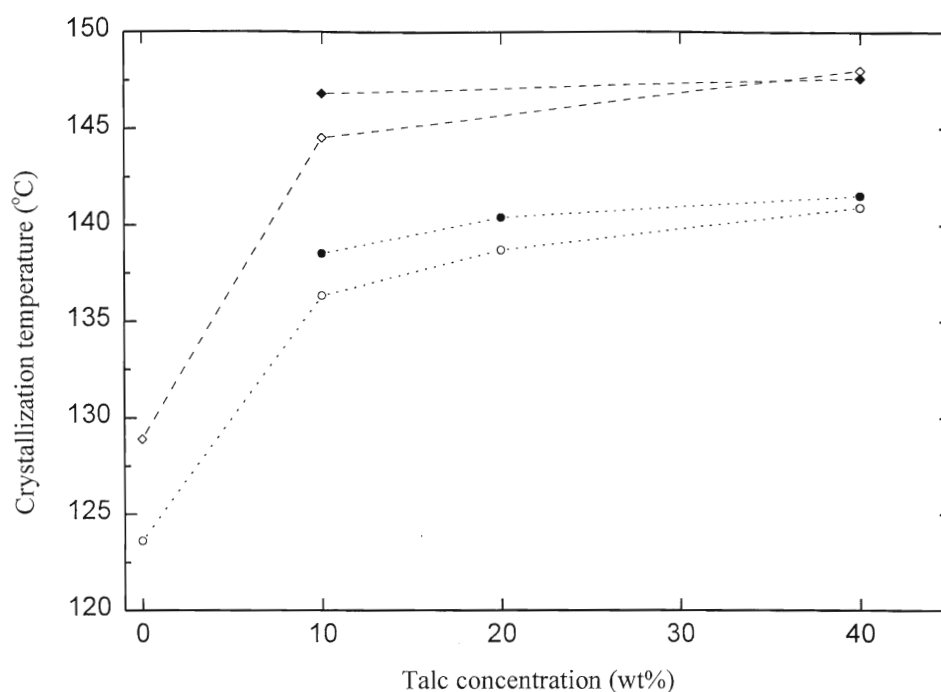


Figure 7. The influence of cooling rates ($\circ = 5\text{ }^{\circ}\text{C min}^{-1}$, $\diamond = 1\text{ }^{\circ}\text{C min}^{-1}$) on the crystallization behaviour of talc filled polypropylene. Filled symbols refer to samples that contain pigment. All samples were continuously sheared at a rate of 0.127 s^{-1} .

3.7 IMPLICATIONS FOR PERFORMANCE

Previous publications have shown that talc reduces the size of spherulites in polypropylene. There are two forms of polypropylene crystals - the α - and β forms, the growth of which depends on temperature and the way in which crystals nucleate. The ratio of α - to β forms influences the mechanical properties of polypropylene⁷. It has been shown that talc is a nucleating agent for the α -crystalline form of polypropylene particularly when functionalised with silane coupling agents^{7,12}. Other materials such as mica or glass flake are known to nucleate the β phase although the formation of this crystalline form is suppressed in the presence of particulate fillers^{7,8}. Some organic pigments can also act as nucleating agents for the β -crystalline form, for example, γ quinacridone.

Talc which nucleates the α -crystalline form of polypropylene reduces the impact resistance of this material but enhances properties that rely on stiffness such as Young's modulus or yield stress. Properties that depend on the matrix material's ductility such as strain to failure are adversely affected as the talc platelets appear to hinder the flow of polypropylene. The impact performance of talc filled material is less than that of the matrix material although this can be improved by coating the platelets with materials such as phosphate. This improvement in impact strength may be due to a more intimate interface between the filler particles and the matrix material or the filler coating may limit the particles' ability to nucleate α -crystals.

Curiously β crystals improve impact performance albeit at the expense of flexural modulus and strength.

There is some evidence to suggest that phthalocyanine blue acts as an α -crystal nucleator in polypropylene. We therefore might expect a further deterioration in the impact performance of talc filled polypropylene coloured with phthalocyanine blue. This is clearly an area where further work is required, not only to establish the extent of the problem but also to find ways of controlling it.

4 CONCLUSIONS

- Adding talc to polypropylene raises both its viscosity and the temperature at which it crystallizes, as expected. The addition of 10 wt% talc raises the crystallization temperature by almost 13 °C. Increasing the concentration of talc to 40 wt% results in an additional 4.5 °C upward rise in crystallization temperature. This behaviour is consistent with talc behaving as a nucleating agent.
- Adding 0.2 wt% phthalocyanine blue to talc filled polypropylene results in an additional increase in crystallization temperature. However the influence of the pigment decreases with increasing talc concentration from ~ 2 °C for polypropylene containing 10 wt% talc to no effect at 40 wt% talc. This behaviour suggests that Phthalocyanineblue is also acting as a nucleating agent and that for high levels of talc (40 wt%) the melt becomes saturated with potential nucleation sites.
- There is no significant difference between the behaviour of melts subjected to either oscillatory or low rate continuous shear during cooling. In this study the maximum shear rate is approximately 3 orders of magnitude less than the melt would experience during its passage through the gate of a cavity mounted on an injection moulding machine. However we note that the melt tends to increase in temperature during its passage through the gate, we would therefore not expect this degree of molecular orientation to remain within the melt as it flows through the cavity.
- The rate at which the melt is cooled has more effect on crystallization than the influence of molecular orientation introduced by low rate shearing.

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