

Effect of pigmentation on the microstructure and properties of rotationally molded polyethylene

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Rotational molding of plastics has experienced growth rates of about 12% per annum over the past decade. As a result, ever more demands are being placed on the quality of the moldings in terms of dimensional control and mechanical properties. With most molding methods for plastics, the use of pigments can have a significant effect on the quality of the product. This is particularly true for rotational molding because there are no stresses to assist with dispersion of the pigment, and the slow cooling rates encourage classic spherulite formation. This paper investigates the use of nucleating and non-nucleating pigments in a rotational molding grade of polyethylene. We demonstrate that the amount of work done on the plastic prior to molding affects the microstructure and the mechanical properties of the end product, often in a positive manner. Turbo-blending of pigments is shown to be problematic, particularly if the pigment is of the nucleating type. The amount of pigment used has little effect on strength but reduces toughness dramatically. © 1998 Kluwer Academic Publishers

1. Introduction

Rotational moulding is a method for manufacturing hollow articles [1]. It differs from most other processes because the molten plastic takes the shape of the mold under very low stresses and cools at a slow rate relative to, say, injection moulding. In the case of crystalline polymers, such as polyethylene, well-developed spherulitic morphologies are formed under such conditions except at the inner surface, where in some circumstances the heating may be too severe, causing the polymer to degrade [2].

Rotomolded polyethylene commercial parts are often colored with pigments. Due to its versatility and economy, dry blending of the pigment with the polymer powder is very common, either by tumble mixing in the mold or by high-speed mixing in turbo-blenders. Previous experience shows that the mixing efficiency of dry blending is poor. Furthermore, because there are no stresses to assist with dispersion of additives in rotational molding, the pigment tends to concentrate at the polymer particle boundaries.

Extrusion compounding and subsequent grinding is a more expensive method of pigmentation of polymers for rotational molding. Nagy and White [3] compared extrusion compounding of pigments to dry blending and reported that it improved the impact strength of rotomolded polyethylene. However Crawford et al. [4] observed that the improvement imparted by extrusion compounding depends on the type of pigment and on the pigment-concentration level. The fact that different pigments lead to different

part behaviour was not explained. The results in this paper suggest that the differences may result, in some cases, from the nucleating activity of the pigments.

Some pigments and many other substances can act as nucleating agents of crystalline polymers. Studies on the nucleating activity of these substances, and its influence on mechanical properties, are usually focused on polymers with a slow crystal-growth rate like polypropylene [5–8]. As polyethylene has a very fast crystal-growth rate, it is not easy to estimate the effect of heterogeneous nucleation on its crystallisation behavior.

The nucleating effect of pigments and other additives on the crystalline structure of polymers depends on the polymer/additive system [9]. For example, titanium dioxide acts as a nucleator when added to polypropylene but does not show that effect when added to polyethylene [10]. Potassium stearate, on the other hand, has the opposite effect [5]. The means by which a nucleator actually works is not well understood, and so it is difficult to predict the nucleating ability of an additive.

The use of nucleating additives causes the spherulite size to decrease [7, 8, 11, 12] and the crystallisation temperature to increase [8, 11], with respect to the base polymer. According to reported studies with polypropylene, the modifications in the microstructure that originate by the presence of nucleating agents improve the modulus of elasticity [5, 12, 13] and the toughness [7] of material.

In this work, the nucleating effect of different pigments was studied when different methods of mixing were used. The effect was assessed in terms of the crystalline morphology of the polymer, the dispersion of the pigment, and the mechanical properties. The effect of the level of pigment was also studied for one type of nucleating pigment.

2. Experimental

The material used in this work was Dupont's Sclair 8504 polyethylene (PE). Two different pigments were used: a non-nucleating blue pigment (sodium aluminium sulphosilicate) and a nucleating red pigment (chromophthal scarlet) supplied by Hampton Colours Ltd. The blue pigment was always used in the amount of 0.15%. The red pigment was used in amounts of 0.05, 0.15 and 0.3%.

The pigments were mixed with the polymer prior to moulding using two different methods:

1. Turbo mixing: the pigment was mixed using a blender (turbo blender Caccia AV0150C) with blades rotating at 1400 rpm until the material reached 50 °C. A batch of virgin PE was turbo-blended to be used as a reference.

2. Extrusion mixing: the pigment was mixed using a Killion KN-150 single-screw extruder with a pelletizer. The extrusion temperature was 195 °C. The granules were ground to a powder using a Wedco Grinder. A batch of virgin PE was also prepared as a reference.

After the mixing stage, the material was rotationally molded in a Caccia 1400 A shuttle-type machine. A cube-shaped steel mould was used to produce 3-mm-thick moldings. The maximum internal temperature reached by the air inside the mold was always around 220 °C. This temperature has been shown [2] to lead to optimum mechanical performance of the plastic material used. Table I identifies the samples and the respective compounding and mixing details.

The thermal properties of the material were measured using a Perkin Elmer differential-scanning calorimeter,

DSC-7. Powder specimens and specimens cut from granules were heated up from 50 °C to 200 °C, cooled down to 50 °C and then heated again to 200 °C. The heating and the cooling rates were 10 °C/min.

The study of the pigment dispersion and the crystalline microstructure of the rotomolded samples was done on microtomed slices with an Olympus microscope, using both common and polarised light. The internal surface of the molded samples was observed using DIC reflection microscopy. The melting and crystallisation behavior of the rotomolded material were studied using a Mettler FP 80 hot-stage fitted onto the polarising microscope. Using heating and cooling rates of 5 °C/min., thin sections of the samples were heated up to 160 °C and then cooled, until all the polymer had crystallised.

The mechanical properties of the samples were measured by impact tests at -20 °C (using a Rosand IFW type 5 instrumented falling dart machine) and tensile tests at room temperature (using an Instron 4505 Universal Testing machine).

3. Results

3.1. Effect of mixing

It was found that, independent of the amount of pigment used, the moldings produced from extrusion compounded material displayed a much smaller spherulitic texture compared to those produced from turbo-blended material (Fig. 1). The same effect was observed by DIC on the inner surfaces of the moldings. The heating of this material in the hot stage microscope up to temperatures above 200 °C, to relax a possible molecular orientation caused by extrusion, and subsequent cooling to recrystallise, did not increase the size of the spherulites. The DSC measurements (Table II) showed that extrusion modified the thermal properties of the polymer. As can be observed in Fig. 2, extrusion caused an increase in the crystallization temperature and in the crystallinity of the polyethylene. These modifications and the increment in the number of nuclei are commonly associated with the effect of nucleating agents [6-11]. However, as this material is not pigmented, it is felt that during extrusion and grinding, some irreversible modifications

TABLE I Identification of the samples

| Sample identification | Type of pigment | Amount of pigment (%) | Mixing method |
|-----------------------|-----------------|-----------------------|----------------------|
| Virg | — | — | — |
| Virgtu | — | — | Turbo blending |
| Virgex | — | — | Extrusion + grinding |
| 0.15nottu | Not nucleating | 0.15 | Turbo blending |
| 0.05nutu | Nucleating | 0.05 | Turbo blending |
| 0.15nutu | Nucleating | 0.15 | Turbo blending |
| 0.3nutu | Nucleating | 0.3 | Turbo blending |
| 0.15notex | Not nucleating | 0.15 | Extrusion + grinding |
| 0.05nuex | Nucleating | 0.05 | Extrusion + grinding |
| 0.15nuex | Nucleating | 0.15 | Extrusion + grinding |
| 0.3nuex | Nucleating | 0.3 | Extrusion + grinding |

TABLE II Thermal properties of the materials

| Sample | T _{cryst.} (°C) | T _{melt.} (°C) | ΔH _{melt.} (J/g) |
|-----------------|--------------------------|-------------------------|---------------------------|
| Virgin | 108.9 (0.3) | 117.8 (1.3) | 135.8 (1.4) |
| Virgin turbo | 109.1 (0.3) | 117.8 (1.3) | 136.0 (1.4) |
| Virgin extruded | 109.5 (0.2) | 117.8 (0.2) | 137.6 (1.0) |
| 0.15notturbo | 109.5 (0.3) | 117.5 (1.3) | 136.0 (1.4) |
| 0.15nuturbo | 110.6 (0.3) | 117.4 (1.3) | 136.4 (1.4) |
| 0.3nuturbo | 110.6 (0.3) | 117.2 (1.3) | 135.8 (1.4) |
| 0.15notext | 110.2 (0.2) | 117.9 (0.2) | 138.3 (1.0) |
| 0.15nuext | 112.7 (0.2) | 115.5 (0.2) | 139.4 (1.0) |
| 0.3nuext | 112.6 (0.2) | 115.7 (0.2) | 139.4 (1.0) |

In brackets-std. deviation. T_{cryst.}-crystallisation temperature T_{melt.}-melting temperature. ΔH_{melt.}- melting enthalpy.

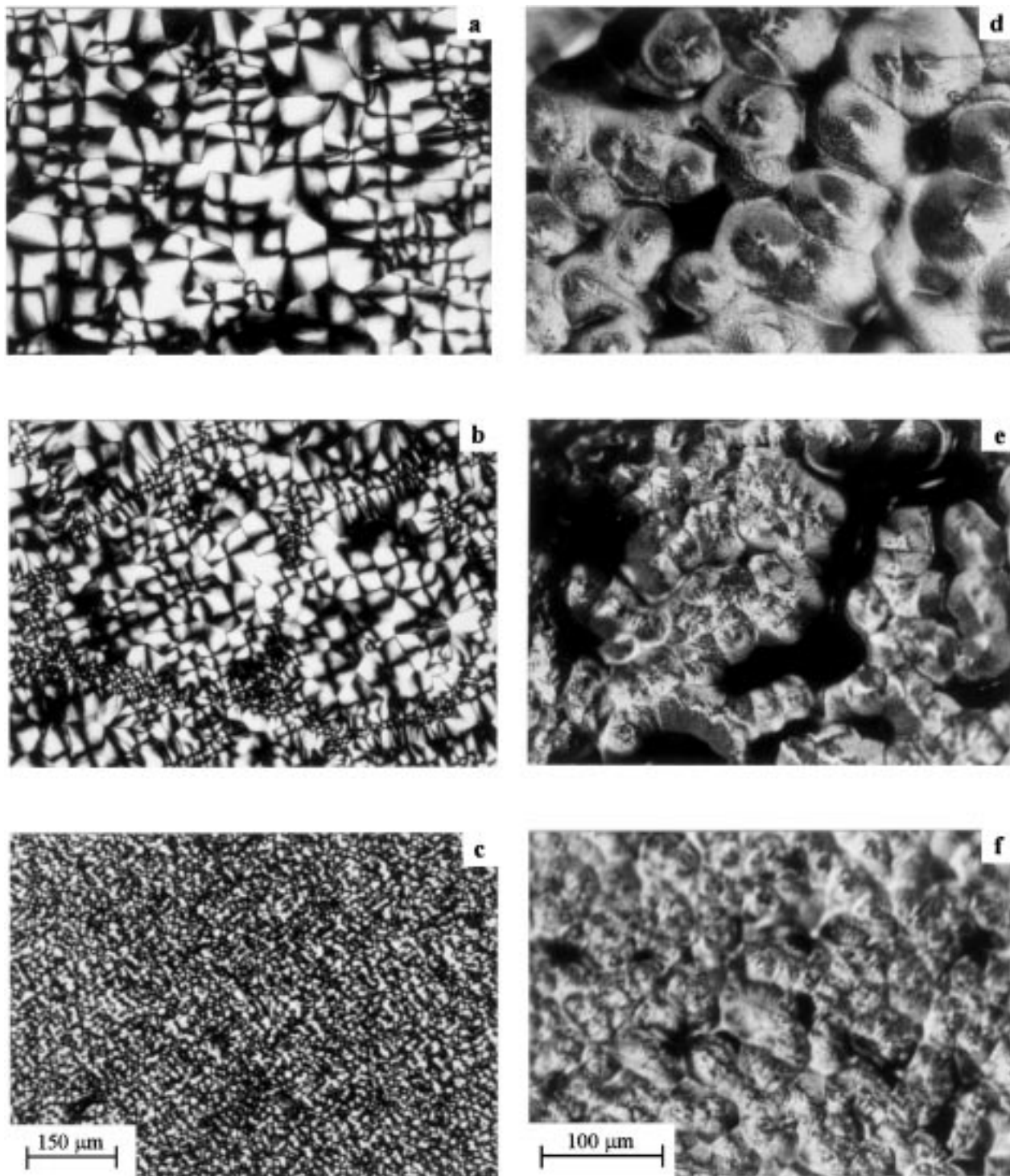


Figure 1 Effect of the mixing method on the microstructure of the samples: a–c polarised light, d–f DIC. a, d – virg b, e – virgtu c, f – virgex.

occurred in the molecular structure of the polyethylene (probably some cross-linking), and this affected its crystallization behavior.

The turbo-blended samples exhibited rows of densely nucleated spherulites located at what appears to be the original powder particle boundaries (Fig. 1b). At these rows, some transcrystalline growth towards the interior of the particles is visible. Away from the rows, the microstructure is identical to that observed in the virgin material. The hot-stage microscope study showed that the row-nucleated spherulites have melting and crystallization temperatures slightly higher ($\sim 0.5^\circ\text{C}$) than those of the remaining material. These observations

suggest that the mechanical action of the blades during turbo-blending caused the material at the particles surface to degrade due to shear heating. The increase in the nucleation rate and crystallization temperature allowed the degraded polymer to nucleate a thin layer at the neighboring material that had not degraded, and to originate the transcrystalline growth.

Table III and Fig. 3 show that the yield stress and the impact strength improve when the material is turbo-blended or extruded prior to moulding. The better mechanical properties obtained with the extruded samples are certainly a consequence of the increase in crystallinity and in the number of tie-molecules associated

with the decrease of the spherulite size. These tie-molecules are known to act as transducers of stress among spherulites and to increase the impact strength of the material. We propose that the improvement in yield stress results from the increase in crystallinity and crystal thickness promoted by the higher crystallization temperature of the extruded material. This is supported by the work of other investigators [14].

In the case of the turbo-blended sample the improvement in properties appears to result from row nucleation at the particles boundaries that probably increased the cohesion between the particles.

TABLE III Mechanical properties of rotationally moulded samples

| Sample | E (GPa) | σ_y (MPa) | σ_b (MPa) | ϵ_b (%) | Ep (J/mm) |
|-----------|-------------|------------------|------------------|------------------|-----------|
| Virg | 0.35 (0.03) | 20.9 (0.8) | 19.7 (1.3) | 848 (87) | 7.7 (0.5) |
| Virgtu | 0.38 (0.05) | 22.0 (0.5) | 24.3 (2.5) | 996 (170) | 8.9 (1.1) |
| Virgex | 0.36 (0.06) | 22.2 (0.7) | 20.0 (3.3) | 838 (141) | 9.2 (1.0) |
| 0.15nottu | 0.40 (0.04) | 22.5 (0.5) | 19.5 (1.5) | 352 (40) | 6.7 (1.2) |
| 0.05nutu | 0.37 (0.04) | 22.0 (0.5) | 15.2 (1.1) | 476 (188) | 6.2 (0.4) |
| 0.15nutu | 0.41 (0.10) | 23.1 (5.1) | 14.6 (3.1) | 181 (97) | 7.8 (1.0) |
| 0.3nutu | 0.37 (0.04) | 22.7 (1.8) | 12.4 (0.8) | 103 (44) | 3.1 (2.2) |
| 0.15notex | 0.36 (0.07) | 22.9 (0.5) | 27.9 (2.4) | 1222 (98) | 9.3 (0.5) |
| 0.05nuex | 0.44 (0.06) | 25.2 (2.5) | 17.2 (1.7) | 534 (110) | 6.5 (0.4) |
| 0.15nuex | 0.42 (0.06) | 25.3 (1.5) | 17.9 (2.0) | 638 (67) | 9.0 (0.7) |
| 0.3nuex | 0.36 (0.05) | 22.6 (1.3) | 16.3 (1.1) | 536 (103) | 6.6 (0.3) |

In brackets-std. deviation. Tensile properties: E-Young modulus; σ_y , σ_b -yield and break stress, respectively; ϵ_b -elongation at break. Impact property: Ep-Peak energy.

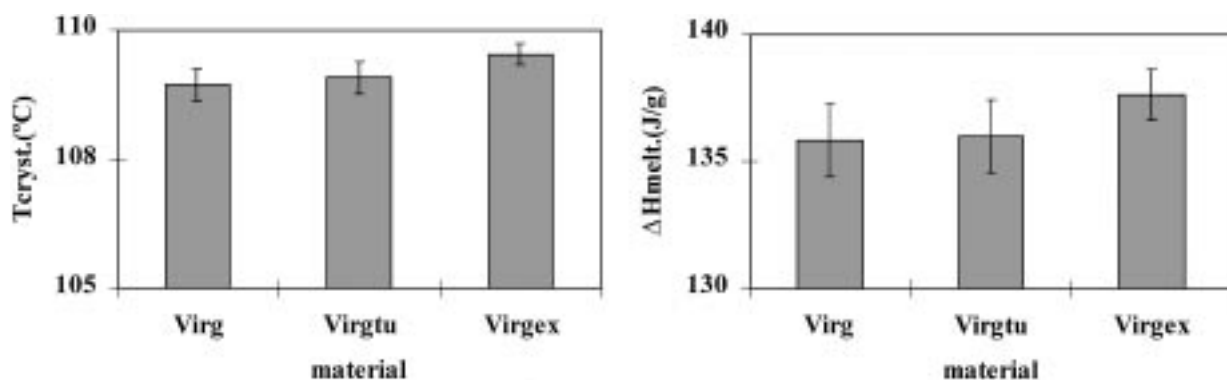


Figure 2 Effect of the mixing method on the thermal properties of the materials.

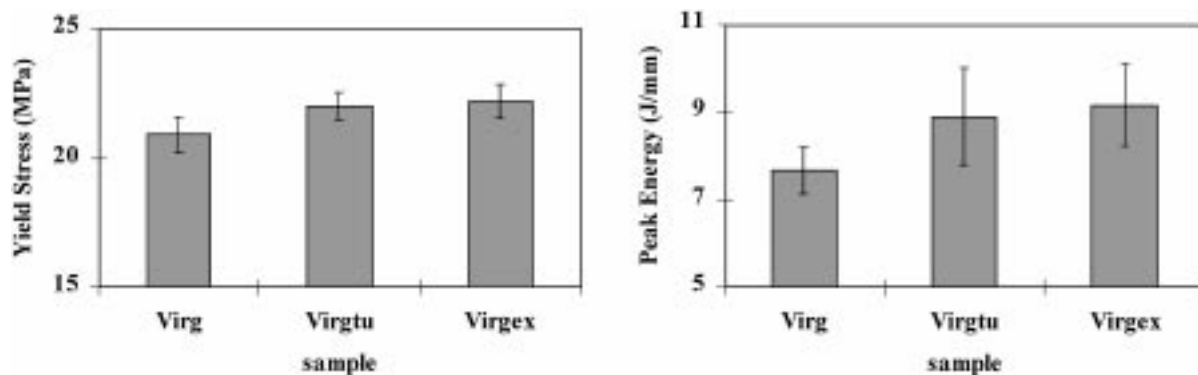


Figure 3 Effect of the mixing method on the mechanical properties of the non-pigmented samples.

3.2. Effect of the type of pigment

The nucleating pigment causes a clear modification of the microstructure of the turbo-blended samples. As is shown in Fig. 4d and e, the concentration of the nucleating pigment at the boundaries of the original particles creates transcristalline textures around them. Similar structures were also observed at the inner surface of these samples, where the tendency of the pigment to concentrate prevents the normal tri-dimensional spherulitic growth (Fig. 4f). In contrast, if the pigment is non-nucleating, the spherulitic texture is identical to that of the virgin material (Fig. 4b and c).

These modifications on the microstructure of the samples are followed by changes of the thermal properties of the material containing a nucleating pigment. DSC results (Table II) show an increase both of the crystallization temperature and of the melting enthalpy when a nucleating pigment is used.

The average yield stress of the turbo-blended samples is not affected by the addition of pigments (see Table III and Fig. 5). However, it should be observed that the standard deviation of the data for samples containing nucleating pigment is much larger. This suggests that to some extent the nucleating effect of the pigment is beneficial, probably because it promotes the adhesion of the particles. However, as this mixing process does not disperse the pigment very well, the zones where it concentrates are very weak. Previous studies on the effect of the dispersion of pigments have shown that the presence of large fragments will induce stress concentration, affecting the tensile strength [15].

The elongation at break and the impact strength of the samples made from turbo-blended material both

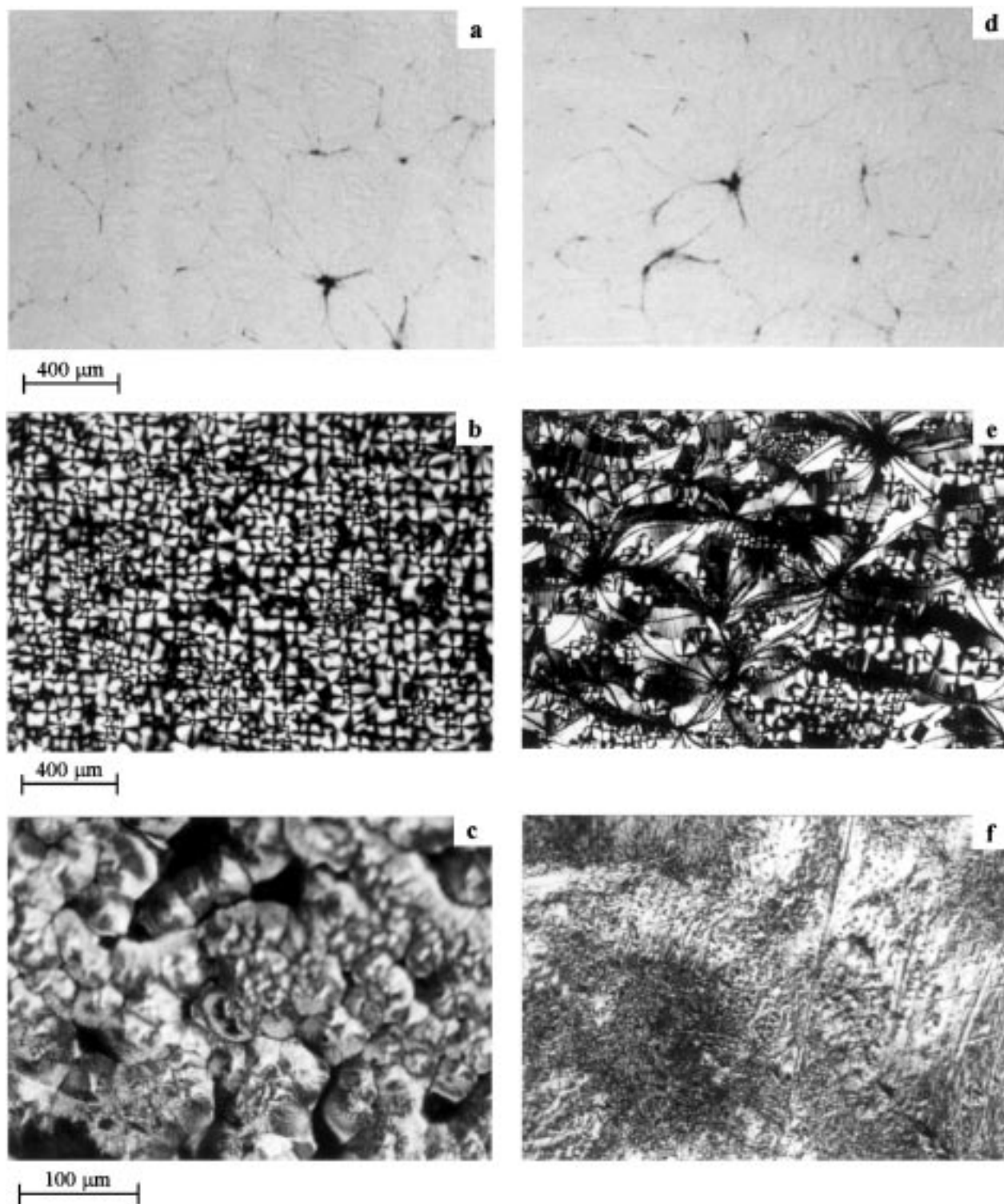


Figure 4 Microstructure of turbo-blended samples: a and d—bright field, b and e—polarised light, c and f—DIC. a–c: 0.15 nottu, d–f: 0.15 nutu.

decrease with the addition of the pigments. This deterioration is caused by the concentration of the pigment at the particles boundaries and at the inner surface of the mouldings (Fig. 6). In falling-weight-impact testing, when the inner molded surface is subjected to the maximum tensile stress, the concentration of pigment and the transcristalline texture at this surface make the material very weak.

Bright-field microscopy revealed that extrusion-compounding promotes good dispersion and uniform

distribution of the pigments (Fig. 7a and d). The use of a nucleating pigment caused the crystalline structure to become finer and to acquire a very complex pattern. As Fig. 8 shows, this complex texture is caused by the grinding process, but the reasons for its formation are not clear. It is evident that the memory of this structure is not erased during the rotational molding process and is reproduced very closely in the molded part.

As was observed for the virgin material (Fig. 1), and again revealed by DIC microscopy at the inner surface

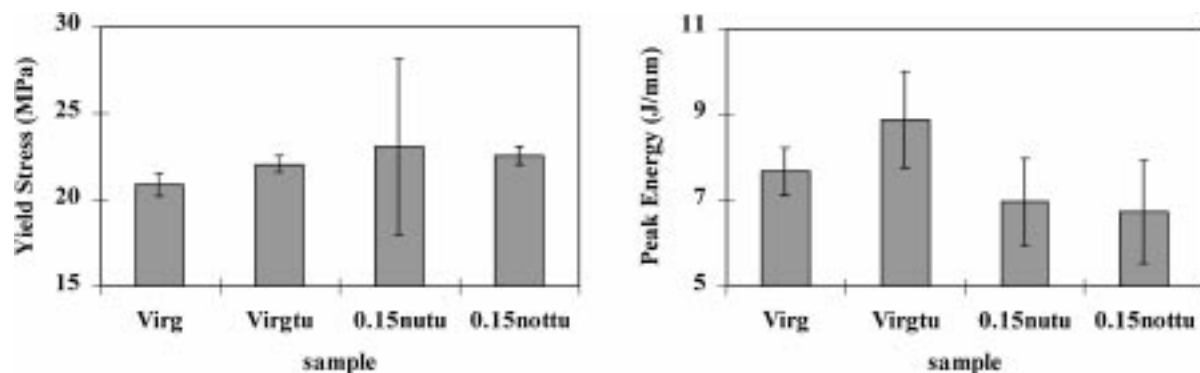


Figure 5 Mechanical properties of the turbo-blended samples.

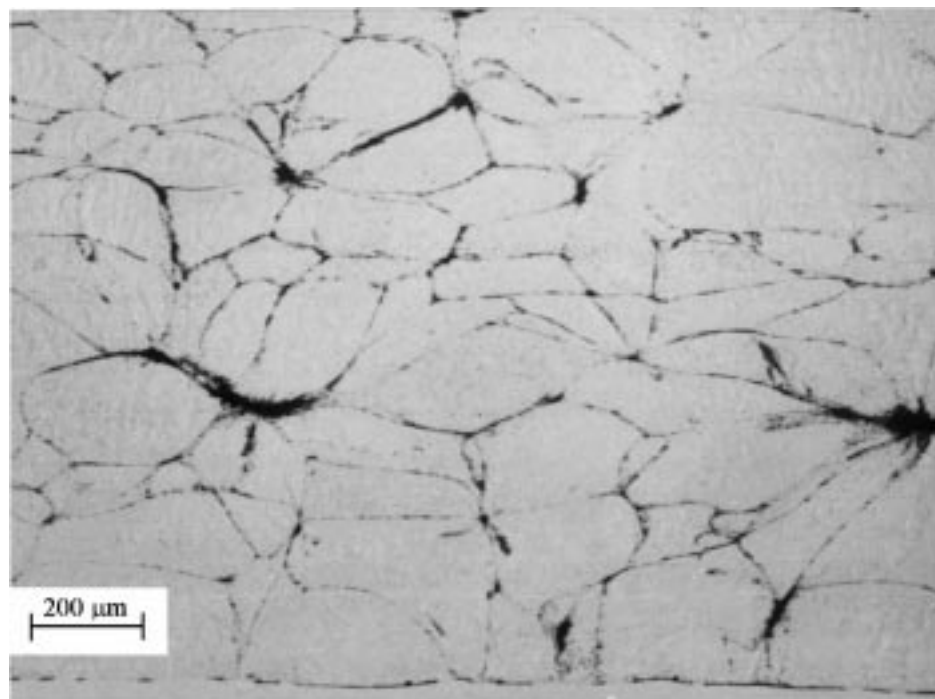


Figure 6 Bright-field micrograph of turbo-blended sample showing the concentration of the pigment at the inner surface.

of the pigmented moldings (Fig. 7c and f), extrusion compounding reduces the size of the spherulitic structure of the polyethylene. The effect is more pronounced in the sample with the nucleating pigment. This illustrates that the nucleating ability of the pigment increases with extrusion mixing, which is in agreement with the results of other investigators [6].

The DSC results confirm the improved nucleating ability of the pigment caused by the extrusion compounding. With this mixing process, the crystallization temperature and the melting enthalpy of the polymer increase more than with turbo-bending (see Table II). The higher mixing efficiency in extrusion increases the number of nuclei available for the polymer to crystallize. This influences not only the spherulite size but also the final crystallinity, contrary to what has been reported for polypropylene [7].

The yield stress improves when the material is extrusion-compounded and ground before molding (see Table III). This improvement is higher when a nucleating pigment is used (Fig. 9), due to the increase

in crystallinity and reduction in size of the crystalline texture, with the consequent increase in number of tie molecules referred to earlier.

The impact strength, measured as the peak energy, increases when the pigments are extrusion compounded (Table III). However, contrary to what was observed for the yield stress, the type of pigment does not appear to affect the impact behavior of the material.

3.3. Effect of the amount of pigment

This study was done only with the nucleating pigment incorporated in different concentrations by turbo-blending and by extrusion compounding.

The DSC measurements on turbo-blended powder and on extruded granules showed in both cases that the increase of the crystallization temperature and of the melting enthalpy caused by the presence of pigment is not affected by its concentration level (Fig. 10). As was already mentioned, the nucleating activity

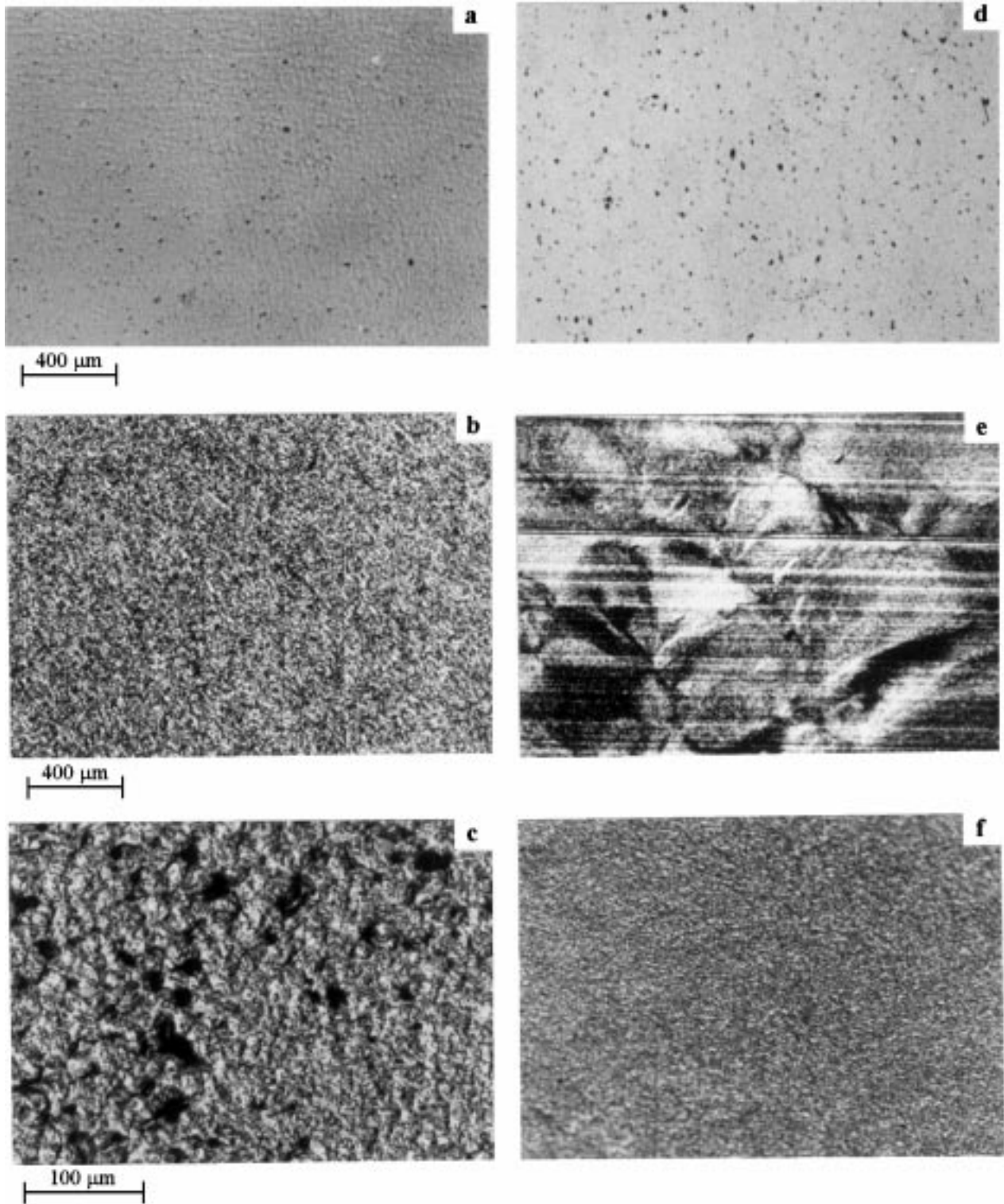


Figure 7 Microstructure of extrusion-compounded samples: a and d – bright field, b and e – polarised light, c and f – DIC. a–c: 0.15 notex d–f: 0.15 nuex.

of the pigment and consequent modification of the crystallization behavior of the polyethylene is stronger in the extrusion-compounded samples.

The tensile properties, namely the yield stress and the strain at break, were clearly affected by the pigment concentration as shown in Table III and Fig. 11. For both mixing processes, the yield stress is a maximum for the pigment level of 0.15%, but in the case of turbo-blended samples, the standard deviation of the data is so high that it is difficult to predict the behavior of the moldings. The strain at break deteriorates

severely when pigment is added. This detrimental effect of the pigment is more severe with the turbo-blended samples than with the extrusion-compounded material. It is suggested that this is the result of the poor dispersion produced by turbo-blending, which leads to stress concentration where the pigment is more heavily concentrated. A similar effect has been observed in studies on the dispersion of titanium dioxide in linear low-density polyethylene and has been related to the size of the agglomerates that are bigger for shorter dispersion times [16].

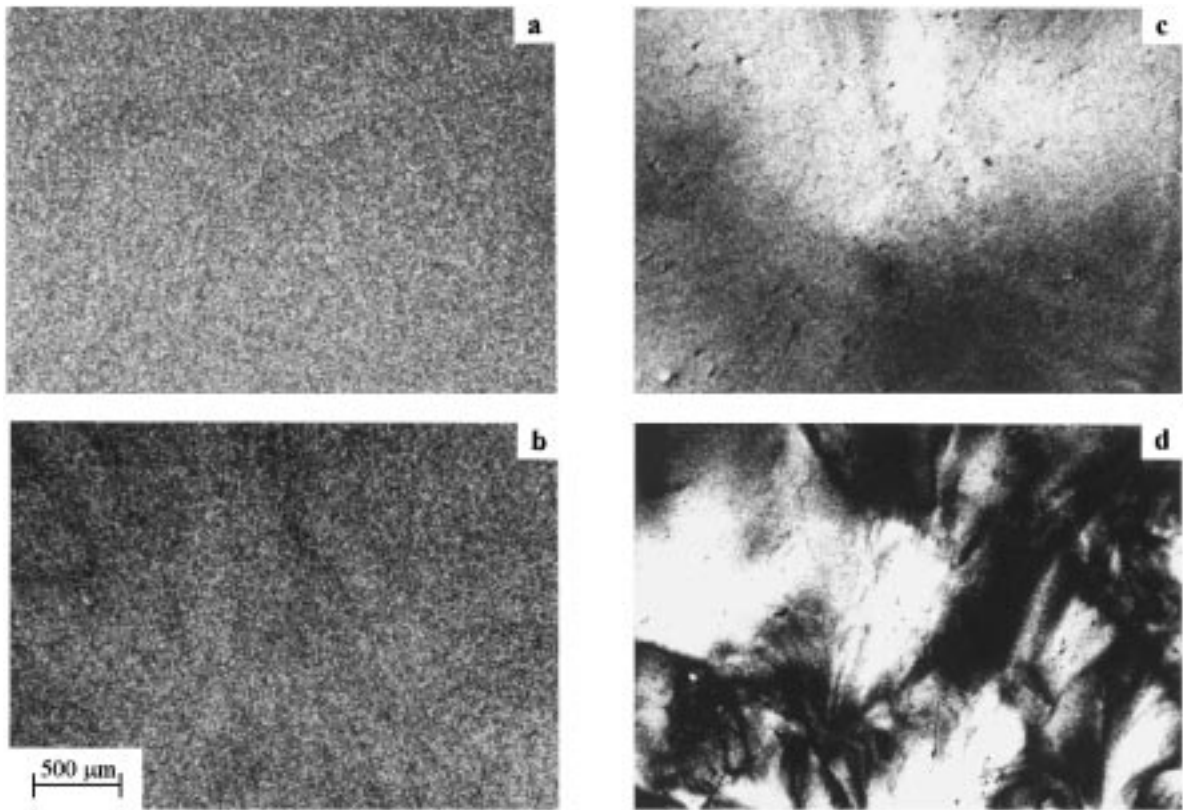


Figure 8 Polarised light micrographs of melt pressings of pigmented materials: a–0.15 notex, extruded granule; b–0.15 notex, ground powder; c–0.15 nuex, extruded granule; d–nuex, ground powder.

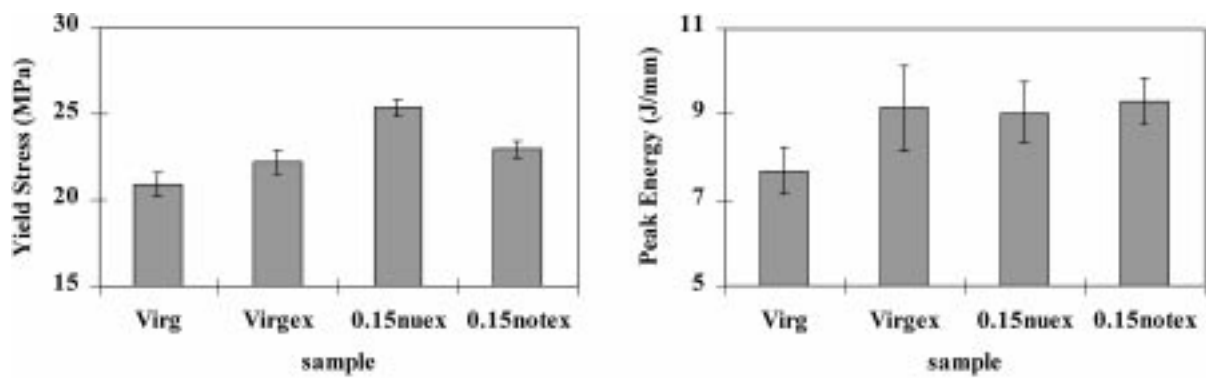


Figure 9 Mechanical properties of the extrusion compounded samples.

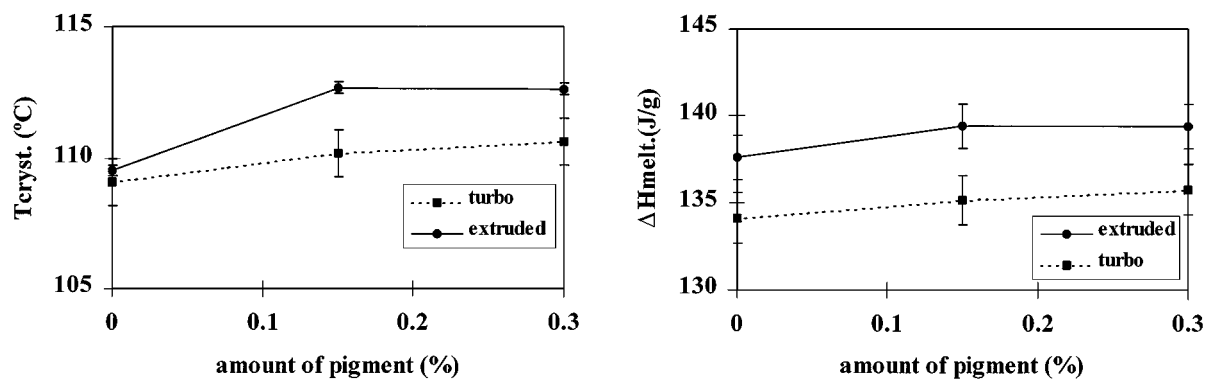


Figure 10 Effect of the level of pigment and mixing method on the thermal properties of the materials.

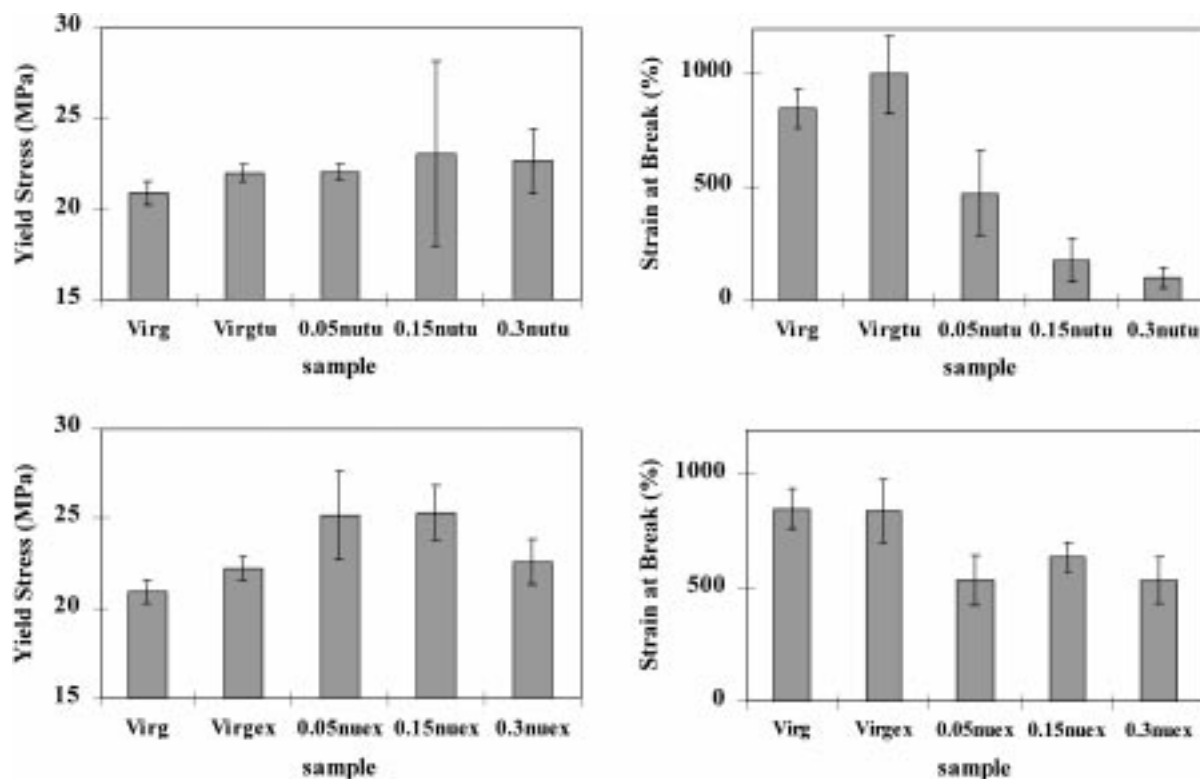


Figure 11 Effect of the level of pigment and mixing method on the tensile properties of the samples.

4. Conclusions

As a result of this experimental investigation of rotomolding of polyethylene with various types and amounts of pigments, the following conclusions have been drawn:

1. If the rotational molding powder is subjected to thermo-mechanical action prior to molding, then the mechanical properties of the end-product are improved.
2. If the thermo-mechanical treatment is imparted by an extruder, then there is a marked decrease of the size of the crystalline texture of the rotationally molded product.
3. Thermo-mechanical treatment through turbo-blending results in a row-nucleated transcrystalline structure around the original powder particles.
4. During rotational molding of turbo-blended plastic powder/pigment, the lack of shear causes the pigment to be trapped at the boundary of the individual powder particles. If the pigment has a nucleating effect, this causes transcrystalline structures that have a major effect on the mechanical properties, causing a very large scatter in the tensile properties of rotomolded products.
5. If a nucleating pigment is turbo blended, the amount of pigment has little effect on the tensile strength, but the strain at break decreases dramatically as the pigment levels increase from 0.05% to 0.3%.
6. If a nucleating pigment is compounded using an extruder, then the decrease in the strain at break is less apparent, and there is a slight increase in the tensile strength of the mouldings.

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