The Effect of Cooling Rate on the Impact Performance and Dynamic Mechanical Properties of Rotationally Molded Metallocene Catalyzed Linear Low Density Polyethylene

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ABSTRACT: This article examines changes to the morphology of rotationally molded metallocene catalyzed linear low density polyethylene brought about by varying the cooling rate during processing. These changes in morphology lead to variations in the impact performance, which is reflected in the dynamic mechanical characteristics of the materials. Various analytical techniques are used in an attempt to explain the differences in impact behavior. Slow cooling is shown to result in high crystallinity, and in the formation of large spherulites, which in turn is detrimental to the impact performance of the material, particularly at low temperatures. The high crystallinity corresponds with a shift in the β transition of the material to a higher temperature, and is shown to result in a higher brittle–ductile transition. A case study was also carried out on samples from a finished part provided by an industrial molder, one section of which failed in a brittle manner when impact tested while the other failed in a ductile manner. Microscopy results showed that the brittle material had large spherulites at the inside surface, while the ductile material showed incipient degradation at this surface, which has previously been shown to be of benefit to impact strength in rotationally molded parts. Dynamic mechanical studies again showed a β transition at a higher temperature in the brittle samples. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1963–1971, 2006

Key words: rotational molding; metallocene; polyethylene; morphology; microscopy; cooling; impact strength

INTRODUCTION

It is well known that the final morphology of a polymer product will be vital in determining its mechanical properties. Being semicrystalline polymers, polyethylenes contain both amorphous and crystalline components. It is the relationship between the amorphous and crystalline components of a polymer that governs the physical properties it exhibits. The structure of a polymer, including, for example, the amount of branching, can affect the degree to which it is able to form crystalline regions, but in addition to this, the level of crystallization can be greatly affected by the way in which it is processed. The effect of using different cooling methods on the morphology, and hence on the impact performance, of rotationally molded metallocene catalyzed polyethylene were investigated in this work.

In the rotational molding process, the relatively stress-free conditions and long cycle times allow classic spherulitic structures to develop. Once a spherulite is nucleated, it will grow until it reaches a neighboring spherulite. In general, the crystallinity of a rotationally molded part is affected by the rate at which it is cooled. Slow cooling results in a product with a higher crystallinity, and the lower nucleation density at higher temperatures gives rise to larger spherulites.

In rotationally molded products, it is known that the inner surface of the molding will have larger spherulites and a higher crystallinity because this surface will cool more slowly than the outer surface will.[1] In addition to this, the spherulites at the inner surface are able to grow freely, as they are not in contact with the mold wall. This gives the inner surface a rough texture. At the outer surface, however, the growth of spherulites is restricted by the presence of the mold wall, and some "transcrystalline structures" can develop, where the polymer crystallizes on the mold wall.

The crystalline structure of a polymer can be affected if degradation occurs during the rotational molding process. Degradation tends to occur at the inner surface of a molding, and can be detected by observing the microstructure of the inside surface. In an undegraded polymer, the spherulites will be of similar size and regularly shaped. When degradation is just incipient, the spherulites become smaller and less perfect. As degradation increases, the spherulitic

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structure gives way to a columnar structure, and eventually the spherulitic structure will break down entirely and an amorphous material develops.[2]

There has been much debate regarding the effect of crystallinity on impact strength, and this is complicated by the fact that the actual size of the crystalline entities can have a separate effect on the degree of crystallinity. Trying to isolate the effects of these separate, but related, factors has been the focus of much research.

Xu et al.[3] investigated this by using different quantities of nucleating agent to change the crystalline morphology of polypropylene. It was found that an increase in the quantity of nucleating agents decreased the spherulite size, but increased the crystallinity. There was an increase in the impact strength of the product with increasing nucleating agent content up until the point where 0.4 wt % of the nucleating agent had been added, and therefore it was proposed that the fineness of the crystalline texture was beneficial to impact strength. Beyond 0.4 wt %, the spherulite size stabilized, but the crystallinity continued to rise. After this point, the flexibility of the polymer chain began to decrease and therefore the capability for energy absorption also decreased, resulting in a decrease in impact resistance. They found that the impact strength was related to spherulite size by eq. (1).

$$\ln \frac{1}{\sigma} \propto D_n \qquad (1)$$

where σ is the impact strength and D_n is the spherulite size.

Heat treatments were also used in this study to vary the crystallinity while keeping the spherulite size constant. In this case it was found that for a given spherulite size the impact strength would initially decrease rapidly with increasing crystallinity, but that beyond a certain level of crystallinity the impact strength would remain relatively constant.

Another study[4] tried to provide a solution to the apparent contradiction shown in some previous work wherein in some cases it was found that increasing crystallinity seemed to improve the tensile properties, but in other cases it seemed to reduce other mechanical properties such as impact resistance. It was found that, for polypropylene, a cooling rate of 0.03°C/s gave an optimum spherulite size for best impact performance. At slower cooling rates, larger spherulite sizes were obtained and the product had a lower impact resistance. It was suggested that slower cooling speeds allowed segregation of impurities and the formation of contraction voids at the boundaries, which led to poorer impact resistance overall.

A third study[5] suggests that there are other factors affecting the impact strength, in addition to the crystallinity and crystal size. The factors listed include the shape and the perfection of both the crystals and the spherulites. This study again suggests that poor impact resistance in specimens with large spherulites is due to the segregation of impurities and the presence of voids. However, it was found that by slowly crystallizing polypropylene glass fiber composites at 134°C and then rapidly quenching in water a significant improvement in impact strength was obtained.

Crystalline domains are usually more brittle than amorphous regions, and can act as stress concentrators. This situation is made worse if the spherulites are very large or if the crystallinity is very high. When the amorphous part of a polymer is brittle, the crystals will decrease the impact strength. When the amorphous part is flexible, and the crystals are small in size, then they can act as reinforcing agents.[6]

In general, it is thought that yield stress will increase almost linearly with increasing crystallinity, but that a very high level of crystallinity will cause brittle failure. The elongation to fracture however will decrease dramatically as crystallinity increases, and impact strength will also usually decrease as crystallinity increases.

This article attempts to highlight how differences in cooling rates can affect the morphology of rotationally molded parts, and how this in turn can affect impact performance.

EXPERIMENTAL

Materials

A metallocene catalyzed linear low density polyethylene (LLDPE) was selected for use in these trials. This material was a Borealis material, grade RM8403, and has a density of 940 kg/m^3 and a melt flow index of 6 g/10 min.

Rotational molding

Moldings with an approximate wall thickness of 3 mm were produced in a 300-mm steel cube mold using a Rotospeed RS-160 independent arm carousel rotational molding machine. In each trial the shot weight used was of 1.8 kg. All the moldings were heated up in an oven at 300°C to a mold internal air temperature of 190°C, and then the mold was removed from the oven.

Three different cooling methods were investigated in this study, and several moldings of each type were produced as detailed here.

1. Water cooling – moldings cooled using two water jets
2. Air cooling – moldings cooled using an air fan
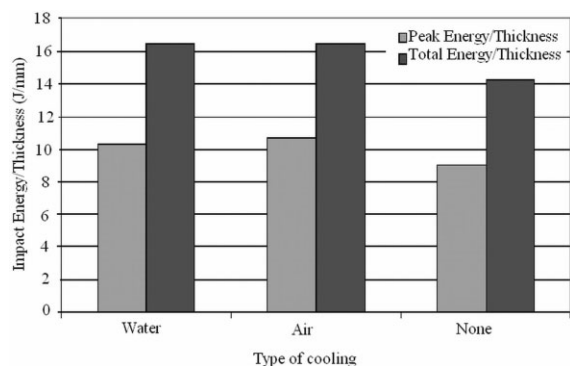3. Quiescent cooling – no forced cooling used

Figure 1 Impact test results at room temperature on moldings cooled in different ways.

The temperature during molding was recorded using a Rotolog device. Temperature recordings were taken at two points on the mold wall, and also a thermocouple was used to measure the temperature of the air inside the mold. This internal air temperature was used to compare cooling rates, as it provides a useful way of averaging out variations in temperature across the mold.

A large 6–mm-thick LLDPE molding, made by an industrial company, that was brittle in some zones and ductile in others was also analyzed to investigate whether the findings of our study could explain the cause of that undesirable behavior.

Impact testing

Impact tests were carried out using a CEAST Fractovis instrumented falling weight impact tester. The dart weighed 3.63 kg, and this was loaded with a mass of 25 kg. Impact samples were machined from the moldings into squares of dimension 60×60 mm^2.

Five impact samples cooled using each of the three methods were impact tested at 20°C and at −40°C. The samples were clamped in the test machine with the outside surface (i.e., the surface that was in contact with the mold) facing up. The samples were impacted from a height of 1 m, and the speed of the dart at impact was ~4.4 m/s.

Dynamic mechanical thermal analysis

A Rheometric Scientific Mark VI DMTA machine was used to carry out dynamic mechanical thermal analysis of each material. Samples of dimension $46 \times 10 \times 3$ mm^3 were mounted in the DMTA machine in the dual cantilever mode. Strain sweeps were first carried out on each material at −100°C and +90°C to determine the range in which linear analysis could be used. A strain of 0.005 was found to be acceptable for all materials in this temperature range.

Temperature ramp tests were carried out for each material between the temperatures of −100°C and +90°C. The heating rate was 2°C/min, and the frequency used was 100 Hz.

Microscopy

The observation of the morphology of the various moldings was carried out in thin sections of ~15 μm, with an Olympus BH2 polarized light microscope. The thin sections were cut across the thickness of the parts, using a Leitz 1401 microtome, and mounted between a glass slide and a cover slip with Canada balsam for the microscopical observation.

RESULTS AND DISCUSSION

Cooling rates

The measured cooling rates for the three cooling regimes were 40°C/min for water cooling, 16°C/min for forced air cooling, and 14°C/min for quiescent cooling in ambient air.

Impact tests

Impact tests were carried out on the moldings at room temperature and at −40°C. The results from these tests are shown in Figures 1 and 2. It can be seen that the moldings with no forced cooling always have the lowest impact strength at both room temperature and at −40°C. The peak impact strength of the air-cooled and water-cooled moldings are very similar, particularly at room temperature, and at −40°C the air-cooled molding has only a slightly lower impact strength than the water-cooled molding. The effect of cooling rate is more significant on the total impact energy than on the peak energy. This supports earlier findings[7] that showed that an increase in crystallinity significantly reduces crack propagation energy.
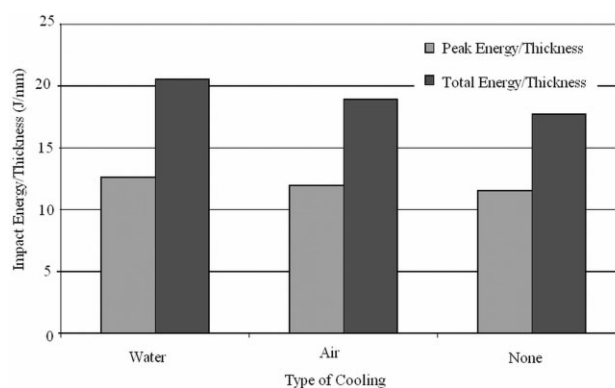

Figure 2 Impact test results at −40°C on moldings cooled in different ways.
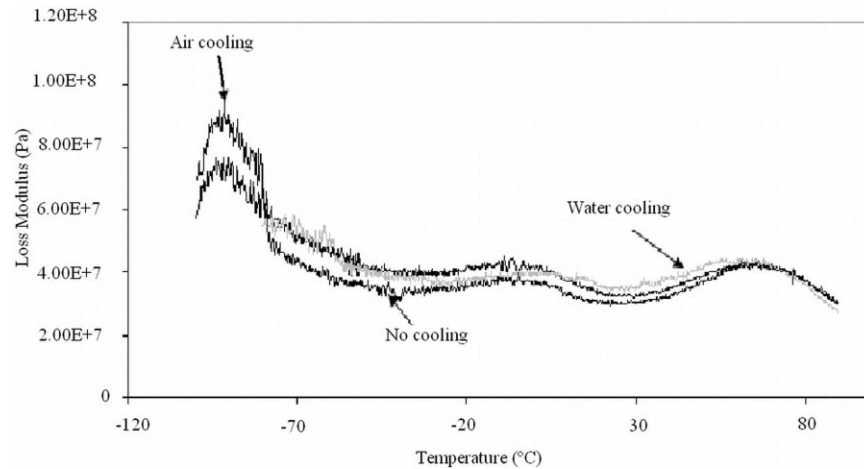
Figure 3 Loss modulus of moldings cooled in different ways.

Dynamic mechanical thermal analysis

The traces obtained from DMTA are shown in Figures 3–5. It can be seen that the loss modulus and tan δ traces are very similar for the air-cooled and water-cooled moldings at −40°C, while at 20°C the water-cooled molding actually has a slightly lower loss modulus, which corresponds to a slightly lower impact peak impact energy at this temperature. The loss modulus for the quiescently cooled molding is lower at both temperatures, as is its peak impact strength. The storage modulus traces indicate that the air-cooled and quiescently cooled moldings have a similar stiffness, and the water-cooled molding has a lower stiffness. This may correspond to the drop in crack propagation energy that is seen in the slower cooled moldings, particularly at −40°C. The tan δ trace for the water-cooled moldings is noticeably higher at elevated temperatures, and so this should correspond to higher impact strength at elevated temperatures.

Microscopy

The observations by polarized light microscopy showed that the moldings were free from bubbles and the crystalline texture was spherulitic all through the thickness of the wall. As Figures 6 and 7 show, the cooling rate had only a marginal effect on the morphology of the moldings. The only difference that can be seen is a small decrease in the size of the spherulites in the part cooled with water, which is a result of fast cooling. This is more evident near the mold, where the cooling is faster. It is thought that this finer structure results in higher impact strength. This is not only related to the smaller spherulites but also to a decrease in the crystallinity. Faster cooling results in a higher amount of amorphous material, which is the flexible part of the structure, more capable of absorbing energy.

At the outer surface some "transcrystalline" structures can be observed [left side of Fig. 7(a, c)] due to crystallization of the polymer being initiated at the surface contacting with the mold wall. Often the inner surface of a molding is prone to degradation because this surface is in contact with the air; however, in this case no degradation was evident.

In the case of the molding quiescently cooled, perhaps more interesting than the increase in the spherulite size is the modifications that the lower cooling rate
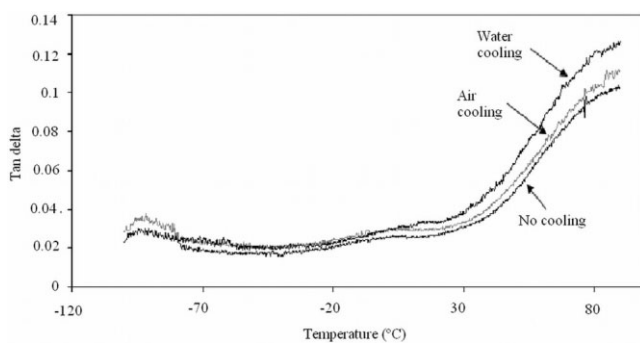

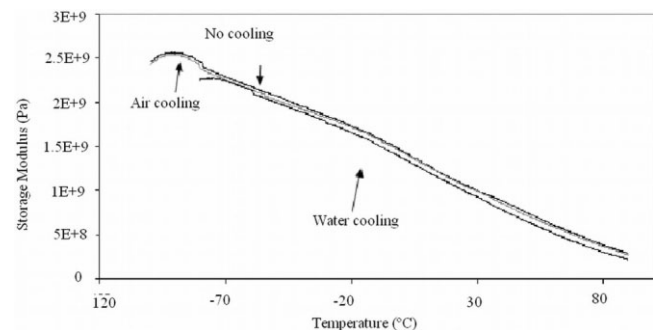**Figure 4** Tan δ of moldings cooled in different ways.

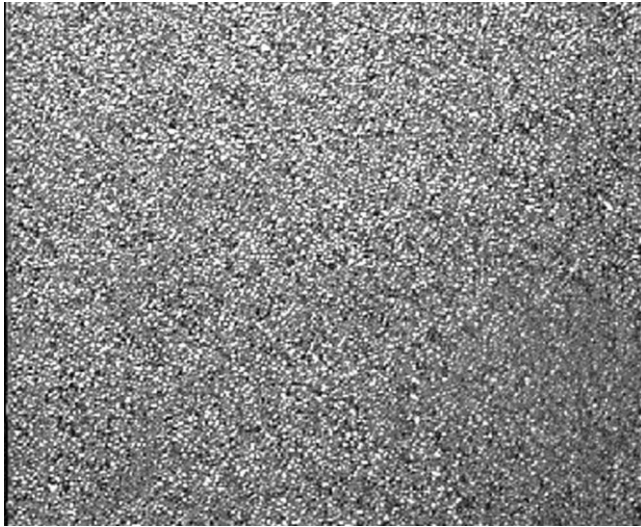**Figure 5** Storage modulus of moldings cooled in different ways.

Figure 6 Polarized light micrograph of molding produced using no forced cooling.

caused in the texture of the spherulites formed close to the inner surface. As Figure 7(d) shows, the slow cooling caused the spherulites to become more irregular than in the fast-cooled specimen [Fig. 7(b)] and to present clearly visible concentric dark rings. The spacing of these rings, which are typical of polyethylene spherulites,[8] is known to increase with the decrease of
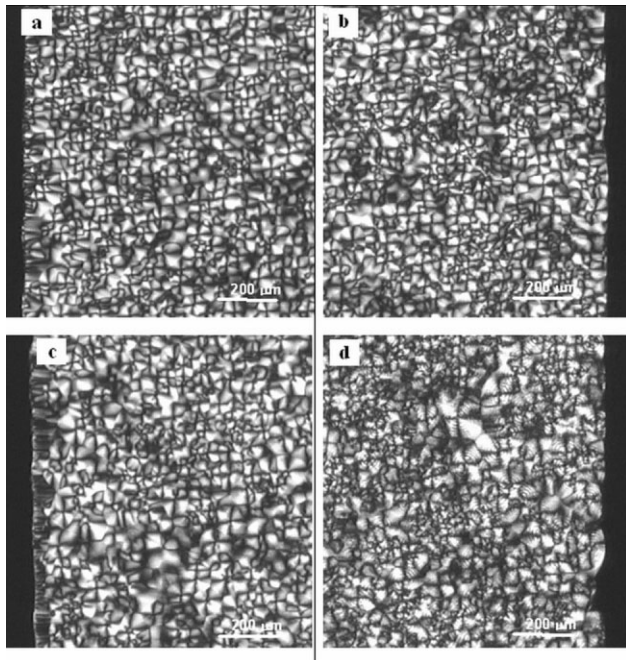

Figure 7 Polarized light micrographs showing the effect of cooling on the morphology of the moldings: (a) water-cooled molding (zone in contact with mold), (b) water-cooled molding (inner free zone), (c) no forced cooling (zone in contact with mold), and (d) no forced cooling (inner free zone).
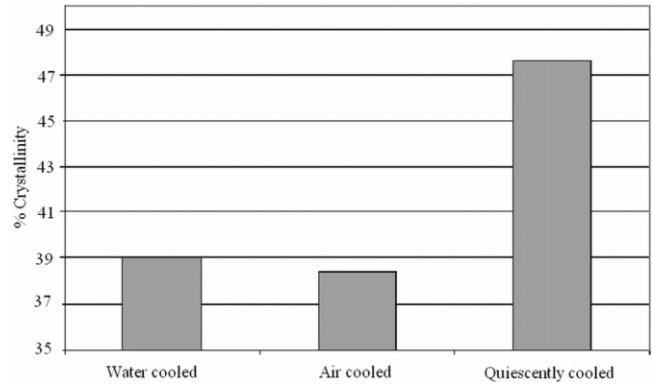

Figure 8 The crystallinity of the outer surface of moldings cooled in different ways.

the molecular weight or with the increase of the crystallization temperature.[9,10] Considering that in the absence of degradation little changes in molecular weight are expected to occur, the coarsening of the rings is the result of the crystallization that occurs at a higher temperature in the slow-cooled sample.

It has been previously shown that very large spherulites are detrimental to impact performance.[3-5] When spherulites are very large, more impurities will be present at the boundaries and this increases the stress concentration considerably.

Differential scanning calorimetry

Differential scanning calorimetry was carried out on samples from the outer and inner surfaces of each molding, and the results are shown in Figures 8 and 9.

The first observation is that there is a very large difference in the crystallinity of the inner and outer surfaces of the air- and water-cooled moldings. As discussed previously, this is due to the inner surface of the molding cooling at a much slower rate than does the outer surface. The crystallinity of the inner and outer surfaces of the quiescently cooled molding are
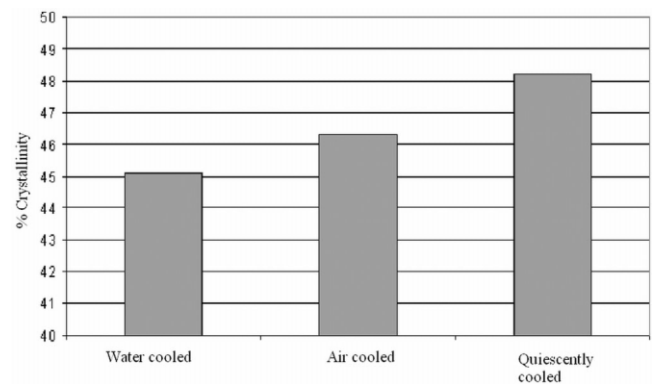

Figure 9 The crystallinity of the inner surface of moldings cooled in different ways.
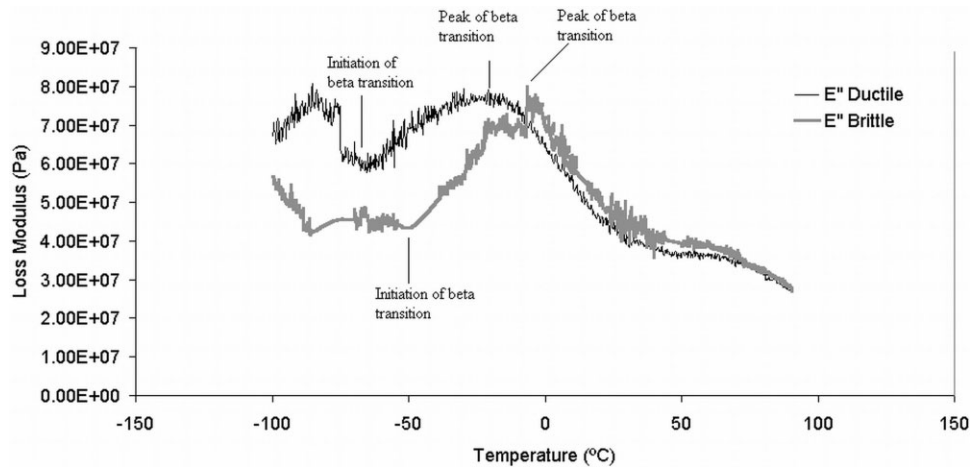
Figure 10 Loss modulus traces of the different parts.

more similar however. This is because this molding takes such a long time to cool that even the crystallinity of the outer surface begins to approach the maximum possible for this particular material.

Second, the rate at which that material is cooled clearly affects the crystallinity of the final molding. This is particularly apparent at the inner surface, where it can be seen that an increase in cooling rate decreases the crystallinity. At the outer surface there is very little difference in the crystallinity of the air- and water-cooled moldings. This can be attributed to the fact that using either cooling method will rapidly cool the outer surface and stop any further formation of crystals.

CASE STUDY: ANALYSIS OF A 6-MM-THICK ROTATIONALLY MOLDED PART

This section describes a study that was carried out to try and understand why two samples from the same rotomolded LLDPE part were failing in different ways, that is, one in a brittle manner when impact tested at −40°C and one in a ductile manner. Dynamic mechanical thermal analysis and microscopy were carried out on the two parts and the results are presented in the following sections.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis of the samples was performed. The tests were carried out between −100°C and +90°C at 100 Hz. The results are shown in Figures 10–12.

It can be seen that the loss modulus of the two materials is very similar at room temperature, but there is a significant drop in the loss modulus of the brittle sample at lower temperatures. This indicates that the brittle sample has less capacity to absorb impact energy at low test temperatures. If the samples are tested at room temperature they should exhibit similar impact resistance.
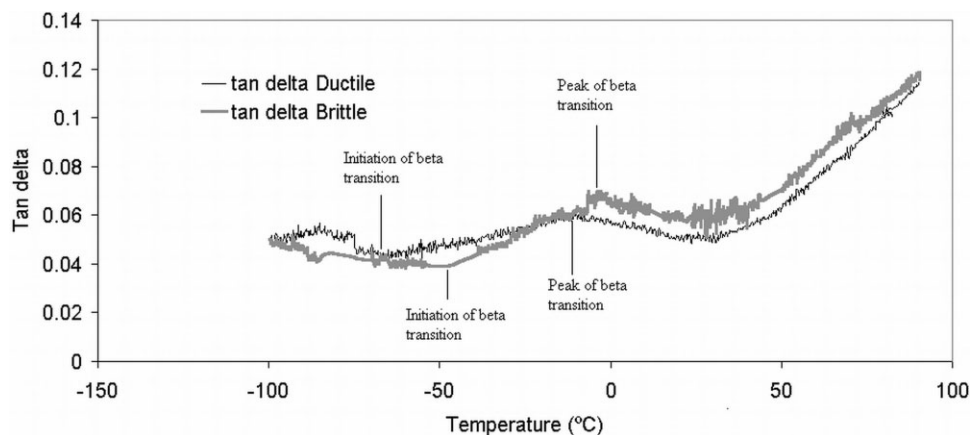

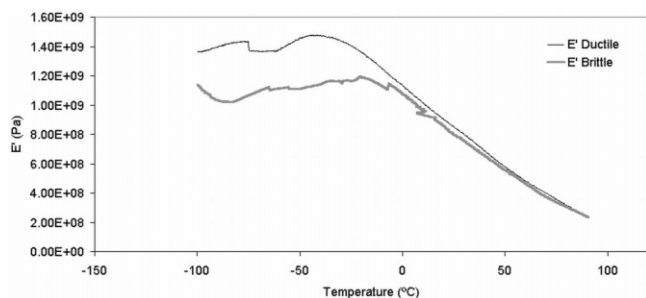**Figure 11** Tan δ traces of the different parts.

Figure 12 Storage modulus traces of the different parts.

Similarly, the tan δ traces show a drop at lower temperatures for the brittle sample. In addition to this, it is clear that the initiation of the β transition is at a much lower temperature in the ductile sample than in the brittle sample. The significance of this has been discussed in a previous work,[11] wherein it has been shown that on the initiation of this transition there is a shift from brittle to ductile failure under impact.

Microscopy

The microscopical analysis of cross sections cut from the brittle and ductile zones of the molding showed that in both zones there is a large variation in the size of the spherulites across the thickness, as can been seen in Figures 13 and 14. These differences arise mainly from the difference in cooling rate between the regions close to the mold wall and those close to the free inner surface, respectively. This difference in cooling rate is increased by the fact that the molding is very thick, ~6 mm, and also by the fact that a fast cooling procedure was used. Although the differences in morphology between the ductile and the brittle sample were not very great, it was visible that the sample with brittle behavior at low temperature shows a large increase in the size of the spherulites from the outer to the inner zone, but in each one of these zones the size is rather uniform. In the ductile sample, although a similar increase in the spherulite size is also observed, the morphology is more heterogeneous than in the brittle sample and a mixture of small and large spherulites are displayed in both the inner and outer zones.

The major differences in morphology of the samples occur at the inner surfaces. As shown in Figure 15(a, b), the brittle sample showed regularly shaped standard spherulites while the ductile one showed in some regions a modified crystalline texture consisting of elongated spherulites close to the inner surface and a large number of small spherulites at the border. However this texture was not uniform.

The modified crystalline texture illustrated in Figure 15(b) is commonly observed at the onset of oxidative degradation. The polymer might have already suffered some chemical modification of the molecular structure but no severe degradation had yet occurred. In a previous work,[12] it was observed that the best impact properties are obtained for the specimens in which degradation is just incipient.

As both samples are taken from the same molding, it may be concluded, from these observations, that the heating or cooling to various parts of the molding was not uniform. The absence of voids in the cross sections shows that the heating was not far from the correct level. What appears evident is that somehow at the ductile zone, due either to the heating being slightly more severe or to the cooling rate being lower, an incipient degradation with some degree of crosslinking of the polymer occurred at the border and this prevented the spherulites from increasing in size that was favorable to the impact behavior. In contrast, at the brittle zone the polymer remained unmodified, and consequently, the crystallization was determined only by the rate of cooling that, being very low, caused the spherulites to grow to a very large size and this generally causes deterioration of the impact strength. These observations lead us to conclude that in case of very thick moldings in the absence of internal cooling
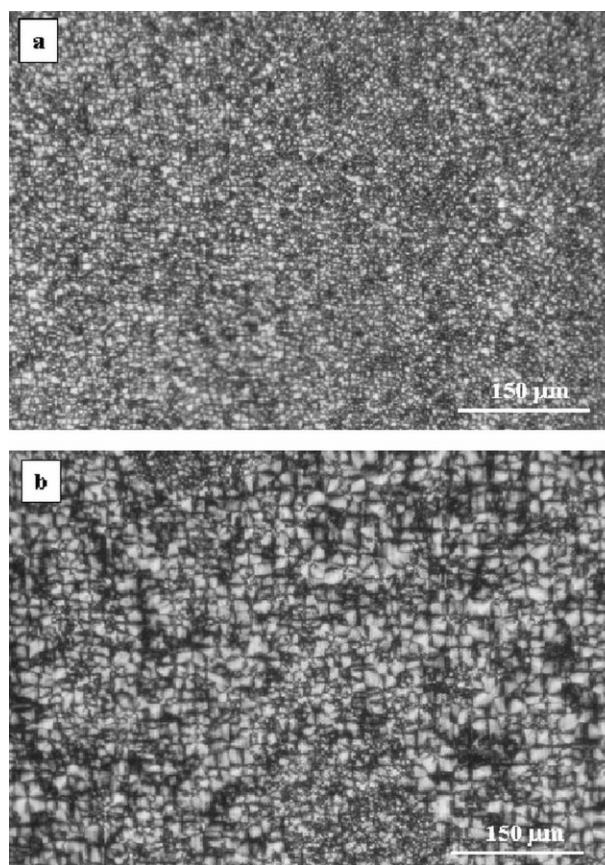

Figure 13 Cross sections of brittle specimen cut from the 6-mm molding observed at low magnification with the polarized light microscope: (a) zone close to the external surface and (b) zone close to the inner surface.
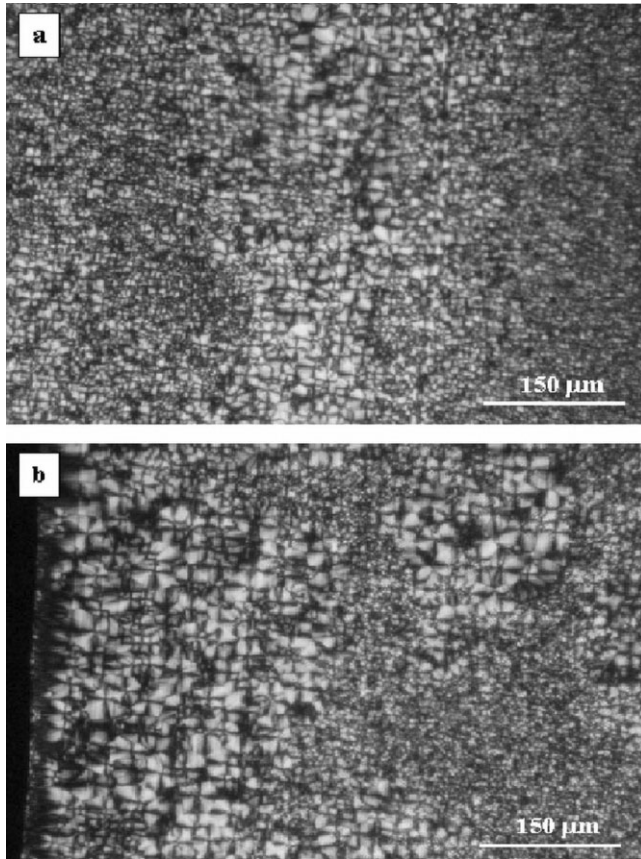
Figure 14 Cross sections of ductile specimen cut from the 6-mm molding observed at low magnification with the polarized light microscope: (a) zone close to external surface and (b) zone close to inner surface.

it is advisable to slightly overheat the part to cause some degree of crosslinking and that by doing so it is possible to avoid the formation of very coarse spherulites at the inner surface and improve the impact behavior.

CONCLUSIONS

The morphology and the crystallinity of polyethylene rotational moldings have been shown to have an extremely important effect upon impact performance. The following conclusions have been drawn from the study:

1. Changing the cooling rate had a much more significant effect on the total energy than on the peak energy of the materials tested, indicating that the higher crystallinity of the slower cooled moldings had the most detrimental effects on the crack propagation energy of the moldings and not on the crack initiation. This is similar to what was proposed earlier, and is due to a higher crystallinity, and larger and less perfect

spherulites, reducing the flexibility and toughness of the material. This agrees with previous research that showed that improving crack initiation resistance by increasing the crystallinity often reduces crack propagation resistance.[13]

2. The changes in morphology were reflected in the DMTA results obtained for the materials. It was seen that the quiescently cooled molding had a lower loss modulus and tan δ than did the other moldings, which indicates that its capacity for energy absorption is less. In addition to this, the storage modulus of this molding was higher, showing that it is stiffer than the faster cooled moldings and therefore more likely to propagate cracks more easily.

3. Microscopy showed that the water-cooled molding had smaller spherulites than did the other moldings and this is another contributing factor to its improved impact performance. It
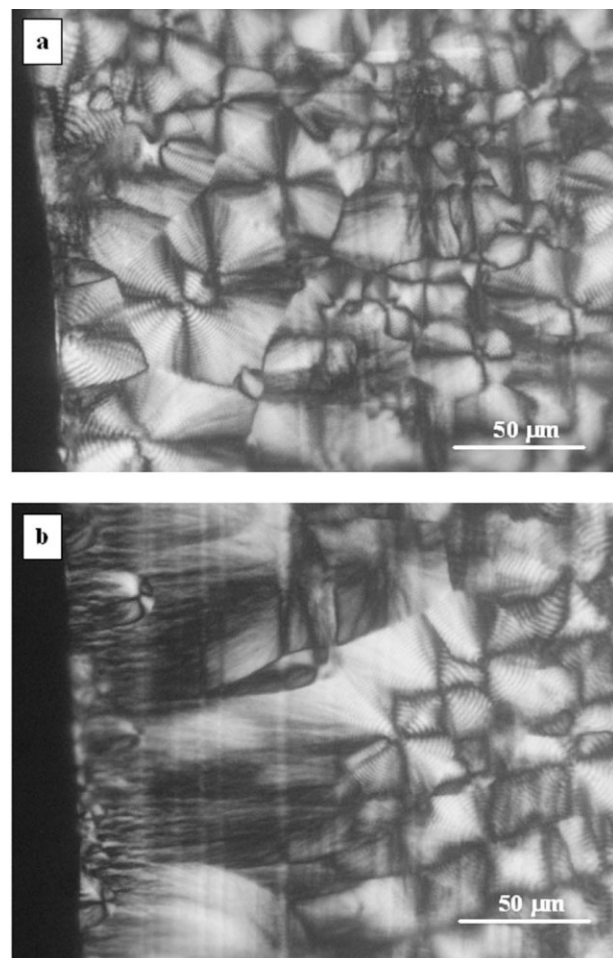

Figure 15 Higher magnification micrographs of the inner surface of the 6-mm molding: (a) brittle specimen under impact testing at −40°C, showing regular randomly nucleated spherulites; and (b) ductile specimen under impact testing at −40°C, showing elongated spherulites below the surface.

was shown that the size of the spherulites may be minimized by cooling moldings rapidly.

4. Results from DSC tests showed large variations in crystallinity between the inner and outer surfaces of both the air- and water-cooled moldings, and this was attributed to differences in cooling rates at the two surfaces. A clear reduction in percentage crystallinity of the inner surface zone can be obtained by using water cooling.

An analysis of the differences between the brittle and ductile zones of a 6-mm molding gave the following conclusions:

1. By carrying out DMTA tests, it was found that the brittle material has a much lower loss modulus at low temperatures, which indicates that it has less capacity to absorb energy. More importantly, it was found, when looking at the tan δ trace, that the β transition of the brittle material started at a much higher temperature than that of the ductile material. As was already discussed, the initiation of the β transition in LLDPE corresponds with a brittle–ductile transition.

2. The microscopy carried out on the samples indicated that the size of the spherulites was much bigger at the inner surface of the brittle sample than in the ductile sample, and this may be linked to its poorer impact performance. This was attributed to differences in heat transfer to and from the mold. This increase in the spherulite size explains the higher initiation of the β transition, and thus the brittle behavior of this sample. In case of thick moldings some degree of crosslinking at the inner surface appears to be beneficial to avoid the formation of very large spherulites.

References

1. Godinho, J. S. Property Variations in Polyethylene Articles Produced by a Variety of Molding Methods; Doctoral Thesis, Queen's University of Belfast, 1997.
2. Cramez, M. C.; Oliveira, M. J.; Crawford, R. J. Proc IMechE Part B: Eng Manuf 2003, 217, 323.
3. Xu, T.; Yu, J.; Jin, Z. Mater Design 2000, 22, 27.
4. Way, J. L.; Atkinson, J. R.; Nutting, J. J Mater Sci 1974, 9, 293.
5. Ismail, Y. S.; Richardson, M. O. W.; Olley, R. H. J Appl Polym Sci 2001, 79, 1704.
6. Daniels, C. A. Polymers: Structure and Properties; Technomic Publishing Company: Lancaster, PA, 1989.
7. Pick, L. T. An Investigation of the Impact Performance of Rotationally Molded Plastics; Doctoral Thesis, Queen's University of Belfast, 2004.
8. Keller, A. J Polym Sci 1955, 17, 291.
9. Janimak, J. J.; Markey, L.; Stevens, G. C. Polymer 2001, 42, 4675.
10. Tanem, B. S.; Stori, A. Polymer 2001, 42, 6609.
11. Pick, L.; Harkin-Jones, E. Proc IMechE Part L: J Mater: Design Appl 2005, 219, 1.
12. Oliveira, M. J.; Cramez, M. C.; Crawford, R. J. J Mater Sci 1996, 31, 2227.
13. Karger-Kocsis, J. Compos Sci Technol 1993, 48, 273.