# The Enhancement of the Mechanical Properties of a High-Density Polyethylene

# GÜRHAN KALAY,<sup>1</sup> RUI A. SOUSA,<sup>1,2</sup> RUI L. REIS,<sup>2,3</sup> ANTONIO M. CUNHA,<sup>2</sup> MICHAEL J. BEVIS<sup>1</sup>

<sup>1</sup> Wolfson Centre for Materials Processing, Brunel University, Uxbridge, Middlesex, UB8 3PH, United Kingdom

<sup>2</sup> Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800 Guimarães, Portugal

<sup>3</sup> INEB Institute for Biomedical Engineering, Laboratory for Biomaterials, Rua do Campo Alegre 823, 4150 Porto, Portugal

Received 4 August 1998; accepted 2 February 1999

ABSTRACT: This paper describes the process optimization in injection molding of highdensity polyethylene (HDPE). Both conventional injection molding and shear controlled orientation (SCORIM) were employed in processing. The process optimization was based on design of experiments and complemented with analysis of variance. Mechanical characterization was carried out by tensile testing. Wide-angle X-ray diffraction and differential scanning calorimetry were used for the structural characterization of the moldings. High-density polyethylene exhibits 7.2 GPa Young's modulus and 155 MPa of ultimate tensile strength following the application of SCORIM processing. These results account for a fourfold increase in Young's modulus and a fivefold increase in ultimate tensile strength compared to conventional injection molding. The maintenance of toughness while enhancing stiffness and strength of the SCORIM moldings is attributable to an oriented morphology developed during shear flow, i.e., shish-kebab structure. The frequency of shearing action has the strongest influence on the morphology development. It is also demonstrated that the studied parameters are very much interdependent. It is possible to achieve substantial gains in mechanical properties of HDPE in SCORIM processing without causing a substantial increase in cycle time. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2473-2483, 1999

**Key words:** high-density polyethylene; injection molding; shear controlled orientation in injection molding (SCORIM); process optimization; design of experiments

# **INTRODUCTION**

It is possible to control the physical properties of semicrystalline polymers by morphology management during processing.<sup>1-6</sup> Shear controlled orientation in injection molding (SCORIM)<sup>1,7,8</sup> has been demonstrated to be an effective processing route for the physical property enhancement of semicrystalline polymers and polymer matrix composites.<sup>1-10</sup> The shish-kebab morphology forming in SCORIM molded<sup>5,11</sup> or high-pressure injection molded<sup>12–14</sup> high-density polyethylene (HDPE) results in substantially improved Young's modulus and tensile strength. Kubát et al.<sup>12,13</sup> reported on the effect of processing conditions on the mechanical properties of HDPE and showed the way to process optimization. The main aim of this paper is to demonstrate the process optimization in SCORIM processing of HDPE, extending our previous paper.<sup>11</sup>

It is worth indicating an observation by Kubát et al.<sup>13</sup> about a mold equipped with an exit cavity, resulting in more enhanced properties for HDPE than a standard mold. The mold with an exit

Correspondence to: G. Kalay.

Journal of Applied Polymer Science, Vol. 73, 2473–2483 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/122473-11

	CMPE
Injection pressure (MPa)	11.3
Holding pressure (MPa)	5.8
Injection time (s)	0.75
Holding pressure time (s)	25
Cooling time (s)	15
Cycle time (s)	41.75
Mold temperature (°C)	40
Melt temperature (°C)	190

Table IProcessing Conditions for theConventional Molding of HDPE

cavity permits the flow of the material from the mold cavity to the exit cavity, which in turn results in further extensional and shear flow in high-pressure injection molding. This results in more homogeneous structure in the molded part.

The molten material is caused, however, to move between the piston's chambers in SCORIM processing, causing a macroscopic shearing action to be applied at the melt–solid interface. Therefore, the requirement for very high cavity pressures of 500 MPa<sup>12</sup> can be dispensed with in SCORIM. The simple principle is causing the material in the mold cavity to move as the solidification progresses from the surfaces of the mold to the core.

Guan et al.<sup>15,16</sup> reported on the structure and properties of self-reinforced HDPE prepared by oscillating packing injection molding, produced by a replication of SCORIM technology in their laboratories. Guan et al.<sup>15,16</sup> further published that Young's modulus and the tensile strength of HDPE have been enhanced from 1 GPa and 23 MPa to 5 GPa and 93 MPa, respectively. In this paper a further improvement above and beyond these values is reported.

## **EXPERIMENTAL**

#### Material

The study material was HDPE, grade HD8621, supplied by DSM Research BV (Geleen, The Netherlands) with a melt flow index of 0.16 g/10 min, a number average molecular weight  $(M_n)$  of 7000, a weight average molecular weight  $(M_w)$  of 210000 and a polydispersity  $(M_w/M_n)$  of 29.

# **Injection Molding**

A Demag D-150 NCIII-K conventional molding machine fitted with a  $SCORIM^1$  head was used to

produce round tensile test bars with 5 mm diameter and 15 mm gauge length.<sup>2</sup> In this work two molding techniques were employed: (1) conventional injection molding and (2) shear controlled orientation injection molding (SCORIM).<sup>1-3</sup> Several processing parameters were studied in the SCORIM processing of HDPE, i.e., holding and piston pressures, frequency of piston movements, and duration of shear applied. The SCORIM processing Mode  $A^2$ was used to induce shear flow in the melt cavity. With Mode A, the SCORIM pistons are reciprocated 180° out of phase with each other. The cycle was completed with the SCORIM processing Mode C<sup>2</sup> as a packing stage. With Mode C, both of the pistons are forced down to impose a static melt pressure in the mold. A SCORIM stage defines the duration of the piston movements and the frequency at which the pistons operate. Four stages were used in all sets of SCORIM moldings The SCORIM stages will be designated sequentially by S0, S1, S2, and S3. The stage S0 is to facilitate filling from one gate only, i.e., one gate is closed by one of the SCORIM pistons being pushed down. The cavity pressure profiles were monitored in order to control any variation during processing and to evaluate the influence of different processing conditions applied in molding. The reader may refer to ref. 2 for the accurate positions of the gates and sprue bushes, and the location of the pressure transducer, which was placed at one of the gates very near to the test bar.

The processing conditions for the conventional molding set CMPE, i.e. conventionally molded polyethylene, are summarized in Table I. The cavity pressure profile for set CMPE is shown in Figure 1.

Four sets were produced for HDPE according to an L4 array. In this array, the processing parameters were the holding pressure and the frequency of piston movement in stages S1 and S2. The sets molded according to the employed design can be described as follows:



Figure 1 Cavity pressure profile for set CMPE.

L4 Array	Low Level	High Level
Holding pressure (MPa)	3.8	6.3
Cycle period <sup>a</sup> (s)	2.0	1.0

Table IILevels of the Processing Parametersfor SCORIM Moldings of L4 Array of HDPE

<sup>a</sup> For each one of the SCORIM stages S1 and S2.

- SC-A at low holding pressures and low frequency of piston movements (3.8 MPa; 0.5 Hz).
- SC-B at low holding pressures and high frequency of piston movements (3.8 MPa; 1 Hz).
- SC-C at high holding pressures and low frequency of piston movements (6.3 MPa; 0.5 Hz).
- SC-D at high holding pressures and high frequency of piston movements (6.3 MPa; 1 Hz).

The details of the processing parameters for this array are summarized in Table II. In order to evaluate the influence of time for the third stage of SCORIM processing, three sets of samples were molded at two levels of holding pressures and the SCORIM pistons pressures, as follows (see Table III):

SC-E, -D, and -F with a total duration of piston's movements of 12, 18, and 24 s (in stage S2) at low holding and piston pressures.



Figure 2 Cavity pressure profile for set SC-C.

SC-G, -H, and -I with a total duration of piston's movements of 12, 18 ,and 24 s (in stage S2) at high holding and piston pressures.

It is important to note that the set SC-D is common to the array already described. Four SCORIM stages were used in all these sets. The difference between these two groups, besides the level of holding and piston pressures used for each case, is the duration of the fourth stage. This last stage is in principle a packing stage. Melt temperatures of 190°C (temperature profile in the barrel: 190/190/180/170/160°C) were used for all the moldings. The processing conditions for all the SCORIM moldings are presented in Table III. The values of piston pressures, which are summarized in Table III for each SCORIM molding, are presented as a percentage of the machine's maximum capacity. The cavity pressure profiles of SC-C and SC-I are shown respectively in Figures 2 and 3. Maximum cavity pressures of approximately 50 MPa are recorded for SC-C. The higher cavity pressures generated for SC-I are clear in Figure 3. It is possible to conclude that the effec-

	L4 Array	SC-E/SC-F	SC-G/SC-H/SC-I
Injection pressure (MPa)	11.3	11.3	11.3
Holding pressure (MPa)	_	6.3	8.8
Injection time (s)	0.75	0.75	0.75
Holding pressure time (s)	38	_	_
Cooling time (s)	15	15	15
Cycle time (s)	44.75	_	_
Mould temperature (°C)	40	40	140
Melt Temperature (°C)	190	190	190
Number of SCORIM stages	4	4	4
Stage time <sup>a</sup> (s)	1, 12, 18, 6	1, 12, -, 6	1, 12, -, 12
Cycle period <sup>b</sup> (s)	1.0, —, —	1.0, 1.0, 1.0	1.0, 1.0, 1.0
Pistons pressure <sup>a</sup> (1.99%)	45, 45, 36, 36	45, 45, 36, 36	55, 55, 46, 46

Table III Processing Conditions for SCORIM Moldings of HDPE

<sup>a</sup> For each one of the SCORIM stages S0, S1, S2, and S3.

<sup>b</sup> For each one of the SCORIM stages S0, S1, and S2.



Figure 3 Cavity pressure profile for set SC-I.

tive macroscopic shear of the melt is strongly dependent on the solidification of the material, which in fact depends on the level of piston pressures and the holding pressure applied. The use of higher piston pressures as in set SC-I results in a very pronounced shear of HDPE. However, the shear heating ought to be considered carefully in setting the piston pressures. There is an optimum pressure and frequency beyond which the material in the mold cavity will remain molten.

# **Mechanical Testing**

The tensile tests were performed on an Instron 4505 tensile testing machine. An Instron 2630 clip-on resistive extensometer was used with 10 mm of gauge length. The tensile test bars were tested in order to determine Young's modulus  $(E_{\text{Young}})$ , the secant modulus at 0.8 % strain  $(E_{0.8\%})$ , the ultimate tensile strength (UTS), the strain at peak (e<sub>p</sub>) and the strain at break point (e<sub>f</sub>). These tests were performed in a controlled environment (23°C and 55% relative humidity). The cross-head speed was 5 mm/min (8.3 × 10<sup>-5</sup> m/s) until 1.5 % strain, to determine accurately the modulus, and then increased to 50 mm/min (8.3 × 10<sup>-4</sup> m/s) until fracture. Seven samples were tested for each condition.

Charpy flexural impact testing was carried out on few samples to prepare specimens for fractographic examination.

#### Wide Angle X-ray Diffraction and Debye Patterns

 ${\rm CuK}_{\alpha}$  radiation was used to obtain X-ray diffraction spectra and Debye patterns. The Debye patterns were gained for selected samples in order to assess the preferred orientation. The diffraction data were acquired at a rate of  $0.02^{\circ} 2\theta$ /s and over a Bragg angle range of  $0^{\circ} < 2\theta < 50^{\circ}$ . The samples were cut parallel to the injection direction with a thickness of 1.5 mm. The Debye patterns were obtained at positions of 1.5 mm from the edge of the moldings. An aperture of 100  $\mu$ m of diameter

was used to define the position and cross-section of the incident X-ray beam.

## Differential Scanning Calorimetry (DSC)

Calorimetric studies were performed in order to examine the crystallinity and the phase relations for the moldings produced by different processing routes. These studies were performed on a differential scanning calorimeter Perkin Elmer DSC 7. Each sample was cut from the middle point of the gauge length of the tensile test bars, with an average weight between 7 and 9 mg. The samples were placed in aluminum pans and heated at a rate of 10.0°C/min from 30 to 180°C.

#### Scanning Electron Microscopy

Scanning electron microscopy was performed for fractographic analysis on selected sets on a Leica Cambridge LS360 scanning electron microscope. All the surfaces were mounted on a copper stub and coated by ion sputtering with an Au/Pd alloy prior to examination.

#### **Statistical Analysis**

Analysis of variance (ANOVA) was applied to the tensile test results according to each design of experiments described. A two-way analysis of variance was performed in sets SC-A to SC-D. The analysis of two controlled parameters is made in a two-way ANOVA. Due to nonorthogonality between groups of sets SC-E, -D, and -F, and SC-G, -H, and -I, which differ in more than one processing parameter at the same time, a one-way analysis of variance was performed for the tensile test results of each group. The effect of only one controlled parameter is considered in a one-way ANOVA. For all cases, an F test, at a 95% confidence level, was applied to test the significance between the sample's averages. Table IV summarizes the results of the analysis of variance for the Young's modulus for SC-A to -D. Table V summarizes the results of the analysis of variance for the ultimate tensile strength for the same moldings. In these tables total sums of squares (SS) is a measure of the total variation present in the data collected for one specific experimental design. In a one-way ANOVA, the total variation can be decomposed into several sources of variation: the variation due to the controlled parameter (main effect) and the variation due to the error (residual). In a two-way ANOVA, the total variation is composed for two additional sources of

Source of Variation	SS	df	V	F
Main effects				
Frequency of piston movements/cycle period	187211.3	1	187211.3	3.23
Holding pressure	2810250.5	1	2810250.5	48.50
Two-factor interaction				
Frequency of piston movements · holding pressure	1304072.5	1	1304072.5	22.50
Residual	927148.4	16	57946.7	
Total	5228682.6	19		

Table IV Analysis of Variance for Young's Modulus for SC-A to SC-D of HDPE

variation: the variation due to the second controlled parameter (main effect) and the variation due to the interaction between the controlled parameters (two factor interaction). The total degree of freedom (df) is defined according to the experimental design and is related to the number of independent comparisons able to be made with data. The degrees of freedom can be decomposed into several sources. As an example and only for a two-way ANOVA, the total degree of freedom is given by the sum of the degrees of freedom associated with the first controlled parameter, the second controlled parameter, the interaction between controlled parameters and the error. The variance (V) is given by the quotient of each sum of squares by the respective degrees of freedom. The error variance or residual variance is a measure of the variation due to uncontrolled factors. The *F* test consists in the ratio of two estimates of individual variance: the variance due to a main effect (or interaction) and the variance due to the error. The significance of this quotient is determined by the degrees of freedom of the numerator, the denominator, and the confidence level desired. Parameters or interactions that present an *F* ratio larger than a defined criterion will be considered relevant and are believed to influence the average value of the population. A detailed description of the mathematical fundamentals of analysis of variance as well as of other statistical analysis, suited to experimental interpretation of data, can be found elsewhere.<sup>17–19</sup>

#### **RESULTS AND DISCUSSION**

#### **Tensile Testing and Statistical Analysis**

Table VI summarizes the tensile test results for CMPE, SC-C, and SC-I. The conventional moldings exhibit an ultimate tensile strength (UTS) of about 30 MPa and a strain at a peak of 3% compared with a 155 MPa UTS and 7% strain at peak for SC-I. This accounts for a fivefold increase in the UTS and a twofold increase in the strain at peak for the HDPE following the application of SCORIM. The CMPE moldings exhibit 1.4 GPa of Young's modulus whereas the SC-I moldings exhibits 7.2 GPa of Young's modulus, representing a fourfold increase in stiffness for moldings processed with SCORIM.

The SC-I were produced with the application of multiple piston movements. However, it is still possible to obtain substantial increase in the mechanical properties of HDPE with fewer piston strokes, which in turn causes only a limited increase in cycle time with SCORIM compared with conventional molding (Figures 1–3). The SC-C moldings exhibit

Table V	Analysis of	Variance for	or the	Ultimate	Tensile	Strength	for	SC-A	to	SC-D	) of [	HDP	E
						···· <b>·</b> · · · · · · · · · · · · · · · ·							

Source of Variation	SS	df	V	F
Main effects				
Frequency of piston movements/cycle period	68.08	1	68.08	2.00
Holding pressure	208.01	1	208.01	6.10
Two-factor interaction				
Frequency of piston movements · holding pressure	139.92	1	139.92	4.10
Residual	545.68	16	34.10	
Total	961.70	19		

Young's Modulus Set (MPa) M		Secant Modulus (MPa)	Ultimate Tensile Strength (MPa)	Strain at Peak (%)	Strain at Break Point (%)
CM	1402 (57)	1145 (38)	29.3 (0.6)	3.1 (0.2)	155.4 (39.6)
SC-C	6455 (202)	5068 (155)	127.6 (2.5)	6.7(1.1)	21.6 (4.9)
SC-I	7241 (98)	5780 (107)	154.9 (3.7)	7.4 (1.0)	21.2 (4.2)

 Table VI
 Tensile Test Data for Both Conventional and SCORIM Moldings of

 HDPE (Standard Deviations Are Shown in Parantheses)

6.7% of strain at peak, 128 MPa of UTS, and 6.5 GPa of Young's modulus. These results prove again a substantial improvement in the mechanical properties of HDPE with SCORIM. The SC-C moldings that were molded at high holding pressures and low frequency of piston movement exhibit the highest of Array 1. These results also indicate an increased toughness for the SCORIM processed HDPE, which is consistent with the previous reports on other semicrystalline polymers.<sup>7–9</sup> The strain at break point for the moldings presented in Table IV may be misleading as the strain values are well beyond the strain at peak and such strain values would not mainly be considered for design purposes in engineering applications despite their indirect importance with respect to stress concentrations and energy absorption. The conventional moldings become fibrous in tensile testing, which in fact can be seen as a drawing process. The SCORIM moldings are not ductile like the conventional moldings processed at relatively low cavity pressures. In fact, the conventional moldings processed at high cavity pressures exhibit much lower values of strain at break.<sup>1–3</sup> Figures 4 and 5 show the impact failure surfaces of a conventional molding processed at high cavity pressures and a SCORIM molding. Both failure surfaces are planar. However, the layered structure of the SCORIM molding is evident, which is consistent with the Debye patterns presented below. Figure 6 shows the superimposed stressstrain diagrams of the conventional molding CMPE, SC-C, and SC-I. It is worth indicating that the results for SC-C and SC-I prove that is possible to achieve substantial gains in mechanical properties in SCORIM processing without causing a substantial increase in cycle time.

Figure 7 plots the variation of Young's modulus for the L4 array. The effect of the frequency of piston movement is pronounced. The interaction between the processing parameters is also evident in Figure 7. Considering the degrees of freedom involved for this array, a processing parameter—or the interaction between processing parameters—will be considered as relevant for a confidence level of 95 % if its F value, presented by analysis of variance, is larger than 4.49.<sup>1</sup> The ANOVA results, presented in Table IV, show that the holding pressure with an F value of 3.23 does not present a relevant importance. The frequency of pistons movement exhibits an F value of 48.50 and is the most important source of variation. The interaction of the processing parameters is the second largest source of variation with an F value of 22.05.

The variation of the ultimate tensile strength as a function of holding pressure is plotted in Figure 8. In this case, the influence of the processing parameters in the total variation is lower. The larger main effect is the frequency of piston movements. The results of analysis of variance presented in Table V confirm this parameter as being the most important main effect with an F value of 6.10. The holding pressure and the two-factor interaction are not believed to influence the average of the population. The stiffness increase of HDPE with SCORIM seems to be favored by high hold-



**Figure 4** The impact failure surface of a conventionally molded HDPE.



**Figure 5** The impact failure surface of a SCORIM molded HDPE.

ing pressures and low frequency of piston movements.

The variation of Young's modulus as a function of the duration of piston movements-by means of the duration of stage S2— is plotted in Figure 9 for two levels of holding and piston pressures. The variation of Young's modulus is reduced with a maximum relative difference between average points of 5% at low level of holding and piston pressures. The effect of the duration of shear applied appears negligible at low holding and piston pressures. A large variation of the Young's modulus occurs at high level of holding and piston pressures. The improvements of 247, 306, and 416% compared with the conventional moldings are achieved for 37, 43, and 49 s of shear applied, respectively. Analysis of variance confirmed the influence of the duration of shear applied, which



**Figure 6** Superimposed stress-strain diagrams of CMPE, SC-C, and SC-I.



**Figure 7** Young's modulus variation for HDPE as a function of holding pressure and frequency of pistons movement:  $(-\phi-)$  1.0 s for compression and relaxation of the pistons;  $(-\diamond-)$  2.0 s for compression and relaxation of the pistons.

presented an F value of 192 (significant at 99% confidence level).

In Figure 10, the variation of the ultimate strength is plotted as a function of the duration of piston movements in stage S2. The influence of the duration of piston movements at a low level of holding and piston pressures appears to be not relevant, according to ANOVA. For these conditions, a threefold increase for the ultimate tensile strength is achieved with SCORIM compared to conventional injection molding. At a high level of



**Figure 8** Maximum stress variation for HDPE as a function of holding pressure and frequency of piston movement:  $(-\phi-)$  1.0 s for compression and relaxation of the pistons;  $(-\phi-)$  2.0 s for compression and relaxation of the pistons.



**Figure 9** Young's modulus variation for HDPE as a function of the duration of piston movement in stage S2 of SCORIM, at two levels of holding and piston's pressures:  $(-\diamondsuit-)$  6.3 MPa of holding pressure and 45/45/36/36% of pressure profile of the pistons;  $(-\bigstar-)$  8.8 MPa of holding pressure and 55/55/46/46% of pressure profile of the pistons.

pressures, the influence of the duration of piston movement is pronounced and presents an F value of 68.91 (significant at 99% confidence level).

The increase of stiffness in SCORIM moldings results from an oriented morphology developed during shear flow. The molecular alignment



**Figure 10** Ultimate tensile strength variation for HDPE as a function of duration of piston movement in stage S2 of SCORIM, at two levels of holding and piston's pressures:  $(-\diamondsuit-)$  6.3 MPa of holding pressure and 45/45/36/36% of pressure profile of the pistons;  $(-\bigstar-)$  8.8 MPa of holding pressure and 55/55/46/46% of pressure profile of the pistons.



**Figure 11** X-ray diffraction profiles from CM, SC-B, and SC-I moldings.

seems to be promoted by the application of high holding pressures, high shear stresses, and longer duration of shear. The frequency of piston movements is also an important parameter. Intermediate frequencies seem to be suitable to achieve enhanced mechanical properties for low durations of shear applied.

# Wide Angle X-ray Diffraction and Debye Patterns

Figure 11 shows the diffraction profiles for CMPE, SC-B, and SC-I. The increase of crystallinity in SCORIM moldings is evident from the greater crystalline peak areas of these moldings. This result is consistent with the DSC investigations presented below. The reflection at  $2\theta$  of 29.91° is present for SCORIM moldings, as a result of the shear imposed during molding, whereas it is not observed in conventional molding for this given orientation of the samples.

The use of longer durations of piston movements and higher holding and piston pressures leads to further enhancement of crystallinity as evident from the results for SC-I. The morphology associated with the oriented SCORIM moldings is a shish-kebab morphology.<sup>2,3,6</sup> As a result, an increase of molecular orientation occurs with the consequent enhancement of stiffness.



Figure 12 X-ray diffraction pattern for CMPE.

Figure 12 shows the Debye patterns gained for CMPE. No preferred orientation is observed as evident by the appearance of continuous Debye rings. However, SCORIM moldings exhibit strongly preferred orientation as shown by the Debye pattern shown in Figure 13.

# **Differential Scanning Calorimetry**

Table VII presents the melting point and the enthalpy of fusion for CMPE, SC-C, SC-G, and SC-I moldings obtained from the DSC analyses. The calculation of the crystallinity for each molding



Figure 13 X-ray diffraction pattern for SC-I.

Table VII DSC Results for CM, SC-B, SC-C, and SC-I Moldings and the Respective Young's Modulus

Set	$T_p$ (°C)	$\Delta H (J/g)$	% Crystallinity	Young's Modulus (MPa)
CM SC-C SC-G SC-I	$130.6 \\ 130.5 \\ 130.5 \\ 131.1$	185.3 203.0 202.3 207.0	$66.9 \\ 73.3 \\ 73.0 \\ 74.7$	$1402 \\ 6455 \\ 4870 \\ 7241$

was based on the value of  $\Delta H^{\rm o}{}_{\rm m}$  of 277 J/g for a 100% crystalline PE.

Figure 14 shows the DSC thermogram for CMPE. A single melting endotherm occurs at 130.3°C for CMPE, which exhibits a mainly spherulitic morphology. Figure 15 shows the DSC thermogram for SC-I. A high temperature melting endotherm appears in addition to the main melting endotherm at 130 °C. This endotherm is associated with the shish-kebab morphology of the SCORIM moldings.<sup>11</sup> Guan et al.<sup>15</sup> also reported this type of multiplicity of the melting endotherms for HDPE exhibiting high modulus values. There is a 6% increase in crystallinity for the SCORIM moldings in comparison to the conventional molding. This is consistent with the enhanced mechanical properties of SCORIM moldings. SC-C presents 73.3% of crystallinity. The increase of the duration of piston movements-that for SC-G to SC-I-leads to an increase of the area of the second melting endotherm peak. As a consequence, the crystallinity further improves to 74.7% for SC-I, which is the highest value of crystallinity achieved for all the moldings produced. The degree of orientation improves for the moldings produced at higher durations of piston movements and higher holding and piston pressures. There appears to be a correlation between the degree of orientation—or stiffness and the intensity of the second melting endotherm.

# **CONCLUSIONS**

The conclusions of this investigation may be summarized as follows:

1. High-density polyethylene exhibits 7.2 GPa Young's modulus following the application of SCORIM processing compared



Figure 14 DSC thermogram for CMPE.

with 1.4 GPa Young's modulus achieved with conventional injection molding. The ultimate tensile strength of the SCORIM moldings is fivefold greater than that of the conventional moldings. These results also indicate maintenance of toughness while enhancing stiffness and strength of the SCORIM moldings compared with the conventional moldings, which is consistent with the previous reports.<sup>1,2,5,10</sup>

- 2. ANOVA was satisfactorily applied for the process optimization in SCORIM processing.
- 3. It is demonstrated that the studied parameters, particularly the piston pressures, the frequency of piston movements, and the holding pressure, are very much interdependent.
- 4. It is evident that the frequency of piston movements has the strongest influence on the morphology development. High fre-



Figure 15 DSC thermogram for SC-I.

quency of piston movements in the SCORIM molding of HDPE are to be avoided, in order not to generate severe shear heating and to allow for the material to solidify.

5. It is possible to achieve substantial gains in mechanical properties in SCORIM processing without causing a substantial increase in cycle time.

These results indicate the merits for further investigation of processing conditions for the optimization of mechanical properties.

We gratefully acknowledge the material supplied by DSM Research (Geleen, Netherlands). The HDPE investigation was carried out within the Brite Euram Programme DECRYPO. The work of Rui A. de Sousa is financially supported by Subprograma Ciência e Tecnologia do 2° Quadro Comunitário de Apoio, Ministério da Ciência e Tecnologia (Portugal).

# REFERENCES

- Kalay, G.; Allan, P. S.; Bevis, M. J. Kunststoffe 1997, 87, 6, 768.
- Kalay, G.; Bevis, M. J. J Polym Sci Polym Phys 1997, 35, 241.
- Kalay, G.; Bevis, M. J. J Polym Sci Poly Phys 1997, 35, 265.
- Kalay, G.; Bevis, M. J. J Polym Sci Polym Phys 1997, 35, 415.

- Kalay, G.; Ogbonna, C. I.; Allan, P. S.; Bevis, M. J. Trans IChemE Part A Chem Eng Res Design 1995, 73, 798.
- Keller, A.; Kolnaar, H. Mat Sci Technol 1997, 18, 191.
- 7. Allan, P. S.; Bevis, M. J. British Patent 2170-140-B (1987).
- Allan., P. S.; Bevis, M. J., Composites Manufact 1990, 1, 79.
- Wang, L.; Allan, P. S.; Bevis, M. J., Plastics Rubber Composites Process Appl 1995, 23, 139.
- Gil, E. M.; Kalay, G.; Allan, P. S.; Bevis M. J. In Polymer Process Engineering 97; Coates, P. D., Ed.; The Institute of Materials: London, 1997; pp. 40-54.
- Ogbonna, C. I.; Kalay, G.; Allan, P. S.; Bevis, M. J. J Appl Polym Sci 1995, 58, 2131.
- Kubát, J.; Månson, J. A., Polym Eng Sci 1983, 23, 86.
- Kubát, J.; Månson, J. A.; Rigdahl, M., Polym Eng Sci 1983, 23, 877.
- 14. Boldizar, A.; Kubát, J.; Rigdahl, M., J Appl Polym Sci 1990, 39, 63.
- Guan, Q.; Shen, K.; Ji, J.; Zhu, J. J Appl Polym Sci 1995, 55, 1797.
- Guan, Q.; Shen, K. Z. Chem J Chinese Univers 1995, 16, 1129.
- 17. Ross, J. P., Taguchi Techniques for Quality Engineering; McGraw-Hill: New York, 1998.
- Schmidt, S. R.; Launsby, R. G. Understanding Industrial Designed Experiments, 4th ed.; Air Academy Press: CO, 1994.
- 19. Montgomery, D. C. Design and Analysis of Experiments, 3rd ed.; Wiley: New York, 1991.