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DESIGNED EXPERIMENT FOR POLYETHYLENE CRYSTALLIZATION BY DSC

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ABSTRACT

A central composite design involving three independent variables was used to define an experimental design matrix of crystallization conditions for polyethylene. The independent variables examined were cooling rate, isothermal crystallization temperature and total time at the crystallization temperature. The crystallization schemes were carried out in the differential scanning calorimeter and the subsequent data from melting thermograms were statistically analyzed in terms of endothermic peak temperatures, peak heights, number of discernible peaks and total heat of fusion. The effect of the independent variables on the well-defined, high temperature endotherm was accurately delineated. However, difficulties were encountered in identifying peaks other than the major peak, and this limited the scope of the statistical analysis.

INTRODUCTION

Typically, in a "controlled" experiment, each independent variable is examined in a one-variable-at-a-time manner while all other variables are held constant. A major drawback of this type of experimentation is that considerable time, effort and cost must be afforded in order to delineate with reasonable precision the relationships between the independent factors and dependent variables. In addition, any non-additive effects (interactions) that might be present will probably not be observed. These difficulties can be avoided in a statistically designed experiment where several control variables are perturbed simultaneously.

In this type of statistically designed experiment, the relationship between each independent or control variable and the associated response of the dependent variable is examined. In the utilization of statistically based experimental design, the objectives are as follows: (1) to deduce which independent variables have the greatest impact on the response; (2) to

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determine if these variables act in an additive manner or if interactions exist; (3) to ascertain if the relationships are linear or non-linear; and (4) to predict outcomes with a reasonable amount of precision [1].

In this study, the experimental design approach was employed to examine the crystallization of linear low density polyethylene (LLDPE) by thermal analysis. This polymer displayed multiple melting endotherms following crystallization from the melt. The number of peaks and their temperatures were dependent on the thermal history of the polymer. Cooling rate, isothermal crystallization temperature and time at the crystallization temperature were used as the control variables in the designed experiment. The objective was to determine if insights into the crystallization process could be attained by performing a designed experiment instead of using the more classical approach of controlled experimentation. A central composite design involving three variables was chosen for this purpose as curvilinear relationships were expected.

EXPERIMENTAL DESIGN

The central composite design comprises three main parts, each consisting of a set of points: cube, star and center. The first part contains the cube points which are represented by the vertices of a k-dimensional "cube" (Fig. 1(a)) where k is the number of independent variables under examination.

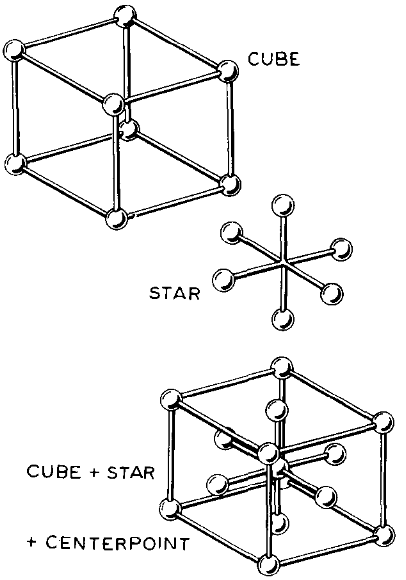

Fig. 1. The central composite design model consisting of : (a) a set of cube points; (b) a set of star points; and (c) the complete factorial cube including the center point.

For this design, the number of cube points equals 2^k. In the second part, the star points, shown in Fig. 1(b), are located at the vertices of a k-dimensional star and their number is defined as $2k$. The final part includes the center points n_0 which can be used to evaluate the non-linear dependence of the response and to estimate pure error. The complete central composite design encompasses $2^k + 2k + n_0$ points or experimental runs for a full factorial "cube" as shown in Fig. 1(c).

The levels of each of the variables are indicated by one of five coded quantities: $-\alpha$, -1, 0, $+1$, or $+\alpha$. The center point is defined to be the case where all variables are positioned at the "0" level. Points at the vertices of the cube are identified by the levels of the variables set to ± 1. When $\alpha > 1$ and $\alpha < 1$, the star points are positioned outside and inside the cube respectively. For statistical reasons not presented here, the distance of the star points from the center of the design was selected to be $\alpha = 2^{k/4} = \pm 1.682$ [2]. In this study, the following three independent variables were evaluated: cooling rate, isothermal crystallization temperature and crystallization time. Owing to the limitation of the differential scanning calorimeter, cooling rates were fixed at 0.31, 0.62, 1.25, 2.5 and 5.0 °C min^{-1}.

The isothermal crystallization temperature range investigated was from 100 to 130 °C. Therefore, 100 (the negative star point) and 130 (the positive star point) were located -1.682 and $+1.682$ units from the center, respectively. The cube points can be evaluated from the relation

$$\text{Coded level} = (\text{SP} - \text{CP})/\text{SF} \tag{1}$$

where SP is the set point (crystallization temperature in this case), CP is the center point and SF is the scale factor. For values of $\alpha = -1.682$ and $\text{CP} = 115$ °C, the evaluated scale factor was 8.9, and subsequently the cube points were determined to be 106 and 124 °C.

The crystallization time used ranged from 1 to 1000 min. Because of the large time range (three orders of magnitude), eqn. (1) used in the logarithmic form

$$\alpha = (\log \text{SP} - \log \text{CP})/\log \text{SF} \tag{1a}$$

Values for CP and SF determined by solving eqn. (1a) for SP equal to 1 and 1000 min. were 32 min. (31.6) and 7.79 respectively. This resulted in cube

TABLE 1

The set points determined from the central composite design for second-order responses and three independent variables

Variable	$-\alpha$	-1	0	$+1$	$+\alpha$
Cooling rate	0.30	0.60	1.25	2.50	5.00
Cryst. temp.	100	106	115	124	130
Cryst. time	1	4	32	246	1000

point times of 4 and 246 min. A summary of the set points and levels employed for the three control variables is shown in Table 1.

EXPERIMENTAL

Linear low density polyethylene (LLDPE), an octene copolymer supplied by Dow Chemical Co. (Freeport, TX), was used in this study. Thermal profiles were performed in a Perkin-Elmer DSC IIC differential scanning calorimeter. About 3 mg of polymer were heated to 170 ° C and held at this temperature for 5 min. The polymer was then cooled at 0.31, 0.62, 1.25, 2.5 or 5 ° C min^{-1} to the isothermal crystallization temperature. The sample was held at this temperature for a predetermined length of time before cooling to 30 ° C at the same cooling rate. Thermograms were collected as the specimen was heated from 30 to 170 ° C at 20 ° C min^{-1}. The 15 experimental trial runs produced from the three-variable central composite design are listed in Table 2. Two of the cube points (trials 2 and 4) and the center point (trial 1) were repeated to give a total of 18 experimental runs.

In addition, specimens were crystallized by cooling at a constant rate of 0.31, 0.62, 1.25, 2.5, 5.0, 10, 20 or 40 ° C min^{-1} from 170 to 30 ° C. Each polyethylene sample was then heated from 30 to 170 ° C as before. Both cooling and heating thermograms were collected for these samples crystallized at a constant cooling rate.

TABLE 2

Experimental trial runs

Trial number	Cooling rate (° C min^{-1})	Crystallization temperature (° C)	Crystallization time (min)
1	1.25	115	32
2	0.60	106	4
3	2.50	124	4
4	2.50	124	246
5	0.60	106	246
6	2.50	106	246
7	0.60	124	246
8	0.60	124	4
9	2.50	106	4
10	0.30	115	32
11	5.00	115	32
12	1.25	100	32
13	1.25	130	32
14	1.25	115	1
15	1.25	115	1000
16 (repeat 2)	0.60	106	4
17 (repeat 4)	2.50	124	246
18 (repeat 1)	1.25	115	32

RESULTS AND DISCUSSION

Heating thermograms collected for trial runs 1 and 9 are shown in Fig. 2. The multiplicity of melting peaks is attributed to polymer fractionation or segregation during the prior crystallization process [3–7]. Molecular fractionation is the separation of molecules from one another during crystallization as a result of differences such as molecular weight and branching characteristics. Consequently, the shape, position and number of melt endotherms were functions of the previous crystallization conditions. In this study, characterization of the thermograms for the 18 experimental trial runs in the designed experiment was achieved in terms of endothermic peak temperatures, peak heights, number of discernible peaks and total heat of fusion.

To aid in the molecular interpretation of the results of the designed experiment, the crystallization and melting characteristics of samples cooled from the melt at constant rates were analyzed. Values of (1) the temperature of the onset of crystallization (2) the exotherm peak temperatures of a sharp crystallization peak and a lower temperature, cooling rate dependent, broad crystallization peak, and (3) the melt peak temperatures of a sharp, high temperature endotherm, an intermediate positioned, cooling rate dependent shoulder on the high temperature endotherm and a lower temperature, broad endotherm are shown in Table 3 as a function of cooling rate. As the cooling rate was increased, the degree of supercooling increased as is commonly observed for semi-crystalline polymers. No significant effect on melt temperature was observed for the highest melting endotherm following crystallization at the faster rates. However, a decline in melt temperature

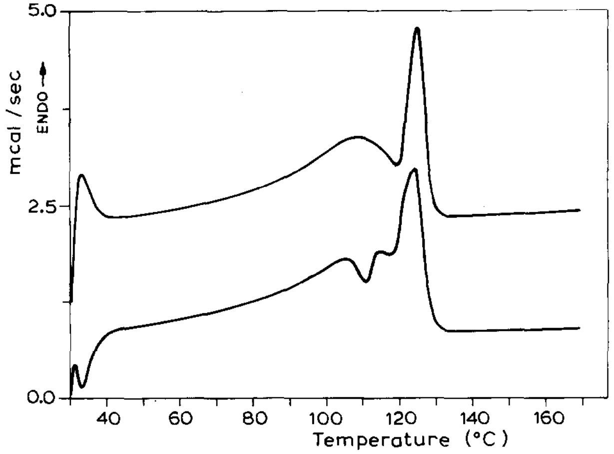

Fig. 2. Thermograms obtained upon heating after crystallization under trial runs 1 and 9 of the designed experiment.

TABLE 3

Crystallization onset temperature, crystallization peak temperatures and melt peak temperatures as a function of cooling rate

Cooling rate (° C min^{-1})	Cryst. onset temp. (° C)	Cryst. temp. (° C)	Cryst. temp. (° C)	Melt temp. (° C)	Melt temp. (° C)	Melt temp. (° C)
0.31	113.8	112.0		124.4		110.4
0.62	112.7	110.7		123.8		109.8
1.25	111.7	109.4	63.8	123.3		109.2
2.5	110.2	107.7	63.6	123.2	122.8	108.9
5.0	108.3	105.6	62.7	123.6	121.9	108.8
10.0	105.9	102.8	60.3	123.5	120.3	108.5
20.0	103.0	99.1	57.2	123.5	119.3	108.1
40.0	98.3	93.5	53.4	123.3	118.0	107.4

with cooling rate was exhibited by the intermediate peak (shoulder) and the broad, low temperature endotherm.

The effect of the independent variables on peak temperature

In the designed experiment, the peak temperature of the highest temperature melting endotherm in each thermogram ranged from 122.9 to 129.2° C. The standard deviation of repeat runs was observed to be 0.2° C. The temperature of this peak T_{max} was observed to be affected by both crystallization time and temperature, but not by cooling rate for the range of rates studied. T_{max} appeared to be a quadratic function of crystallization temperature, with its maximum melt temperature occurring for the crystallization temperature of 115° C. This temperature is just above the crystallization onset temperature determined from the constant cooling rate study (Table 3), and so isothermal crystallization should occur after a brief induction period. However, at the lower crystallization temperatures, primary crystallization commenced and under some thermal profiles progressed towards completion during sample cooling to the isothermal crystallization temperature. At 130° C the polyethylene was molten; thus, crystallization occurred under constant cooling rate conditions. It is expected that isothermal crystallization at 124° C would occur only if sufficient induction time (hold time) was allotted and that at least a portion of the molecules associated with T_{max} would crystallize during the subsequent cooling.

Although T_{max} increased as a function of time, the function did not appear to be a simple, linear one because T_{max} rose significantly between 246 and 1000 min at 115° C. This suggests that long times were required for secondary crystallization where the previously crystallized polymer molecules reorganized into a more orderly structure [7].

The temperature of the lowest temperature peak T_{left} ranged between 98.6 and 109.8 °C. The standard deviation of repeat trials was quite high at 1.8 °C. This can be attributed to the difficulty in identifying peaks other than the major one. The only discernible effect on the position (temperature) of the low temperature peak was the crystallization temperature and, as with T_{max}, there appeared to be a hold temperature at which T_{left} was a maximum. This temperature is somewhere between 110 and 115 °C. No other effects (cooling rate or time) were noted.

The effect of the independent variables on peak height

The range of peak heights, P_{max} for T_{max}, was from 6.8 to 10.5 cm with a standard deviation for repeat runs of 0.33. The two factors found to significantly affect the peak height were the cooling rate and an interaction between time and temperature. Cooling rate was observed to have a negative effect on peak height with P_{max} declining by an estimated 0.6 cm per doubling of the cooling rate. A decrease in peak height with cooling rate was also observed in the constant cooling rate experiments.

The interaction of time and temperature is best described by Table 4 which illustrates the average peak height as a function of time and temperature. At the elevated crystallization temperature (124 °C), the length of time held at that temperature had little or no effect on the peak height. However, as the temperature was lowered, the longer the hold time the greater the peak height. Also, for short hold times (4 min), the crystallization temperature had little or no effect on the peak height. However, as the length of time increased, the lower the crystallization temperature the higher the peak. This can be attributed to secondary crystallization, where amorphous molecules crystallize and/or where previously crystallized molecules reorganize [7]. The latter would result in a narrower, higher melting endotherm.

The peak height of the lowest temperature peak P_{left} varied between 2.5 and 3.5 cm. The standard deviation for replicate runs was estimated to be 0.15 cm. No significant effects of cooling rate, crystallization temperature or

TABLE 4

The effect of crystallization time and temperature on the peak height of the high temperature peak

Crystallization temperature (°C)	Crystallization time (min)	P_{max} (cm)
106	4	7.7
124	4	7.7
106	246	9.8
124	246	7.5

TABLE 5

The effect of crystallization temperature and time on the ratio of peak height P_{max}/P_{left}

Crystallization temperature (°C)	Crystallization time (min)	P_{max}/P_{left}
106	4	2.40
124	4	2.65
106	246	2.80
124	246	2.47

time were observed for this characteristic. Again, this could be due to the degree to which separation of peaks is possible.

The ratio of the height of the tallest peak (P_{max}) to the height of the low temperature peak (P_{left}) was also considered as a response. This ratio varied between 2.06 for run 15 to 2.92 for run 5. The standard deviation from replicate runs was 0.06. The peak ratio was observed to be significantly affected by the cooling rate and the interaction between time and temperature. This is similar to that observed for P_{max}; P_{max} was affected by these variables while P_{left} was not. Thus, as the cooling rate was increased, the ratio of the peaks decreased. Time–temperature results are illustrated in Table 5, variation in time at low temperature having more of an influence on the peak ratio than variation in time at high temperature.

Effect of the independent variables on the heat of fusion

The total heat of fusion varied between 17.6 and 22.0 cal g^{-1} with a standard deviation for repeated runs of 1.1. Because of variability and the difficulty in identifying peaks, no significant information could be obtained.

Effect of the independent variables on the number of discernible peaks

The number of observed peaks per set of conditions ranged between two and, at least, four. Here, in particular, the separation of peaks is critical, and given the data, no clear statistical causes for peak existence could be identified. In this regard, the power of the designed experiment was limited for the prediction of the melting behavior under particular crystallization conditions.

SUMMARY

Crystallization of polyethylene was performed according to the scheme defined by the central composite designed experiment. Thermograms obtained during the heating cycle were statistically analyzed in terms of endothermic peak temperatures and heights, number of discernible peaks and total heat of fusion. The effects of cooling rate, isothermal crystallization temperature and time spent at the isothermal crystallization temperature on the well-defined, high temperature endotherm were determined. The analysis indicated that the melt temperature of this high temperature peak was affected by crystallization time and temperature, while factors affecting its peak height were cooling rate and an interaction between crystallization time and temperature. Cooling rate had a negative effect on the peak height of the endotherm. The only major effect on the melt temperature of the lowest temperature endotherm was isothermal crystallization temperature; no effects on peak height could be discerned owing to difficulties in the separation of endotherm peaks.

It is expected that this mode of analysis could be enhanced by using techniques which allow further peak definition. The ultimate goal of this kind of study is to be able to predict a priori the features of thermograms from the information supplied by statistical analysis of a designed experiment. This could allow insights into the molecular aspects of polymer crystallization and melting, with a minimum use of resources.

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