Studies of Glycolysis of Poly(ethylene terephthalate) Recycled from Postconsumer Soft-Drink Bottles. II. Factorial Experimental Design

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ABSTRACT: Glycolysis temperature, glycolysis time, and amount of catalyst are important factors affecting the glycolysis of recycled poly(ethylene terephthalate) (PET) flakes. A 2^3 factorial experimental design is applied to study the main, two-factor interaction, and three-factor interaction effects of glycolysis temperature, glycolysis time, and amount of catalyst on the glycolysis of recycled PET flakes. In this study cobalt acetate is used as the glycolysis catalyst. The sequence of the main effects on the glycolysis conversion of the recycled PET flakes in ascending order is glycolysis time < glycolysis temperature < amount of catalyst. The sequence of the two-factor interaction effects on the glycolysis conversion of the recycled PET flakes in ascending order is glycolysis temperature versus the glycolysis time < glycolysis time versus the amount of catalyst < glycolysis temperature versus the amount of catalyst. The three-factor interaction effect is significantly related to the glycolysis conversion of the recycled PET flakes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 956–962, 2001

Key words: factorial experimental design; recycled poly(ethylene terephthalate) flake; glycolysis temperature; glycolysis time; amount of catalyst; glycolysis conversion

INTRODUCTION

Experimental designs and their statistical analyses have been well developed and applied widely in many research areas, such as basic science, engineering, sociology, and so forth. The main advantage of the experimental design is that it can cover a larger area of the engineers' experimental interest and obtain unambiguous results at a minimum cost.[1,2] Because this technique is powerful and easy to handle, the factorial experimental design is one of the most commonly used methods to realize the effects of some independent variables that significantly affect the final experimental results.

Bambrick[3] studied the fusion characteristics that are the dependent variables of poly(vinyl chloride) (PVC) compounds (fusion time, fusion temperature, and fusion torque) by using a Rheocord System 40 torque rheometer equipped with a three piece Rheomix 600 bowl and roller mixing blades. He applied a central composite design of the experiment to find the optimal formulation of additives for PVC compounds by changing the following six independent formulation variables: the amounts of impact modifier, paraffin wax, calcium stearate, ester wax, and processing aid. Chen and Lo[4] applied a 2^3 factorial experimental

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design to study the main, two-factor interaction, and three-factor interaction effects of three independent blending conditions (starting temperature, rotor speed, and totalized torque) on the heat of fusion of PVC/CPE/OPE blends [Chlorinated polyethylene (CPE) oxidized polyethylene (OPE)].

Currently, poly(ethylene terephthalate) (PET) is widely used in the manufacture of soft-drink bottles for replacing PVC and glass bottles. However, it is difficult to naturally decompose PET bottles. The disposal of a large number of PET bottles has caused serious environmental problems.[5,6] Since the green revolution movement starting in the 1980s, researchers have begun to focus on recycling and management of plastics waste.[7,8] Today PET bottles have become one of the most valuable and successfully recyclable materials. Glycolysis of recycled PET flakes can yield bis-2-hydroxyethyl terephthalate (BHET) monomer. BHET has been widely used in the production of unsaturated polyesters and rigid or flexible polyurethanes.[9] In previous work[10] we found that the glycolysis temperature, glycolysis time, and amount of catalyst are important factors affecting the glycolysis conversion of recycled PET flakes. In order to realize the main, two-factor interaction, and three-factor interaction effects of these three independent glycolysis variables on the glycolysis conversion of recycled PET flakes, a 2^3 factorial experimental design (three independent variables with high (+), and low (−) levels) was conducted.

EXPERIMENTAL

Materials

Commercial clear PET soft-drink bottles were recovered, washed, and cut into 0.4 × 0.4 cm flakes for recycling evaluation. These recycled PET flakes were dried for the glycolysis experiments. The recycled PET flakes were blow-molding grade (IV = 0.85 in 60% phenol/40% tetrachloroethane). Ethylene glycol (EG) and cobalt acetate were purchased from Katayama Chemical. All reagents were used without further purification.

Glycolysis Experiment

A 1000-mL four-necked flat-bottom reactor was used for all glycolysis experiments. It was equipped with a thermometer and a reflux condenser. A stirrer was put in the reactor to ensure proper mixing. Cobalt acetate was used as the glycolysis catalyst in this study. The ratio of EG:PET used in the glycolysis experiments was 2:1 (w/w). The weights of EG and recycled PET flakes were 160 and 80 g, respectively. In order to ensure limited water content in the reactor it was heated to 110°C and held at this temperature for at least 2 min.

After the specified glycolysis experiment was finished, the reactor was removed from the hot plate and 200 mL of boiling water was slowly added into the reactor. Then the whole product mixture was quickly filtered using a copper screen with a 0.05 × 0.05 cm pore size. The undepolymerized PET flakes were collected, dried, weighed, and labeled as the PET fraction. The conversion for the glycolysis of recycled PET flakes was defined as below:

$$\text{glycolysis conversion} = \frac{A - B}{A}$$

where A represents 80 g of recycled PET flakes and B represents the weight of undepolymerized PET flakes.

Experimental Design

Figure 1 shows the standard figure of a 2^3 factorial experimental design. The glycolysis temper-

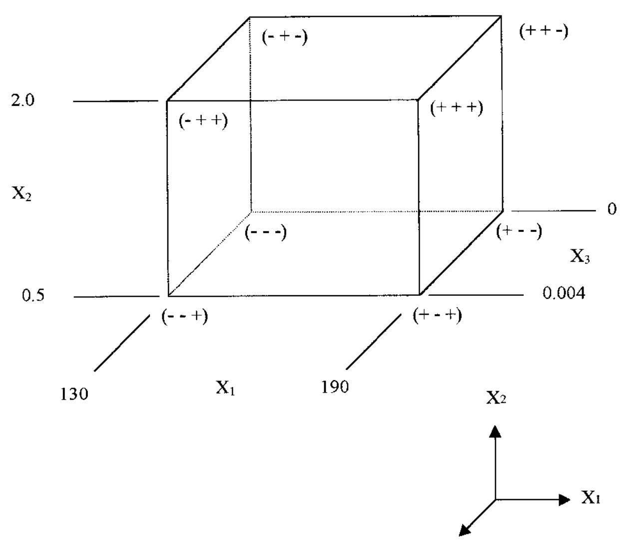

Figure 1 A diagrammatic representation of the standard ordering of a 2^3 factorial experimental design (X_1, glycolysis temperature; X_2, glycolysis time; X_3, amount of catalyst).

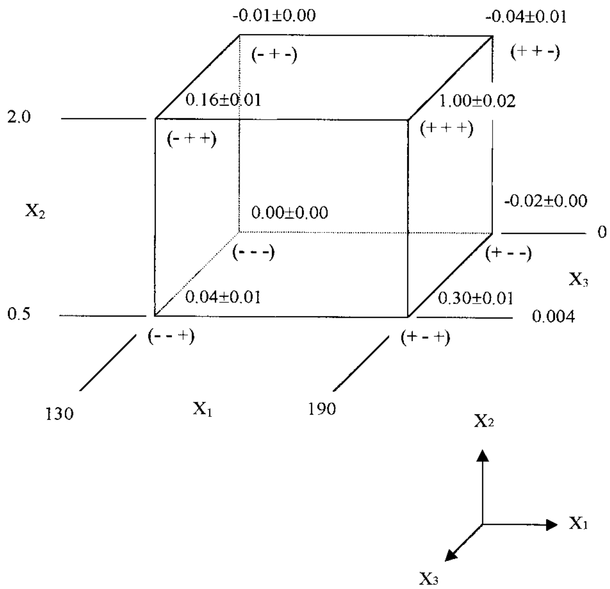

Figure 2 A diagrammatic representation of the observed yields (glycolysis conversion) and the standard ordering of experiments of the glycolysis of recycled PET flakes.

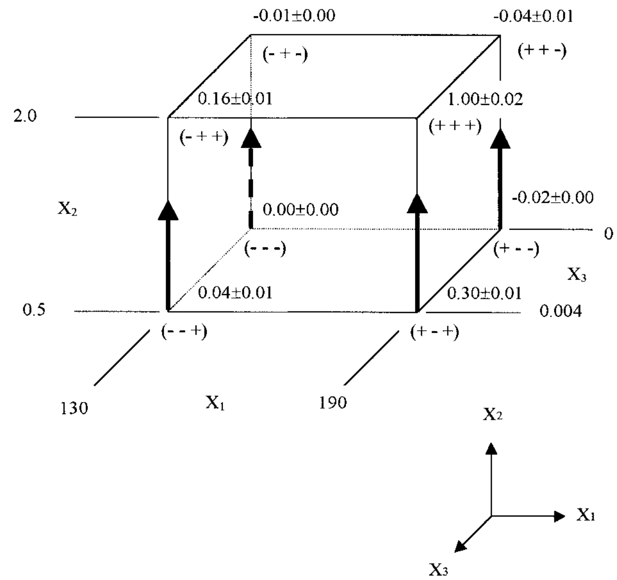

Figure 4 The determination of the main effect of the glycolysis time (X_2) on the glycolysis conversion of recycled PET flakes.

ature (X_1), glycolysis time (X_2), and amount of catalyst (X_3) were chosen as the independent variables. Two levels, high (+) and low (−), were also defined for each independent variable. Thus, a 2^3 factorial experimental design has eight runs, the first in standard order being (− − −) and the last in standard order being (+ + +). For the glycolysis temperature, 190 and 130°C were chosen as the high and low levels, respectively; for the glycolysis time, 2.0 and 0.5 h were chosen as the high and low levels, respectively; and or the amount of catalyst, 0.004 and 0 mol were chosen as the high and low levels, respectively. The glycolysis conversion of recycled PET flakes was studied as the dependent variable.

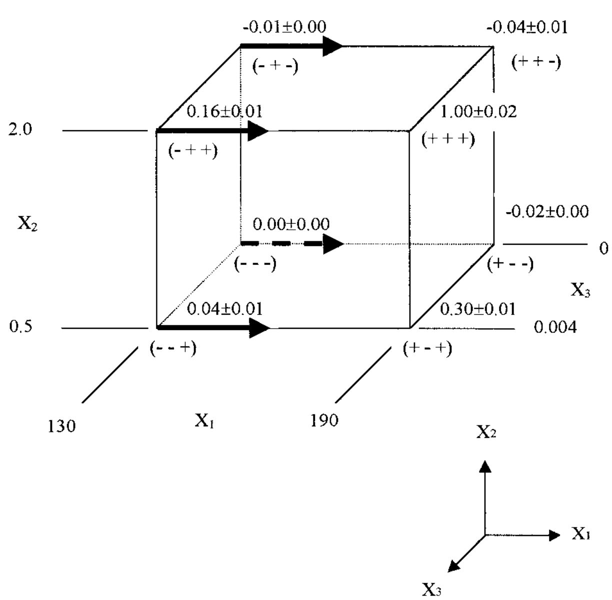

Figure 3 The determination of the main effect of the glycolysis temperature (X_1) on the glycolysis conversion of recycled PET flakes.

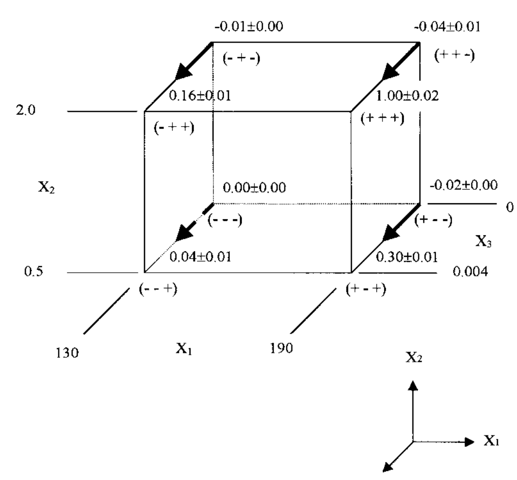

Figure 5 The determination of the main effect of the amount of catalyst (X_3) on the glycolysis conversion of recycled PET flakes.

Table I Main Effect of Glycolysis Temperature (X_1) on Glycolysis Conversion of Recycled PET Flakes

X_1	X_2	X_3
1.00–0.16 = 0.84	2.0	0.004
0.30–0.04 = 0.26	0.5	0.004
−0.04–(−0.01) = −0.03	2.0	0
−0.02–0.00 = −0.02	0.5	0

X_2, glycolysis time; X_3, amount of catalyst. The average (main effect of glycolysis temperature) was [0.84 + 0.26 + (−0.03) + (−0.02)]/4 = 0.26.

Table III Main Effect of Amount of Catalyst (X_3) on Glycolysis Conversion of Recycled PET Flakes

X_3	X_1	X_2
1.00–(−0.04) = 1.04	190	2.0
0.16–(−0.01) = 0.17	130	2.0
0.30–(−0.02) = 0.32	190	0.5
0.04–0.00 = 0.04	130	0.5

The average (main effect of amount of catalyst) was [1.04 + 0.17 + 0.32 + 0.04]/4 = 0.39.

RESULTS AND DISCUSSION

Figure 2 shows the observed yields (glycolysis conversion) and the standard ordering of glycolysis experiments for recycled PET flakes. There are three negative glycolysis conversions shown in Figure 2. This is because without any amount of catalyst, no glycolysis reaction occurs. On the other hand, some EG molecules may react with the recycled PET flakes and result in the final weight being higher than 80 g. Therefore, the glycolysis conversion is negative.

Figures 3, 4, and 5 represent the determinations of the main effects of the glycolysis temperature, glycolysis time, and amount of catalyst, respectively. According to the definition, the main effect of the controlled independent variable is the average of the difference between the values at the high level (+) and the values at the low level (−). Tables I, II, and III illustrate the results of the main effects of the glycolysis temperature, glycolysis time, and amount of catalyst, respectively. Comparing the results of these tables, the main effect of the amount of catalyst is nearly twice that of the glycolysis time and one and half that of the glycolysis temperature.

Table II Main Effect of Glycolysis Time (X_2) on Glycolysis Conversion of Recycled PET Flakes

X_2	X_1	X_3
1.00–0.30 = 0.70	190	0.004
0.16–0.04 = 0.12	130	0.004
−0.04–(−0.02) = −0.02	190	0
−0.01–0.00 = −0.01	130	0

The average (main effect of glycolysis time) was [0.70 + 0.12 + (−0.02) + (−0.01)]/4 = 0.20.

Figures 6, 7, and 8 illustrate the determinations of the glycolysis temperature versus the glycolysis time, the glycolysis temperature versus the amount of catalyst, and the glycolysis time versus the amount of catalyst interaction effects, respectively. According to the definition, the two-factor interaction effect of the glycolysis temperature versus the glycolysis time (X_1 vs. X_2) is equal to half the difference [(0.41 − 0.12)/2 = 0.15] between the average glycolysis temperature effect with a glycolysis time of 2.0 h {[0.84 + (−0.03)]/2 = 0.41} and the average glycolysis temperature effect with a glycolysis time of 0.5 h {[0.26 + (−0.02)]/2 = 0.12}. The glycolysis temperature versus the amount of catalyst interaction effect (X_1 vs. X_3) is equal to half the difference {[0.55 − (−0.025)]/2 = 0.29} between the average

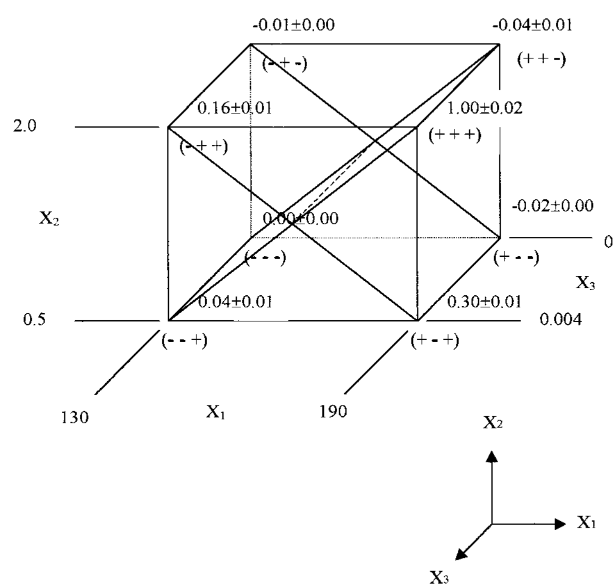

Figure 6 The determination of the glycolysis temperature versus the glycolysis time interaction effect (X_1 vs. X_2) on the glycolysis conversion of recycled PET flakes.

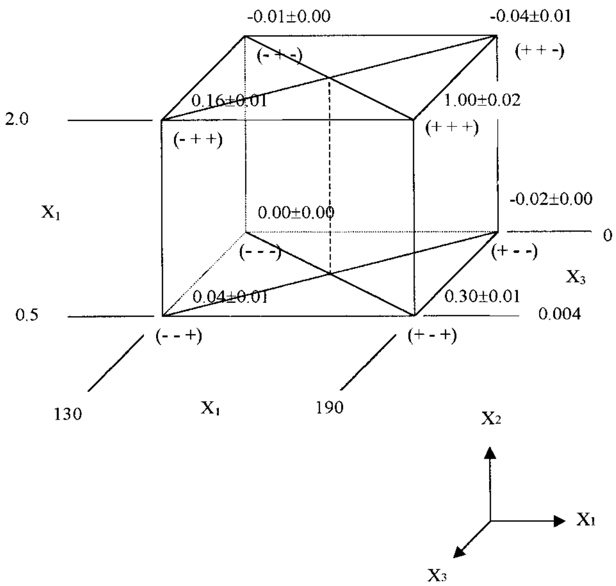

Figure 7 The determination of the glycolysis temperature versus the amount of catalyst interaction effect (X_1 vs. X_3) on the glycolysis conversion of recycled PET flakes.

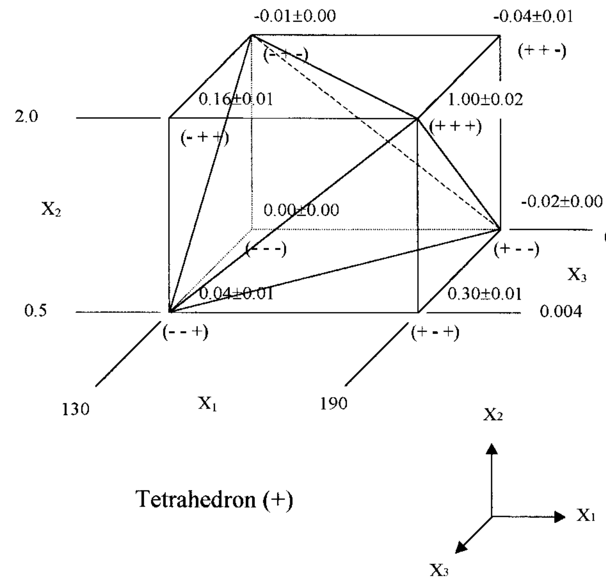

Figure 9 The determination of the three-factor interaction effect (glycolysis temperature vs. glycolysis time vs. amount of catalyst, X_1 vs. X_2 vs. X_3) on the glycolysis conversion of recycled PET flakes [(+) tetrahedron].

glycolysis temperature effect with 0.004 mol catalyst [(0.84 + 0.26)/2 = 0.55] and the average glycolysis temperature effect with 0 mol catalyst {[−0.03 + (− 0.02)]/2 = −0.025}. Similarly, the glycolysis time versus the amount of catalyst interaction effect (X_2 vs. X_3) is equal to half the difference {[0.41 − (−0.015)]/2 = 0.21} between the average glycolysis time effect with 0.004 mol catalyst [(0.70 + 0.12)/2 = 0.41] and the average glycolysis time effect with 0 mol catalyst {[−0.02 + (−0.01)]/2 = −0.015}.

Consider the individual comparisons of the effect of the glycolysis temperature (X_1). There are two available measurements from the experiment to estimate the three-factor interaction effect of the glycolysis temperature versus the glycolysis time versus the amount of catalyst (X_1 vs. X_2 vs. X_3): one for 0.004 mol catalyst {[(0.84 − 0.26)]/2 = 0.29} or for 0 mol catalyst {[−0.03 − (−0.02)]/2 = −0.005}. The difference between these two estimates is a measure of consistency for each glycolysis time of 2.0 h {[0.84 − (−0.03)]/2 = 0.435} and 0.5 h {[0.26 − (−0.02)]/2 = 0.14}. Half this difference {0.29 − (−0.005)]/2 = 0.15 or (0.435 − 0.14)/2 = 0.15} is defined as the three-factor interaction effect of the glycolysis temperature versus the glycolysis time versus the amount of catalyst (X_1 vs. X_2 vs. X_3).

The same results are obtained from either the effect of the glycolysis time (X_2) individual comparisons or the effect of the amount of catalyst (X_3) individual comparisons. As in the main effects and the two-factor interactions, the estimate of the three-factor interaction can be obtained from the difference between the average of the

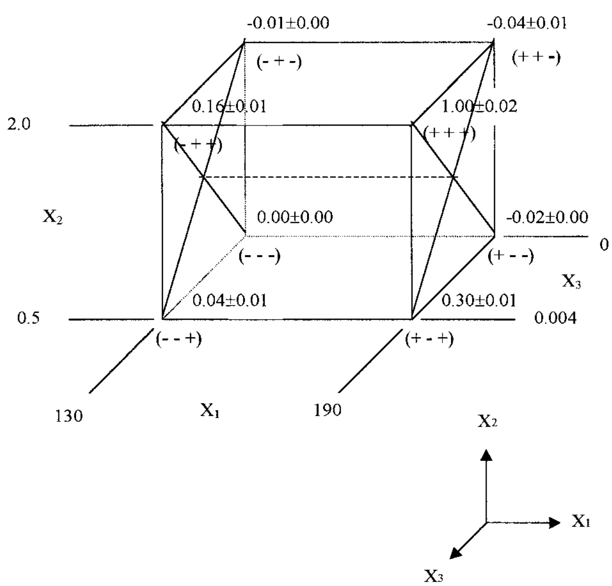

Figure 8 The determination of the glycolysis time versus the amount of catalyst interaction effect (X_2 vs. X_3) on the glycolysis conversion of recycled PET flakes.

vertices of the (+) tetrahedron (Fig. 9) and the average of vertices of the (−) tetrahedron {Fig. 10; i.e., [1.00 + 0.04 + (−0.01) + (−0.02)]/4 − [0.16 + 0.30 + (−0.04) + 0.00]/4 = 0.15}.

Table IV illustrates the summary of the main, two-factor interaction, and three-factor interaction effects of the glycolysis conversion of recycled PET flakes. It shows that the sequence of the main effects on the glycolysis conversion of recycled PET flakes in ascending order is glycolysis time < glycolysis temperature < amount of catalyst. This is because without any amount of catalyst, the glycolysis of recycled PET flakes cannot occur, even at the high levels of glycolysis temperature and glycolysis time. Similarly, at the same amount of catalyst, the glycolysis temperature affects the glycolysis conversion of recycled PET flakes more significantly than the glycolysis time. This is because the glycolysis temperature reflects the input energy that affects the glycolysis processing of recycled PET flakes. Therefore, the amount of catalyst and glycolysis temperature are the first and second most important factors, respectively.

The sequence of the two-factor interaction effects on the glycolysis conversion of recycled PET flakes in ascending order is glycolysis temperature versus glycolysis time < glycolysis time versus amount of catalyst < glycolysis temperature versus amount of catalyst. The amount of catalyst is the most important individual factor. Furthermore, the glycolysis temperature is the second important individual factor. Therefore, the interaction effect between the glycolysis temperature and the amount of catalyst is the highest in determining the glycolysis conversion of recycled PET flakes. Similarly, the interaction effect between the glycolysis time and amount of catalyst is second in order in determining the glycolysis conversion of recycled PET flakes. In addition, the interaction effect between the glycolysis temperature and glycolysis time is third in order. The three-factor interaction effect is still significantly related to the glycolysis conversion of recycled PET flakes. From the results of Table IV, we can obtain a prediction equation[11]

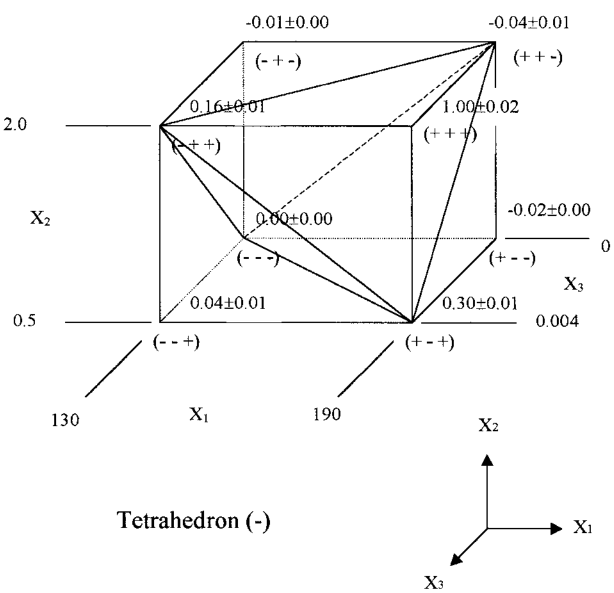

Figure 10 The determination of the three-factor interaction effect (glycolysis temperature vs. glycolysis time vs. amount of catalyst, X_1 vs. X_2 vs. X_3) on the glycolysis conversion of recycled PET flakes [(−) tetrahedron].

Table IV Summary of Main, Two-Factor, and Three-Factor Interaction Effects of Glycolysis Conversion of Recycled PET Flakes

	Interaction Effect	
Main Effect	Two Factor	Three Factor
$X_1 = 0.26$	X_1 vs. $X_2 = 0.15$	X_1 vs. X_2 vs. $X_3 = 0.15$
$X_2 = 0.20$	X_1 vs. $X_3 = 0.29$	
$X_3 = 0.39$	X_2 vs. $X_3 = 0.21$	

$$\hat{Y} = \bar{Y} + 0.13X_1 + 0.10X_2 + 0.195X_3 + 0.075X_1X_2 + 0.145X_1X_3 + 0.105X_2X_3 + 0.0737X_1X_2X_3$$

where: $\hat{Y}$ = the predicted response

$\bar{Y}$ = 0.179 (the average of all response values from the experimental data)

X_1, X_2, X_3 = +1 (if high level) or −1 (if low level)

CONCLUSIONS

A 2^3 factorial experimental design was successfully applied to study the main, two-factor interaction, and three-factor interaction effects of glycolysis temperature, glycolysis time, and amount of catalyst on the glycolysis conversion of recycled PET flakes. The sequence of the main effects on the glycolysis conversion of recycled PET flakes in ascending order was glycolysis time < glycolysis temperature < amount of catalyst. The sequence of the two-factor interaction effects on the glycolysis conversion of recycled PET flakes in ascending order was glycolysis temperature versus glycolysis time < glycolysis time versus amount of catalyst < glycolysis temperature versus amount of catalyst. The three-factor interaction effect was still significantly related to the glycolysis conversion of recycled PET flakes. The prediction equation[11] was

$$\hat{Y} = 0.179 + 0.13X_1 + 0.10X_2 + 0.195X_3 + 0.075X_1X_2 + 0.145X_1X_3 + 0.105X_2X_3 + 0.0737X_1X_2X_3$$

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