Application of Factorial Experimental Design to Demonstrate the Influence of Processing Conditions on the Fusion of Poly(vinyl chloride)/Chlorinated Polyethylene/Oxidized Polyethylene Blends

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ABSTRACT: Poly(vinyl chloride) (PVC)/chlorinated polyethylene (CPE)/oxidized polyethylene (OPE) blends were prepared in a Haake torque rheometer at various temperatures, rotor speeds, and totalized torques. A 2^3 factorial experimental design was applied to study the main two-factor interaction, and three-factor interaction effects of temperature, rotor speed, and totalized torque on the heat of fusion of PVC/CPE/OPE blends, which were examined using differential scanning calorimetry. The sequence of the main effects on the heat of fusion of PVC/CPE/OPE blends, in ascending order, is temperature < rotor speed < totalized torque. The sequence of the two-factor interaction effects on the heat of fusion of PVC/CPE/OPE blends, in ascending order, is temperature vs rotor speed < temperature vs totalized torque < rotor speed vs totalized torque. The three-factor interaction effect is not significantly related to the heat of fusion of PVC/CPE/OPE blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2755–2761, 1999

Key words: factorial experimental design; poly(vinyl chloride); chlorinated polyethylene; oxidized polyethylene; differential scanning calorimetry

INTRODUCTION

Experimental designs and their statistical analyses have been well developed and applied widely in many research areas, such as basic science, engineering, sociology, etc. The main advantage of the experimental design is that it can cover a larger area of 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.

The fusion of poly(vinyl chloride) (PVC) compounds is highly dependent upon the additives and the rotor speed, as well as its thermal history in a batch mixer. Bambrick et al.[3] studied the fusion characteristics, which are the dependent variables, of 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. They applied a central composite design of the experiment to find the optimal formulation of additives for PVC compounds by changing the following six independent formula-

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tion variables: amounts of impact modifier, paraffin wax, calcium stearate, ester wax, and processing aid. Chen et al.[4] reported that the starting temperature, rotor speed, and totalized torque (TTQ) were the three major factors to affect the heat of fusion of a PVC compound prepared by a Haake Torque Rheometer equipped with a three-sectioned mixing chamber and two interchangeable rotors. In order to realize the main two-factor interaction and three-factor interaction effects of these three independent blending variables on the heat of fusion of PVC/chlorinated polyethylene (CPE)/oxidized polyethylene (OPE) blends, a 2^3 factorial experimental design [three independent variables with high (+), and low (−) levels] is applied.

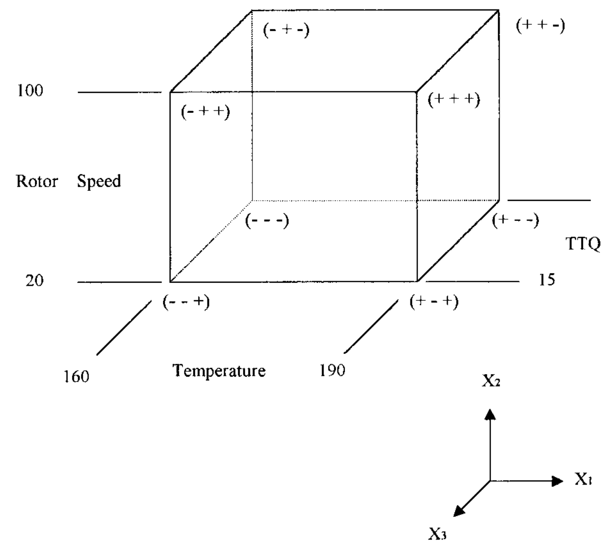

Figure 1 Diagrammatic representation of the standard ordering of a 2^3 factorial experimental design.

EXPERIMENTAL METHOD

Preparation of PVC/CPE/OPE Blends

The materials used in this study are suspension PVC masterbatch powder, containing 100 parts PVC grain particle (MW ≈ 150,000), 5 parts CPE (impact modifier; MW ≈ 160,000; chlorine content ≈ 36%), 0.3 parts OPE (MW ≈ 3000; acid number ≈ 6–8), 1.5 parts processing aid (K120N), 1.0 part wax (XL165), 1.0 part calcium stearate, and 1.5 parts tin stabilizer (T-137). The Dow Chemical Company supplies all samples.

All PVC/CPE/OPE blends were prepared by a Haake Torque Rheometer (Rheocord 90) equipped with an electrically heated mixing head and two noninterchangeable rotors. The sample weight was 65 g for all runs. PVC samples were charged into the mixer at various starting temperatures and rotor speeds, and removed when the set totalized torque (kgm-min) was reached in a Haake Torque Rheometer.

Figure 1 shows the standard figure of a 2^3 factorial experimental design. Processing temperature, rotor speed, and totalized torque 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 will have eight runs, the first in standard order being (− − −), and the last in standard order being (+ + +). For processing temperature, 190 and 160°C were chosen as high and low levels, respectively. For rotor speed, 100 and 20 rpm were chosen as high and low levels, respectively. For the totalized torque, 15 kg-m-min and 1 kg-m-min were chosen as high and low levels, respectively. The heat of fusion of a PVC/CPE/OPE blend is studied as the dependent variable here. Several different fusion assessment methods have been well developed.[5] Recently, the differential scanning calorimetry (DSC) thermal analysis[6–9] is commonly used because it is very convenient and quick. In this study, DSC thermal analysis is used to determine heat of fusions of PVC/CPE/OPE blends.

DSC Thermal Analysis

PVC/CPE/OPE blends prepared by the Haake Torque Rheometer were cut randomly, approximately 10 mg each, and characterized by the SEIKO 220C Automatic Cooling Differential Scanning Calorimeter. For further thermal analysis, samples were heated from room temperature to 270°C at the heating rate of 20°C/min. Three DSC measurements were required for each sample in order to obtain an average value of the heat of fusion. This average value was chosen as the dependent variable of the 2^3 factorial experimental design for PVC/CPE/OPE blends.

RESULTS AND DISCUSSION

Figure 2 shows the DSC thermal analysis curves of PVC compounds blended in a Haake Torque Rheometer at various temperatures.[4] A DSC trace of PVC powder has an endothermic baseline shift at the glass transition temperature (T_g) (ap-

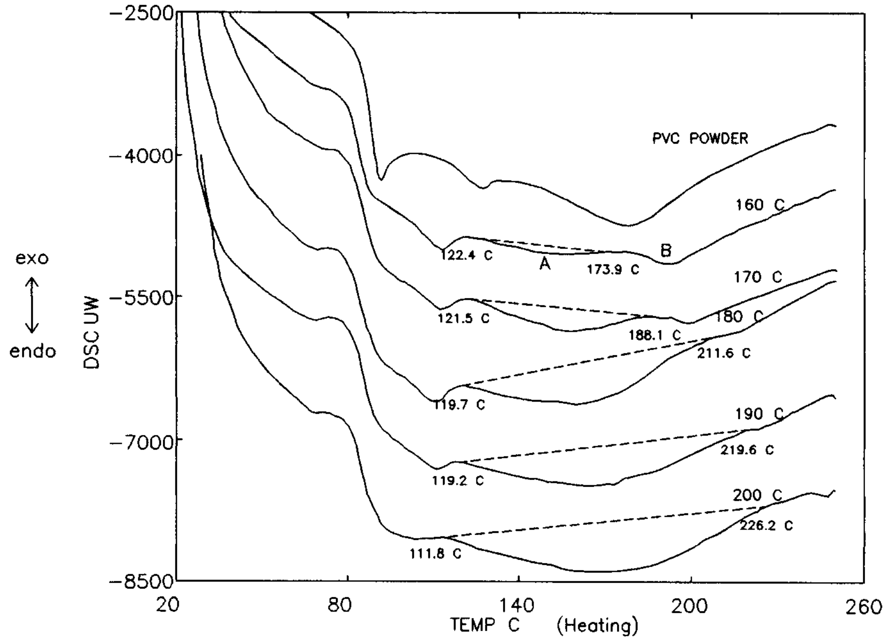

Figure 2 DSC thermal analysis curves of PVC compounds processed in a Haake Torque Rheometer at rotor speed = 60 rpm, TTQ = 10 kg-m-min, and various temperatures.[4]

proximately 80°C). There are two peaks, A and B, in DSC traces. Peak B stands for the endothermic energy of the PVC crystals that are not melted in a Haake Torque Rheometer. When the processing temperature increases, this peak decreases in size and shifts to a higher temperature. Gilbert et al.[5,6] suggested that the size decrease was due to the melting of less perfect or smaller crystallites and the temperature shift was caused by annealing of unmelted crystallites. Peak A is related to the endothermic energy of the PVC crystals melted in a Haake Torque Rheometer and recrystallized after cooling at room temperature. Peak A was measured to determine the heat of fusion of the PVC compound. Figure 3 shows the observed yields (heat of fusion; mJ/mg) and the standard ordering of experiments for PVC/CPE/OPE blends. Figures 4, 5, and 6 represent the determinations of the main effects of temperature, rotor speed, and TTQ, 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 low level (−). Tables I, II, and III illustrate the results of the main effects of temperature, rotor speed, and TTQ, respectively.

Figures 7, 8, and 9 illustrate the determinations of temperature vs rotor speed, temperature vs TTQ, and rotor speed vs TTQ interaction effects, respectively. According to the definition, the two-factor interaction effect of temperature vs rotor speed (X_1 vs X_2) is equal to half the difference [(2.60 − 2.64)/2 = −0.02] between the average temperature effect with rotor speed = 100 rpm

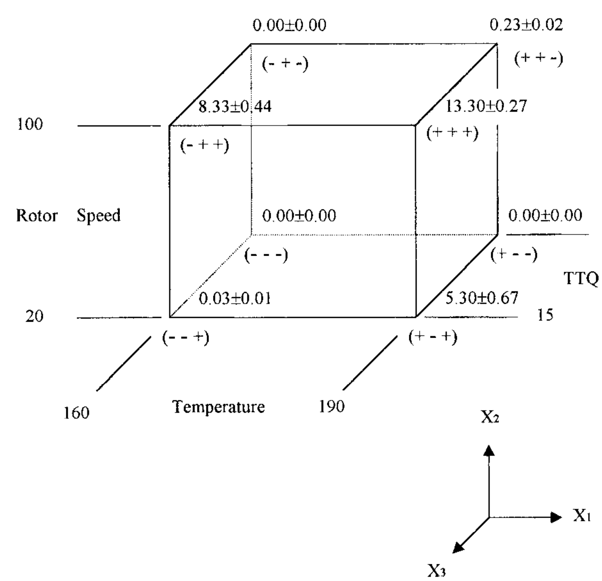

Figure 3 Diagrammatic representation of the observed yields (heat of fusion: mJ/mg) and the standard ordering of experiments of PVC/5phr CPE/ 0.3phr OPE blend.

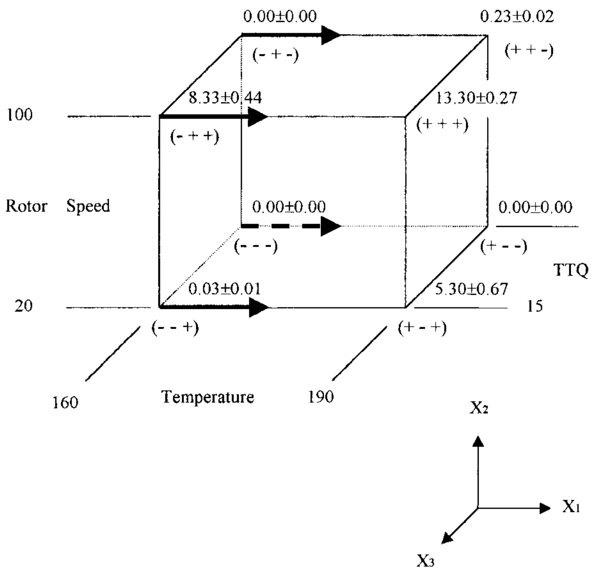

Figure 4 Determination of the main effect of temperature (X_1) of PVC/5phr CPE/0.3phr OPE blend.

[(4.97 + 0.23)/2 = 2.60] and the average temperature effect with rotor speed = 20 rpm [(5.27 + 0.00)/2 = 2.64]. Temperature vs TTQ interaction effect (X_1 vs X_3) is equal to half the difference [(5.12 − 0.12)/2 = 2.50] between the average temperature effect with TTQ = 15 [(4.97 + 5.27)/2 = 5.12] and the average temperature effect with TTQ = 1 [(0.23 + 0.00)/2 = 0.12]. Similarly, rotor speed vs TTQ interaction effect (X_2 vs X_3) is equal to half the difference [(8.15 − 0.12)/2 = 4.02]

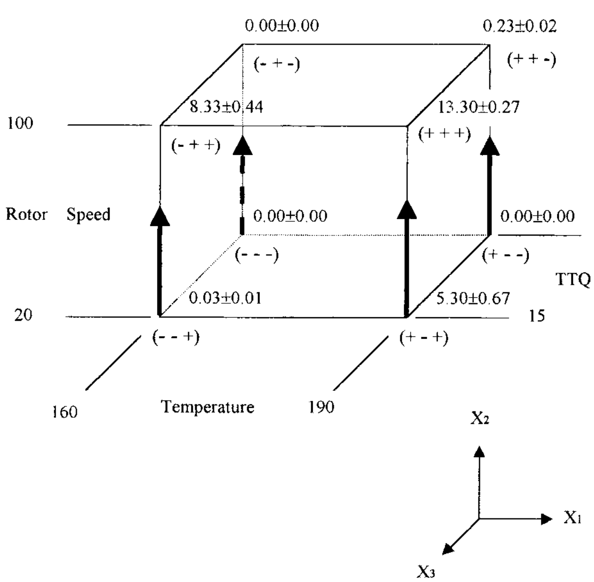

Figure 5 Determination of the main effect of rotor speed (X_2) of PVC/5phr CPE/0.3phr OPE blend.

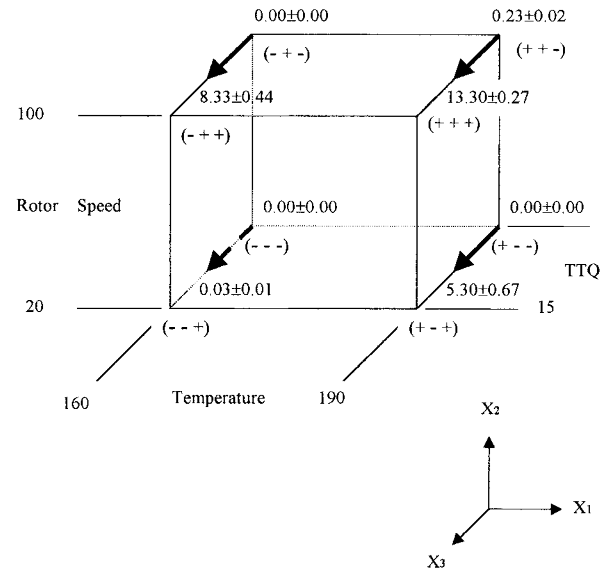

Figure 6 Determination of the main effect of TTQ (X_3) of PVC/5phr CPE/0.3phr OPE blend.

between the average rotor speed effect with TTQ = 15 [(8.00 + 8.30)/2 = 8.15] and the average rotor speed effect with TTQ = 1 [(0.23 + 0.00)/2 = 0.12].

Consider the individual comparisons of the effect of temperature (X_1). There are two available measurements from the experiment to estimate the three-factor interaction effect, temperature vs rotor speed vs TTQ (X_1 vs X_2 vs X_3), one for each TTQ, TTQ = 15 kg-m-min: [(4.97 − 5.27)]/2 = −0.15, TTQ = 1 kg-m-min: [(0.23 −0.00)]/2 = 0.12. The difference between these two estimates is a measure of consistency for each rotor speed, rotor speed = 100 rpm: [(4.97 − 0.23)]/2

Table I The Main Effect of Temperature (X_1) on PVC/CPE/OPE Blends

Effect of Temperature (X_1), Individual Comparisons	Conditions Where Comparisons are Made: Rotor Speed (X_2)	TTQ (X_3)
(13.30 − 8.33) = 4.97	100	15
(5.30 − 0.03) = 5.27	20	15
(0.23 − 0.00) = 0.23	100	1
(0.00 − 0.00) = 0.00	20	1

Average (main effect of temperature): (4.97 + 5.27 + 0.23 + 0.00)/4 = 2.62

Table II The Main Effect of Rotor Speed (X_2) on PVC/CPE/OPE Blends

Effect of Rotor Speed (X_2), Individual Comparisons	Conditions Where Comparisons are Made	
	Temperature (X_1)	TTQ (X_3)
(13.30 − 5.30) = 8.00	190	15
(8.33 − 0.03) = 8.30	160	15
(0.23 − 0.00) = 0.23	190	1
(0.00 − 0.00) = 0.00	160	1
Average (main effect of rotor speed): (8.00 + 8.30 + 0.23 + 0.00)/4 = 4.13		

= 2.37, and rotor speed = 20 rpm: [(5.27 − 0.00))/2 = 2.64. Half this difference, (−0.15 −0.12)/2 = −0.14 or (2.37 − 2.64)/2 = −0.14, is defined as the three-factor interaction effect of temperature vs rotor speed vs TTQ (X_1 vs X_2 vs X_3).

The same results will be obtained from either the effect of rotor speed (X_2) individual comparisons or the effect of rotor speed (X_2) individual comparisons. As in the case of 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 vertices of (+) tetrahedron (Fig. 10) and the average of vertices of (−) tetrahedron (Fig. 11), i.e., [(13.30 + 0.03 + 0.00 + 0.00)/4 − (8.33 + 5.30 + 0.23 + 0.00)/4] = −0.14.

Table IV illustrates the summary of the main two-factor interaction, and three-factor interaction effects of PVC/CPE/OPE blends. It shows that the sequence of the main effects on the heat of fusion of PVC/CPE/OPE blends in ascending order is temperature < rotor speed < TTQ. This is because at the low TTQ (1 kg-m-min) the processing time of the PVC resin particles is very short and the PVC resin particles cannot be fused together well, even at the high levels of temperature and rotor speed. Similarly, at the same TTQ, the rotor speed affects the heat of fusion of PVC/CPE/OPE blends more significantly than temperature does. This is because the rotor speed dominates the mechanical energy (torque) and the uniformity of the heat transfer in the mixer. Therefore, TTQ and rotor speed are the first and second most important factors, respectively.

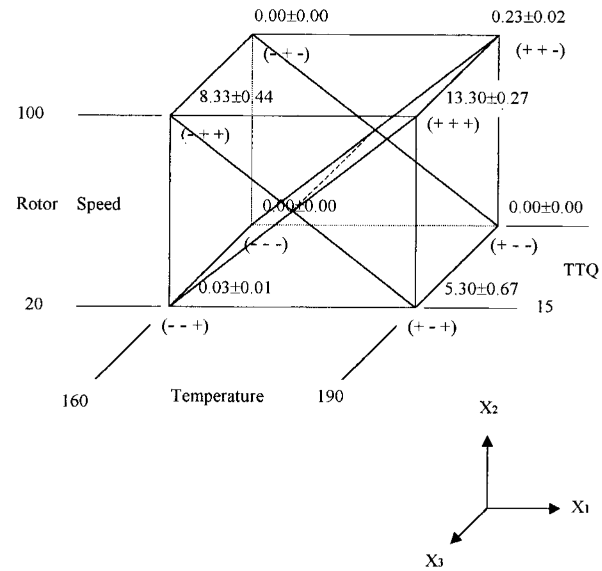

Figure 7 Determination of the temperature vs. rotor speed interaction effect (X_1 vs $X2$) of PVC/5phr CPE/0.3phr OPE blend.

The sequence of the two-factor interaction effects on the heat of fusion of PVC/CPE/OPE blends, in ascending order, is temperature vs rotor speed < temperature vs TTQ < rotor speed vs TTQ. The TTQ, which is the most important individual factor, is equal to the integral of torque by time. Furthermore, the torque inside the mixer

Table III The Main Effect of TTQ (X_3) on PVC/CPE/OPE Blends

Effect of TTQ (X_3), Individual Comparisons	Conditions Where Comparisons are Made	
	Temperature (X_1)	Rotor Speed (X_3)
(13.30 − 0.23) = 13.07	190	100
(8.33 − 0.00) = 8.33	160	100
(5.30 − 0.00) = 5.30	190	20
(0.03 − 0.00) = 0.03	160	20
Average (main effect of TTQ): (13.07 + 8.33 + 5.30 + 0.03)/4 = 6.68		

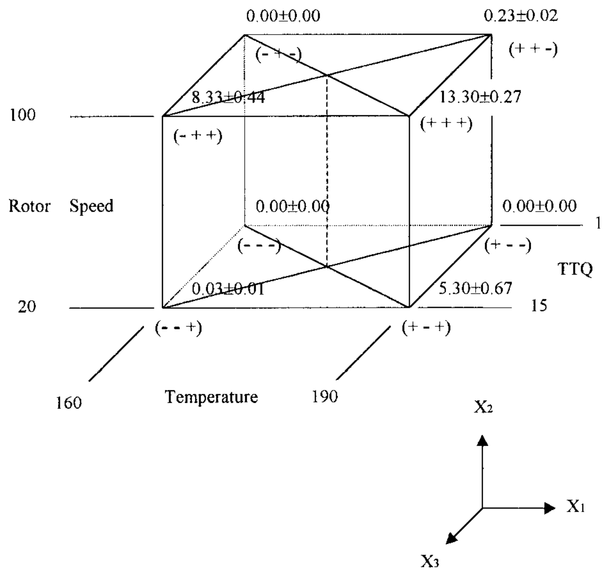

Figure 8 Determination of the temperature vs TTQ interaction effect (X_1 vs X_3) of PVC/5phr CPE/0.3phr OPE blend.

is mostly contributed by the rotor speed. Therefore, the interaction effect between rotor speed and TTQ is the most important factor in determining the heat of fusion of PVC/CPE/OPE blends. Torque in the mixer is also affected by the mixer temperature because the melt viscosity of the PVC/CPE/OPE blend changes with respect to the mixer temperature. Therefore, the interaction

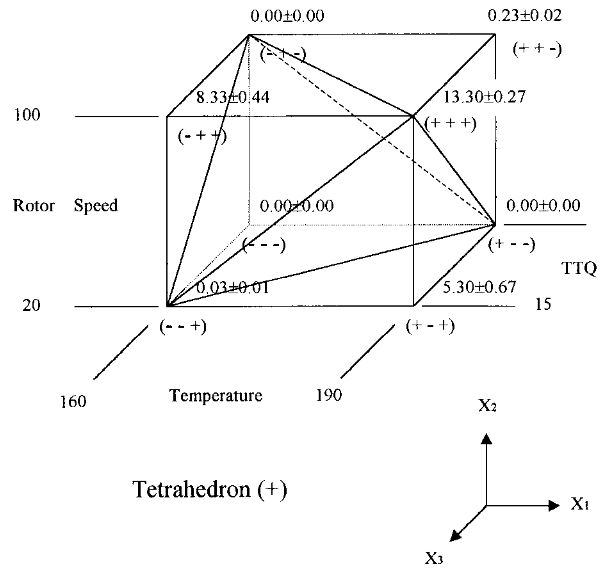

Figure 10 Determination of the three-factor temperature vs rotor speed vs TTQ interaction effect (X_1 vs X_2 vs X_3) of PVC/5phr CPE/0.3phr OPE blend [Tetrahedron(+)].

effect between temperature and TTQ is the second most important factor in determining the heat of fusion of PVC/CPE/OPE blends. Because there is no significant interaction between rotor speed and temperature in the mixer, the interaction effect between rotor speed and temperature

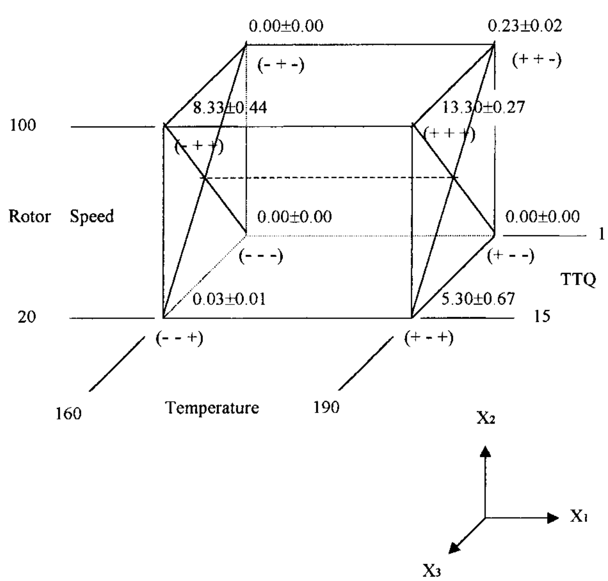

Figure 9 Determination of the rotor speed vs TTQ interaction effect (X_2 vs X_3) of PVC/5phr CPE/0.3phr OPE blend.

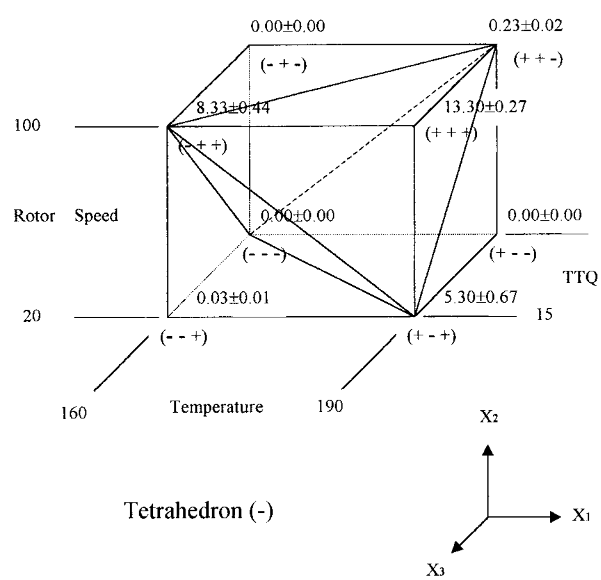

Figure 11 Determination of the three-factor temperature vs rotor speed vs TTQ interaction effect (X_1 vs X_2 vs X_3) of PVC/5phr CPE/0.3phr OPE blend [Tetrahedron(-)].

Table IV Summary of Main, Two-Factor Interaction, and Three-Factor Interaction Effects of PVC/CPE/OPE Blends

Main Effect	Two-Factor Interaction Effect	Three-Factor Interaction Effect
$X_1 = 2.62$	X_1 vs $X_2 = -0.02$	X_1 vs X_2 vs $X_3 = -0.14$
$X_2 = 4.13$	X_1 vs $X_3 = 2.50$	
$X_3 = 6.68$	X_2 vs $X_3 = 4.02$	

is not significantly related to the heat of fusion of PVC/CPE/OPE blends. Since the interaction effect between rotor speed and temperature is not significant, the three-factor interaction effect is not significantly related to the heat of fusion of PVC/CPE/OPE blends. By definition, an effect is not significant when the value of an effect is between 1 and −1.

DSC thermal analysis has attracted attention because it provides a convenient, quantitative measure of the heat of fusion and uses a very small sample (approximately 10 mg). The main disadvantage of thermal analysis is that some additives may interfere with the final results because the sample size is very small.

CONCLUSIONS

The sequence of the main effects on the heat of fusion of PVC/CPE/OPE blends, in ascending order, is temperature < rotor speed < TTQ. The sequence of the two-factor interaction effects on the heat of fusion of PVC/CPE/OPE blends, in ascending order, is temperature vs rotor speed < temperature vs TTQ < rotor speed vs TTQ. The three-factor interaction effect is not significantly related to the heat of fusion of PVC/CPE/OPE blends. In industry, the processing temperature normally used for rigid PVC is around 190°C or less, therefore we considered that the maximum processing temperature is 190°C. If the maximum processing temperature was raised dramatically, the results might be somewhat changed. But at higher processing temperature, PVC is easy to be degraded. DSC thermal analysis is a very convenient and quick method to assess the fusion level of PVC/CPE/OPE blends, but this technique may result in error due to the fact that the sample analyzed weighs only 10 mg.

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