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Applications of a statistical model to the analysis of the kinetic parameters in isothermal and non-isothermal crystallization of polymer blends based on PVDF

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In this work the classical Scheffé model is applied to the study of isothermal and non-isothermal crystallization of blends based on the systems PVDF, PMMA and PVA. In the light of the results obtained the validity of the model proposed is assessed. The authors endeavour to contribute to the discussion on the compatibility of these materials, which latter aspect is of utmost relevance when interpreting the properties presented by these polymer blends. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The well-known pyro-piezoelectric activity of polyvinylidene fluoride (PVDF) has stimulated several research projects on this polymer in recent years[1,2], taking into account the potential interest of its application in the field of sensors. It is also known that the pyro-piezoelectrical activity of PVDF is attributed to the ferro-electric orientation of the crystalline dipoles in their beta-phase[3]. This is the reason why their existence conditions the pyro-electricity of these materials. Furthermore it has been recognized[4] that certain copolymers based on PVDF do not only possess the above-mentioned beta-form, but their pyro-piezoelectrical activity is greater than that of the PVDF homopolymer. This latter finding explains the intense research activity deployed in the development of new, PVDF-based pyro-piezoelectric materials through copolymerization reactions[5], through physical blends with other polymers[6,7] or through the incorporation of highly active ceramics into different polymer systems[8].

The research we have been developing for quite some years[9,10] pursues these very objectives, with the ultimate aim of synthesizing new pyro-piezoelectric polymers based on polymer blends or composites obtained by means of incorporation of different ceramics into the previously synthesized polymer systems. The condition to be fulfilled by the new systems is that they possess better electrical, mechanical and/or economic properties than pure PVDF.

Within our project, this work embarks upon an aspect which, to date and to judge from the literature, has not been dealt with by any group of researchers. We refer to the application of statistical methods in the need-tailored design of new materials based on polymer blends. Thus a study was conducted to determine the kinetic crystallization parameters under isothermal and non-isothermal conditions of a sample series planned according to the method proposed by Scheffé. Subsequently the model applied was assessed as to its suitability in the light of our findings. In case it proved adequate, a simple method would become available for the design of new materials from the polymers under study.

EXPERIMENTAL

Materials

All the polymers studied were commercial products and were used as received. The polyvinylidene fluoride (PDVF) used was SOLEF 6010 supplied by Solvay (Germany) ($M_w/M_n = 4.5$); the polyvinyl acetate (PVA) was a Hoechst (Germany) product (Mowilith 50)

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($M_w = 260\,000$) and the polymethyl methacrylate (PMMA) was supplied by Repsol, S.A. (Spain).

Blends were prepared in a Brabender Plasticorder using a thermoplastic mixing chamber type W60 preheated at 180°C. Rotor speed was set at 60 rpm; 10 min of mixing were sufficient to generate a steady-state torque response, indicating uniform dispersion of the components.

Methods

Isothermal crystallization from the melt was studied using a Perkin–Elmer model DSC 7 differential scanning calorimeter (d.s.c.) operating in a N_2 atmosphere. The following procedure was employed: the samples were kept for 5 min at 493 K to destroy their thermal history and then quenched (350 K min^{-1}) to their crystallization temperature T_c. The melting temperature T_m of each sample after isothermal crystallization at T_c were calculated by heating the sample directly from T_c to T_m at a heating rate of 5 K min^{-1}. The crystallinity fraction X_T of the samples was determined at each T_c by the ratio of H_f^* to the fusion enthalphy of the PVDF sample with 100% crystallinity, taken as 104.75 J g^{-1}.

A Mettler TA4000 was used for the non-isothermal measurements. As in isothermal crystallization, each sample was held at 493 K for 5 min in order to remove all thermal history. Then it was cooled at a rate of 1, 2, 5, 10 and 20 K min^{-1} to total crystallization. The fraction of polymer crystallized at a certain temperature and time, the onset temperature, and the peak temperature were determined from the non-isothermal exotherm. Finally, the crystallized sample was heated at a rate of 10 K min^{-1} and the endotherm was recorded.

A software NEMROD was used to calculate the coefficients for the cuadratic canonic model and further plot of the ternary diagrams corresponding to the isoresponse curve for each property studied.

RESULTS AND DISCUSSION

Statistical design

As set out above in order to obtain new materials with desirable properties, the usual procedure is to prepare, at random, more or less complicated mixtures of the different components and to select the most suitable empirically.

In the present paper, the classical Scheffé Simplex design[11], which is well suited for this kind of problem[12], but which has never been applied to mixtures of polymers, has been used. So, this work deals with binary and ternary blends of the three polymers where the following condition is fulfilled: $\Sigma_i X_i = 1$ where X_1, X_2 and X_3 are the weight percentages of PVDF, PVA and PMMA, respectively.

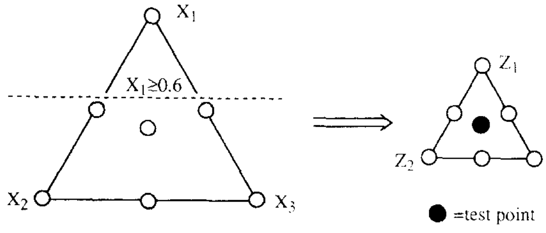

Figure 1 Initial experimental domain schematic representation and subsequent transformation in the constraint model. The test point has been chosen in the middle of the experimental domain

There are two complementary objectives regarding the general problem of mixtures: to find the proportions of the compounds required to optimize one or more properties of the mixture, and to obtain an empirical equation which satisfactorily describes the properties of the mixture over the whole area which might be used.

In the general case, the empirical mathematical models, also named equation of response surfaces, are polynomials[13,14], and correspond to the development of Taylor serial functions. To determine the coefficient of a particular model, Scheffé proposed the study of mixtures whose compositions are distributed symmetrically in a 'simplex' lattice over the experimental range. This kind of design contains a number of points equal to the coefficients in the corresponding polynomial which allows the equations to be solved directly.

In our case, although we had selected initially seven different blends represented in *Figure 1*, we could confirm through direct observations by means of thermal optical microscopy (TOM), that only blends with PMMA content makes up less than 60% in the blend, present crystallization capacity. So, we applied to our problem, a constraint Scheffé model with pseudocomponents (*Figure 1*) and seven new mixtures were prepared according to the plan

Exp. no.	Blends	Composition, wt% PVDF/PVA/PMMA	Variables Z_1	Z_2	Z_3
1	PVDF	100/0/0	1	0	0
2	FA64	60/40/0	0	1	0
3	FM64	60/0/40	0	0	1
4	FAM622	60/20/20	0	0.5	0.5
5	FA82	80/20/0	0.5	0.5	0
6	FM82	80/0/20	0.5	0	0.5
7	FAM811	80/10/10	0.5	0.25	0.25

With the results of experiments 1–6 and using the software Nemrod[15], coefficients for a cuadratic model

$$y = b_1Z_1 + b_2Z_2 + b_3Z_3 + b_{12}Z_1Z_2 + b_{13}Z_1Z_3 + b_{23}Z_2Z_3 \qquad (1)$$

where calculated, while experiment 7 was used as test in the model.

For the purpose of implementing a complete characterization of the crystallization processes taking place in these blends, measurements were taken at different crystallization temperatures and cooling rates. For this work, however, and by way of example, we present results obtained by applying the model to the parameters resulting from monitoring the crystallization processes at 415 K for isothermal crystallization and at a rate of 1 K min^{-1} for non-isothermal crystallization, the comments, however, being applicable to all other conditions.

Isothermal crystallization

From a theoretical point of view, it was first Avrami[16] and then Evans[17] who demonstrated that in isothermal conditions the change in crystallinity with time can be monitored by thermal analysis (d.s.c.) through the evolution of crystallization heat and can be readily expressed in the equation

$$X = 1 - \exp(-Kt^n) \qquad (2)$$

where X is the volume fraction of material crystallized at time t, K is a temperature-dependent constant that contains nucleation and crystal growth rate (rate constant), and n is a whole number whose value depends on the crystallization mechanism and the shape of crystal growth (fibril, disc, spherulite). The Avrami parameters n and K are determined by taking the double logarithm of equation (2) to yield a plot of $\log[-\ln(1-X)]$ vs $\log t$. From the expression[18]

$$K = \ln 2/t_{1/2}^n \qquad (3)$$

the half time, $t_{1/2}$, can be obtained, i.e. the time taken for 50% of the total crystallization to occur.

Table 1 lists the respective blend compositions, the values of T_m^0 (equilibrium melting point), as well as Avrami's parameters and the $t_{1/2}$ values corresponding to each crystallization temperatures (T_c). Coefficient values and calculated test for T_m^0, n and $\log K$ obtained by applying the model are collected in *Table 2*.

The equilibrium melting point values were obtained by means of the Hoffman–Weeks method[19] and as it can be observed, all the blends under study, binary as well as ternary blends, have a lower T_m^0 than the pure PVDF (*Figure 2*). So, for the binary blends PVDF/PVA it was observed that the drop of $T^0_{m,PVDF}$ as a consequence of increasing PVA content in the blend is notably more prominent for high PVDF concentrations, whereas the binary blends PVDF/PMMA, apart from generating a lesser depression of the melting point, are much more regular over the whole range of concentrations. With regard to the ternary blends, it must be stressed, on the one hand, that the higher the amorphous polymer portion, the greater the depression of the melting point, and on the other hand that for the same level of

Table 1 Equilibrium melting point, Avrami's parameters and $t_{1/2}$ values at different crystallization temperatures

Sample	Composition PVDF/PVA/PMMA (wt%)	T_c (K)	T_m^0 (K)	n	log K	$t_{1/2}$ (min)
PVDF	100/0/0	415	450.8	2.6	−0.039	0.88
		417		2.7	−0.502	1.05
		419		2.7	−1.054	1.29
		421		2.8	−1.756	1.63
		423		2.9	−2.458	2.05
		425		2.8	−2.969	2.50
FA82	80/20/0	415	449.0	2.2	−0.191	0.92
		417		2.5	−0.633	1.11
		419		2.6	−1.252	1.41
		421		2.7	−2.068	1.87
		423		2.8	−2.931	2.47
		425		2.8	−3.603	3.23
FA64	60/40/0	409	446.2	2.3	−0.168	0.92
		411		2.7	−0.678	1.13
		413		2.6	−1.152	1.36
		415		2.7	−1.926	1.78
		417		2.7	−2.763	2.40
		419		2.8	−3.704	3.32
FM82	80/0/20	413	445.5	2.3	−0.065	0.88
		415		2.6	−0.503	1.05
		417		2.6	−1.040	1.29
		419		2.8	−1.823	1.68
		421		3.0	−2.745	2.22
		423		3.2	−3.787	2.94
FM64	60/0/20	405	448.0	2.7	−0.735	1.15
		407		2.7	−0.990	1.27
		409		2.9	−1.531	1.50
		411		3.0	−1.920	1.69
		413		2.9	−2.325	1.99
		415		2.8	−2.884	2.50
FAM811	60/30/10	413	450.1	2.3	−0.046	0.87
		415		2.6	−0.594	1.06
		417		2.6	−1.048	1.31
		419		2.7	−1.722	1.65
		421		2.9	−2.578	2.17
		423		2.9	−3.290	2.78
FAM622	50/30/20	407	446.6	2.4	−0.073	0.89
		409		2.7	−0.487	1.05
		411		2.8	−0.942	1.23
		413		2.9	−1.480	1.48
		415		3.0	−2.330	1.94
		417		2.9	−3.050	2.54

Table 2 Coefficients values and calculated test obtained by applying the model to the parameters obtained under isothermal conditions

Coefficients	T_m^0	n	$\log K$
b_1	450.8	2.6	−0.039
b_2	446.2	2.7	−1.926
b_3	448.0	2.8	−2.884
b_{12}	−7.6	1.4	−5.390
b_{13}	−1.6	−2.0	5.082
b_{23}	−6.4	−0.6	7.608
FAM811 (exp.)	450.1	2.6	−0.594
FAM811 (cal.)	447.4	2.6	−0.688

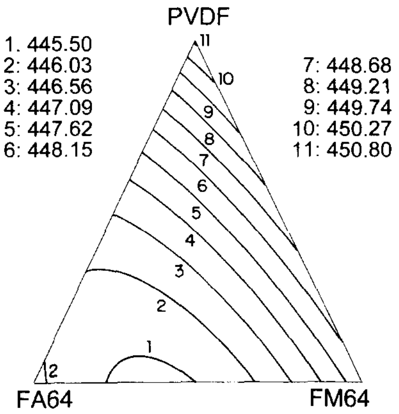

Figure 2 Response-surface contours for the equilibrium melting point

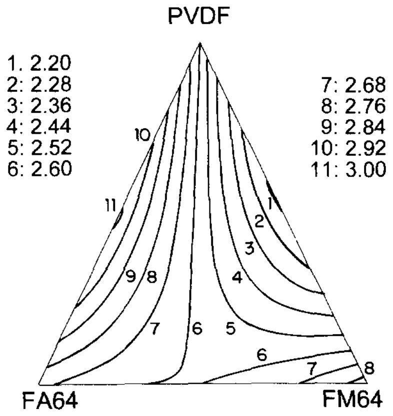

Figure 3 Response-surface contours for Avrami's exponent obtained in isothermal conditions at 415 K

polyvinylidene fluoride in the blend, $T^0_{m,\mathrm{PVDF}}$ is lower when the major amorphous polymer is PVA. This fact comes to suggest, according to the criterions of Flory and Nishi-Wang, that these are compatible blends. According to these theories an amorphous polymer is miscible with a semicrystalline polymer when it is capable of reducing its melting temperature significantly. This reduction is a function of the composition of blend.

The values of Avrami's exponent (*Figure 3*) found in our samples are highly similar among themselves ranging from 2 to 3 whereby it can be inferred that PVDF adopts the same growth geometry independent of T_c and blend composition and as for many macromolecules n is close to three and a picture of thermal heterogeneous nucleation followed by spherulitic growth is acceptable.

With respect to the rate constant (*Figure 4*) in all samples a drop in the crystallization rate constant is observed, with the exception of the binary PVDF/PMMA blends with a high semicrystalline polymer content, where the PVDF rate constant practically remains unaltered. Considering the binary PVDF/PVA blends with a high PVDF portion, $\log K$ increases (and hence K decreases) as a function of decreasing PVA content. Nevertheless, for PVDF percentages around 65%, K increases upon PVA addition. The PVDF rate constant hardly changes in the binary PVDF/PMMA blends until the amorphous polymer approaches 20%, at which concentration K diminishes inversely proportional to increasing PMMA content. Likewise, for the ternary blends a differentiation can be made as a function of PVDF content. For high concentrations the rate constant increases with PMMA content, until the amorphous polymer reaches a threshold, situated in a broad area of constancy, and then K is observed to drop to even lower values than the ones found experimentally.

The fact that having inferior, in general, constants makes us think there is a certain grade of likeness between the polymers that hinders the movement of the segments towards the surface of the crystal in formation. So, it is indicative of a certain compatibility between them.

The same information is reached by the data obtained when studying the behaviour of $t_{1/2}$ (*Figure 5*).

Non-isothermal crystallization

The analysis of non-isothermal crystallization can be followed by applying the Ziabicki[20] equation which is an extension of the Avrami equation and is used to describe the morphological variation as a function of cooling rate.

The kinetics of non-isothermal crystallization can be characterized by determining the constants Z_t and n'' occurring in the equation:

$$\log[-\ln(1-X(t)] = n''\log t + \log Z_t \qquad (4)$$

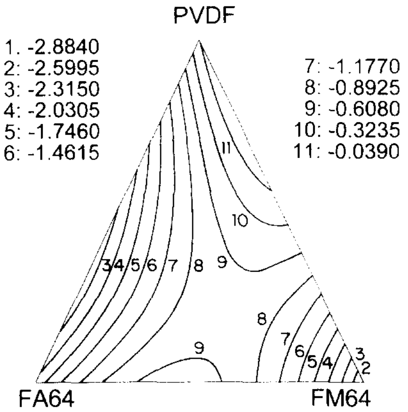

Figure 4 Response-surface contours for $\log K$ obtained in isothermal conditions at 415 K

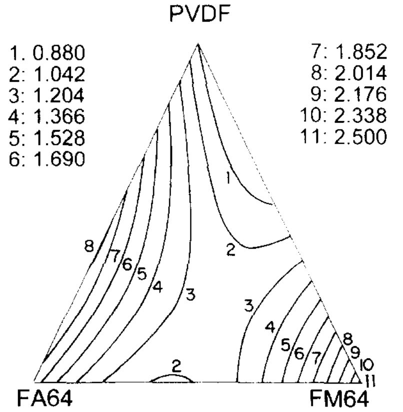

Figure 5 Response-surface contours for $t_{1/2}$ obtained in isothermal conditions at 415 K

Table 3 Values obtained from non-isothermal crystallization at different cooling rates

Sample	Composition PVDF/PVA/PMMA (wt%)	β (K min^{-1})	n''	$\log Z_t$	$t_{1/2}$ (min)
PVDF	100/0/0	1	2.4	−1.97	1.93
		2	3.6	−1.98	1.56
		5	2.9	−0.31	0.98
		10	2.8	0.41	0.78
		20	2.3	0.61	0.67
FA82	80/20/0	1	3.7	−2.64	1.85
		2	2.9	−1.03	1.26
		5	2.5	−0.09	0.90
		10	2.0	0.35	0.70
		20	1.4	0.41	0.57
FA64	60/40/0	1	4.3	−3.59	2.13
		2	3.9	−2.00	1.54
		5	4.4	−0.79	1.01
		10	2.8	0.39	0.76
		20	2.9	0.77	0.68
FM82	80/0/20	1	3.2	−2.58	1.98
		2	3.7	−1.79	1.48
		5	4.2	−0.77	1.10
		10	2.9	0.21	0.82
		20	2.0	0.51	0.65
FM64	60/0/40	1	4.1	−3.57	2.21
		2	3.6	−2.21	1.67
		5	3.8	−1.16	1.23
		10	3.0	−0.23	0.96
		20	2.6	0.21	0.80
FAM811	80/10/10	1	3.8	−2.92	1.97
		2	4.6	−2.44	1.57
		5	3.3	−0.31	0.98
		10	2.8	0.23	0.81
		20	2.4	0.50	0.69
FAM622	60/20/20	1	3.8	−3.02	2.03
		2	4.1	−2.21	1.58
		5	3.4	0.53	1.05
		10	2.5	0.20	0.79
		20	2.7	0.41	0.75

Table 4 Calculated model coefficients and test point values obtained by applying the model to the non-isothermal data

Coefficients	n''	$\log Z_t$	$t_{1/2}$
b_1	2.4	−1.97	1.93
b_2	4.3	−3.59	2.13
b_3	4.1	−3.57	2.21
b_{12}	1.8	−0.96	−0.88
b_{13}	1.8	0.52	−0.76
b_{23}	−4.0	4.01	0.00
FAM811 (exp.)	3.8	−2.92	1.93
FAM811 (cal.)	3.5	−2.58	1.89

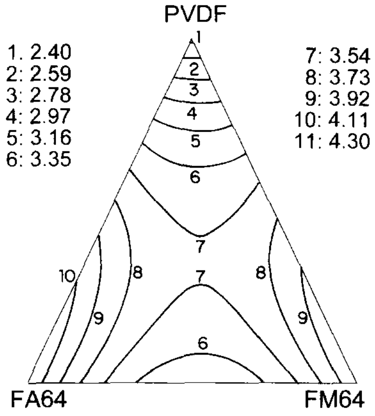

Figure 6 Response-surface contours for n'' obtained in non-isothermal conditions at a crystallization rate of 1 K min^{-1}

The rate constant Z_t is equivalent to the Avrami rate constant in isothermal crystallization kinetics; n'' is the morphological exponent; and $X(t)$ is the crystalline fraction at the time t. n'' at a specific cooling rate is obtained from the slope of a plot of $\log[-\ln(1-X)]$ vs $\log t$. In the Ziabicki analysis, the effects of the cooling rate on the crystalline morphology are indicated by the dependence of the exponent n'' on the cooling rate. The intercept in the logarithm plot gives the parameter $\log Z_t$. The final form of Z_t has to be corrected for the cooling rate

$$\log Z_c = \log Z_t/\beta \tag{5}$$

When applying the Ziabicki equation (up to a maximum of 60% conversion) the data adjust almost perfectly to a straight line for small rate values. For higher rates the data deviate from strict linearity, although in none of the cases is a ratio below 0.97 obtained.

Table 3 compiles the n'', $\log Z_t$ and $t_{1/2}$ values obtained in the non-isothermal conditions described above and *Table 4* collects the corresponding coefficient and test point values. In general terms, the n'' values range from 2 to 4 (*Figure 6*) and, in spite of observing a wide zone of compositions where it hardly varies, a straightforward relationship between n''-variation and composition proves impossible to establish. More useful information can be retrieved from analysing the behaviour of the rate constant. As can be concluded from *Figure 7*, all the blends present a lower value than that of unblended PVDF. For the binary blends (PVDF/PVA as well as PVDF/PMMA) this value decreases inversely proportional to the amorphous polymer content. In the ternary blends, and for one and the same PVDF portion, a slight increase is observed with increasing replacement of PVA by PMMA, until a central zone is reached, where the value of the rate constant practically does not vary, and then it begins to decrease. In other words, the behaviour shows perfect analogy to the one commented on when discussing crystallization under isothermal conditions. The fact that the rate constants of the blends are consistently lower than that of pure PVDF explains the circumstance that the time needed to reach 50% transformation in these samples is longer than the span required by unblended PVDF under the same conditions. As can be seen in *Figure 8*, with increasing amorphous polymer percentage in the blend (with the exception of the samples with extremely high PVDF and PMMA portions) the time to reach 50% transformation of the crystallizable material is becoming shorter. This phenomenon, the same as under isothermal conditions, is indicative of the fact that there exists a certain difficulty in moving the macromolecular segments in the crystallization processes, as a consequence of the macromolecular affinity of PVDF with either of the amorphous polymers.

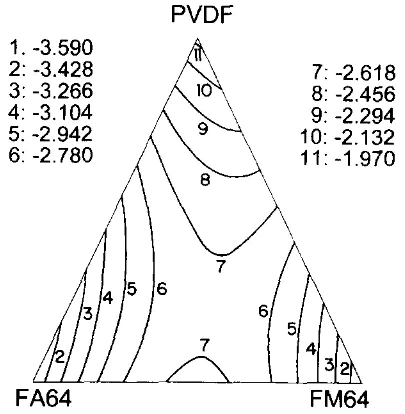

Figure 7 Response-surface contours for $\log Z_t$ obtained in non-isothermal conditions at a crystallization rate of 1 K min^{-1}

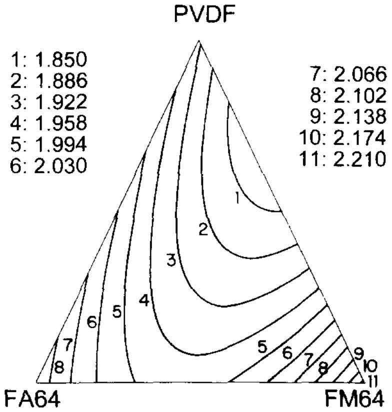

Figure 8 Response-surface contours for $t_{1/2}$ obtained in non-isothermal conditions at a crystallization rate of 1 K min^{-1}

CONCLUSIONS

Interpretation of these findings allows for two conclusions. Firstly, the Scheffé model proposed to examine these systems has proved to be totally satisfactory, as it is capable of reliably reproducing this behaviour. This is of enormous relevance, because, apart from the fact that its application to the study of ternary blends is a novelty, it allows us, once the coefficients of the equation have been determined, to obtain, for each response, its exact value for any composition without the need of experimental determination. In addition it becomes possible to select the range of concentrations where the behaviour of a certain property is the most adequate, i.e. in a certain way the best suited material as a function of the properties required can now be designed.

The second conclusion refers to blend compatibility, which is known to be an extremely relevant aspect, when dealing with polymer blends, whose properties are expected to be better than those of the individual components. In the light of the data discussed in this paper it is legitimate to conclude that the experimental blends have proved to be compatible.

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