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Application of a statistical method to study the spherulitic growth of polymer blends

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Summary

This paper has two objectives. Firstly, to plan experimental blends (based on PVDF, PMMA and PVA) according to a statistical method proposed by Scheffé and subsequently to apply the model to the study of the spherulitic growth of PVDF with the aim of assess its suitability. In case it proved adequate, a simple method would become for the design of new materials from the polymer under study.

Introduction

The relevance of polyvinylidene fluoride (1,2) as regards its potential application in the field of sensors in general and of robotics in particular is based on its excellent pyro-piezoelectric properties discovered by Kwei in 1969 (3).

As is well known polyvinylidene fluoride shows polymorphism and it exits in five crystalline phases, designated as α, β, γ, δ, ε (4,5). If the polymer is crystallized from the melt at atmospheric pressure, it produces an α-phase in which the polymer backbone is in a trans-gauche-trans-gauche configuration. In this conformation there are two molecules per unit cell (6), and the dipoles of these two molecules are oriented in opposite directions, canceling each other to produce a net moment of zero. Therefore, this form is neither polar nor does it exhibit piezoelectric or pyroelectric properties (7). The β-phase is composed of two trans-planar chains in an orthorombic unit cell (8). The dipoles of the monomer units in the polymer chain backbone are aligned so that self-cancellation among them does nor occur and therefore spontaneous polarization arises (9). The polyvinylidene fluoride crystal in this phase is polar and exhibits piezoelectric and pyroelectric properties.

It has been recognized that certain co-polymers (10) based on polyvinylidene fluoride do not only possess the above-mentioned β-form, but their pyro-piezoelectrical activity is greater than that of the homopolymer. This latter finding explains the intense research activity deployed in the development on new polyvinylidene fluoride-based pyro-piezoelectric materials through co-polymerization reactions (11), through physical blends with other polymers (12,13) or through the incorporation of highly active ceramics into different polymer systems (14).

The research we have been developing for quite some years (15,16) 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 the pure polyvinylidene fluoride homopolymer.

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 researches. 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 spherulitic growth 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.

Theoretical background

Lauritzen-Hoffman analysis

Lauritzen and Hoffman (17-19) developed a chain-folding kinetics to describe the crystal growth of macromolecules from a solution and the melt. This kinetic theory, as opposed to the classical nucleation theory, which emphasizes the characterization of the equilibrium aspects of polymer crystals, essentially remains a nucleation theory; yet the interest does not focus only on the formation of the nucleus, but emphasizes subsequent growth.

Under normal circumstances, flexible linear molecules crystallize in the form of thin platelets, whose upper and lower surfaces consist of an array of molecular folds. These folded structures, which crystallize from the melt, are referred to as "chain-folded lamellae". The lamellae grow to form spherulites, so commonly encountered in crystallized linear polymers.

The Lauritzen-Hoffman growth rate of polymer crystals, G, expressed in terms of length/time, can be formulated as:

$$\ln G + U^*/R(T_c - T_\infty) = \ln G_0 - K_g/T_c(\Delta T)f \qquad /1/$$

K_g is defined as:

$$K_g = xb\sigma\sigma_e T_m{}^0/k\Delta H \qquad /2/$$

x is equal to 2 or to 4 depending on regime since the L-H theory indicates that crystal growth is characterized by three regimes depending on T_c, or more specifically on supercooling (ΔT, defined as $T_m{}^0$-T_c). Although originally conceived to be applied to homopolymers, the L-H theory has also been used in the case of polymer-diluent systems (20-22) and polymer blends (23,24). In the case of crystalline/amorphous polymer systems, the amorphous polymer is expelled from the growing crystals. Hence it will concentrate mainly at the interface and from there attempt to diffuse towards the amorphous region. If, however, the diffusion process is poor, amorphous polymer concentration at the interface will remain high. As a consequence, spherulitc growth rate will slow down, and the growth process will be governed by displacement phenomena. For this and other reasons the Lauritzen and Hoffman theory has been modified and redefined by Hoffman himself (25), and the modified equation which describes the spherulitc growth rate of a crystallizable polymer in the molten phase, containing a second polymer which acts as a diluent, can be expressed in the following way:

$$\ln G - \ln \Phi_2 + U^*/R(T_c\text{-}T_\infty) - 0.2T_m{}^0\ln \Phi_2/\Delta T = \alpha = \ln G_0 - K_g/T_c(\Delta T)f \qquad /3/$$

where Φ_2 is the volume fraction of crystalline polymer. G_0 is the pre-exponential factor which is constant and independient of temperature.

Thus, if α is plotted against $1/T_c(\Delta T)f$, a straight line should be obtained with slope K_g and intercept $\ln G_0$. Hoffman found T_∞=T_g-30K and U^* = 1500 cal mol^{-1} by fitting the crystallization kinetic data for various polymers (26).

The glass transition temperature of PVDF was calculated from thermal measurements (27) and the T_gs corresponding to the different blends by appliyng the Wood equation (28).

The equilibrium melting temperature (T_m^0) was obtained by the Hoffman-Weeks method (29).

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 (30), which is well suited for this kind of problems (31), 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: $\sum_i X_i = 1$ where X_1, X_2 and X_3 are the weight percentages of PVDF, PVA and PMMA, respectively.

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 (32,33), and correspond to the development of Taylor serial functions. To determine the coefficients of a particular model, Scheffé proposed the study of mixtures whose compositions are distributed symmetrically in a "simplex" lattice over the experimental range. In this kind of design the number of points equals the coefficients in the corresponding polynomial which allows the equations to be solved directly.

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

exp. n°:	**BLENDS**	**Composition, wt-%**	**VARIABLES**		
		PVDF/PVA/PMMA	**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 experiencies 1-6 and using the software Nemrod (34), coefficients for a cuadratic model were calculated:

$$y = b_1 Z_1 + b_2 Z_2 + b_3 Z_3 + b_{12} Z_1 Z_2 + b_{13} Z_1 Z_3 + b_{23} Z_2 Z_3 \qquad /4/$$

Experience 7 was used as test. Agreement between experimental and calculated (using the obtained equation) values would be a good validation of the statistical model.

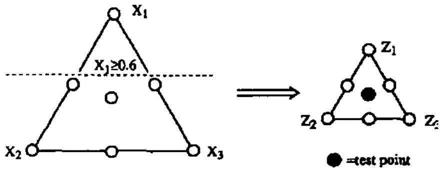


Fig. 1- Initial experimental domain schematic representation and subsequent transformation in the constraint model

Experimental

Materials

All the polymers studied were commercial products and were used as received: The polyviylidene fluoride (PVDF) was Solef 6010, supplied by Solvay (M_w/M_n=4.5); the polyvinyl acetate (PVA) was Mowilith 50, a Hoechst product (M_w=260000) and the polymethyl methacrylate (PMMA) was supplied by Repsol, S.A.

Blending

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 and ten minutes of mixing were enough to get uniform dispersion of the components.

Methods

The spherulitic growth rate, G, was studied on films obtained through melting slabs of approximately 10 µm thickness, utilizing a Jenaval light microscope equipped with a hot stage Mettler FP82. First the films were molten at 493 K with the aim of deleting their thermal history and then quenched to the selected crystallization temperature. During crystallization micrographs were obtained at different intervals with a pentacon B 100M camera.

Table 1.- Composition blends, T_c and radial growth rate for different crystallization temperatures.

SAMPLE	Composition, wt-% PVDF/PVA/PMMA	T_c (K)	G (µm/min)
PVDF	100/0/0	435	0.73
		434	1.13
		433	1.40
FA82	80/20/0	432	0.36
		434	0.26
		436	0.16
FA64	60/40/0	426	1.12
		427	0.57
		429	0.29
FM82	80/0/20	431	0.78
		432	0.42
		435	0.27
FM64	60/0/40	425	1.01
		426	0.33
		429	0.26
FAM811	80/10/10	433	0.26
		435	0.15
		437	0.09
FAM622	60/20/20	423	0.56
		425	0.36
		427	0.22

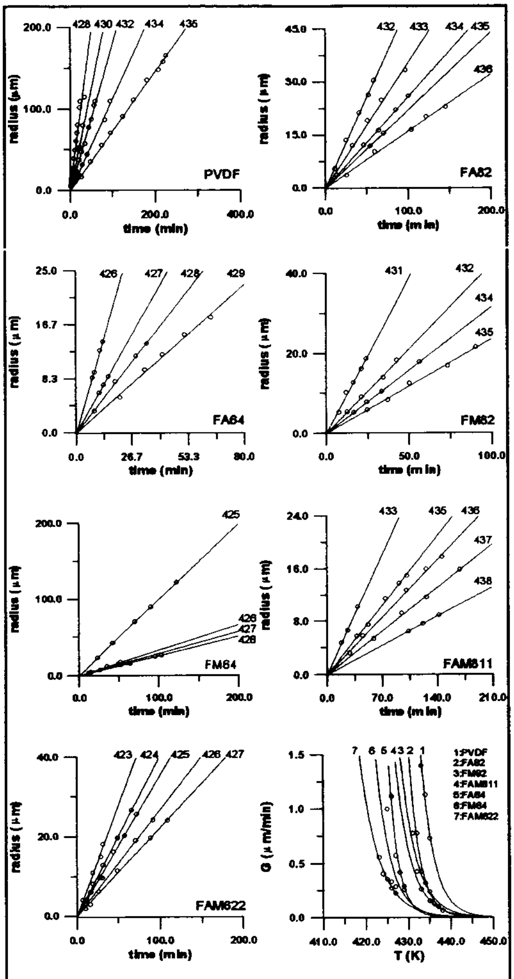


Fig. 2.- crecimiento readial de las diferenes muestras y G

Results and discussion

In Figure 2 it can be observed the behaviour of G versus temperature for all the samples studied. G was obtained from the slope of the straight line which is obtained when plotting the experimental spherulitic radius against time (for each crystallization temperature) (see also Figure 2).

Table 1 compiles the G, T_c values and the composition of the blends. Table 2 compiles de K_g and ln G_0 results obtained from the Lauritzen-Hoffman analysis and Table 3 the coefficients and calculated test result for both parameters.

Plotting each equation, the corresponding response-surface contours are obtained such as they are shown in Figures 3 and 4.

In Figure 2 it can be observed that, as was to be expected, the spherulitic radius increases over time for all crystallization temperatures, and the spherulites in the different blends grow almost linearly. In some cases we could observe a non-linear behavior in a self-retarding fashion: the retarding obstacle is a depletion layer which is formed around the growing crystal; PVDF crystallization always involves ejection of the amorphous polymer. When this latter polymer concentrates at a certain site, depletion zones are formed.

Regarding the G_0 values it must be pointed out that: a) it is higher in pure PVDF than in the blends; b) for the pairs of blends FA82-FM82 and FA64-FM64 (both with the same amorphous polymer content) the values are slightly lower for the blends containing PMMA. This can be explained by the fact that, as is well know, the crystallization process is only possible in the temperature range between T_m^0 and T_g. When an amorphous polymer is added and acts as a diluent, i. e. if it presents a certain degree of compatibility with the crystalline polymer, the T_m^0 - T_g range is reduced. Thus, as the T_m^0 corresponding to samples FA82 and FM82 are very similar and T_g of FA82 is lower than that of PMMA, the polymer chains possess greater mobility in the former, and hence radial growth rate will be higher. A third feature, c) is that G_0 diminishes inversely proportional to the amorphous fraction, i. e. $G_{0,FA82}>G_{0,FA64}$. The line of reasoning to explain this fact is analogous to what was stated above.

Table 2.- T_gs, T_m^0 s and results of the Lauritzen-Hoffman analysis.

SAMPLE	T_g (K)	T_m^0 (K)	K_g x 10^4 (K^2)	ln G_0
PVDF	244.4	450.8	2.8	9.9
FA82	258.5	449.0	3.3	8.7
FA64	272.6	446.2	3.4	7.4
FM82	274.1	448.0	2.9	8.4
FM64	303.8	445.5	3.6	7.1
FAM811	266.3	450.1	3.1	8.9
FAM622	288.2	446.6	3.2	6.7

The nucleation factor (Table 2) which basically depends on the free energy available to form a critical size nucleus, is determined from the slope of the straight line, which is obtained when plotting α against $1/T_c(\Delta T)f$ in equation /3/. Regarding these values it must be stressed that they are very similar to those of the pure homopolymer, i.e. the free energy necessary to form a critical size nucleus is of the same order. There antecedents in the bibliography (35) which support the assumption that a drastic drop of the K_g value of the blend vis à vis that of the homopolymer is indicative of the existence of incompatibility.

If we observe Figure 4 it is possible to take out some additional information: in general the blends present a higher value than that of unblended PVDF. For the binary blends (PVDF/PVA as well as PVDF/PMMA) this value increases inversely proportinal to the amorphous polymer content. In the ternary blends, and for one and the same PVDF portion, a slight decrease is observed with increasing replacement of PVA by PMMA, until a central zone is reached, where the value of K_g practically does not vary, and then it begins to increase.

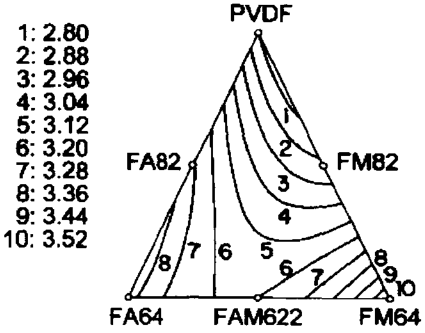
Table 3.- Coefficients values and calculated test obtained by appliying the model to the parameters calculated from the L-H analysis.

Coefficients	**K_g**	**G_0**
b_1	2.8	9.9
b_2	3.4	7.4
b_3	3.6	7.1
b_{12}	0.8	0.2
b_{13}	-1.2	-0.4
b_{23}	-1.2	-2.2
FAM811 (experimental)	3.1	8.9
FAM811 (calculated)	3.0	8.4

Conclusions

The interpretation of these findings allows the following conclusions: First, the Scheffé model proposed to examine these systems has proved to be totally satisfactory, as it is capable of reliably reproducing this behaviour (the values corresponding to G_0 and K_g experimental and calculated are practically the same).This is of considerable 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.

Fig.3- Response-surface contours for K_g



Another conclusion is connected with the blend compatibility. As is well known this is an extremely relevant aspect when dealing with polymer blends. Spherulitic growth rate is diminished in all blends, as compared to the unblended homopolymer, the differential becoming greater with increasing amorphous polymer portion in the blends. This is in good agreement with the general criterion that, when a crystallizable polymer is blended with an amorphous polymer, and this latter acts as a diluent (i.e. if it has a certain affinity with the crystalline polymer), compatible blends can be former. As a consequence, the T_m^0 - T_g range, within which crystallization is possible, will decrease, and at a given crystallization temperature the migration rate of the macromolecular segments towards the crystal-forming sites will be slower. This, in turn, translates into a reduction in radial growth rate.

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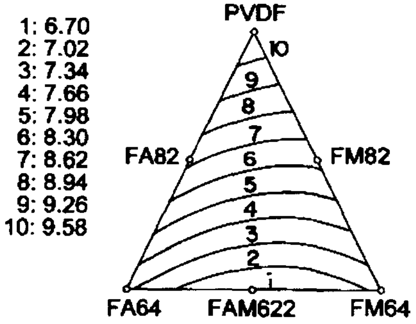
Fig.4- Response-surface contours for G_0



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