Extrinsic conducting and superconducting polymer systems: 1. Analysis of the structure of PVDF/PS blends containing copper and carbon black fillers

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This paper reports on the obtention of two extrinsic conducting polymer systems by means of copper and carbon black filler incorporation into a polymer system consisting of a poly(vinylidene fluoride)/polystyrene (PVDF/PS) blend. With the aim of analysing the influence exerted by copper and carbon black on the morphology, microstructure and compatibility of the systems under study, the glass transition temperatures as well as isothermal and non-isothermal crystallization kinetics were determined for the different systems. The dynamic mechanical and calorimetric results demonstrated on the one hand that carbon black produces partial compatibilization of the PVDF/PS system, while on the other hand they prove both copper and carbon black to be capable of modifying the microstructure and morphology of the initial system.

(Keywords: poly(vinylidene fluoride); polyblends; conducting polymer systems)

INTRODUCTION

The insulating properties of polymers are one of the most important characteristics of these materials. In recent times[1-7], however, conducting and superconducting polymer systems have been synthesized, which apart from the usual characteristics of polymers (castability, good mechanical properties, lightness, low cost, etc.) provide for a large number of electrical and electronic features with the result that in many cases and for certain applications they have succeeded in replacing metals.

Among the different conducting polymer systems, one has gained special importance. Such a system is obtained by means of incorporating conducting metallic or non-metallic fillers in powder or fibre form into polymers or polymeric systems. The resulting composites are known as extrinsic conducting polymer systems, their most important electrical characteristic being that their conductivity is a consequence of electrical charge transfer between conducting islands dispersed throughout the polymeric matrix. In order to overcome the insulating nature of the polymer, it is necessary to provide for percolation[8-11] to exist between the conducting particles so that charge transfer can take place, or to arrange for these particles to be positioned in the closest possible proximity so that electron transfer can take place through a tunnelling mechanism.

The conductivity of extrinsic conducting polymers depends not only on the filler concentration but also on the intrinsic properties of the conducting material, the usual characteristics of the polymer system and the nature of the interaction between both. It is known that both the nature of the polymeric system acting as the matrix in extrinsic conducting polymer systems and certain surface properties, such as surfactance[2], play an essential role in determining the degree of conductivity and the transfer mechanism. This is the reason why at present research is focusing on new polymeric systems in an attempt to achieve maximum conducting or superconducting efficiency. Among the different superconducting polymer systems, special emphasis is placed on the composites based on YBaCuO, one of the most important superconducting ceramics.

In this series of articles, we will use a basic polymer system consisting of blends of poly(vinylidene fluoride) (PVDF) and polystyrene (PS) in an investigation of the influence of copper (Cu) and carbon black (N) on the structure and electrical properties of the composites.

This first paper pursues the thermal and dynamic mechanical characterization of the different composites with the purpose of gaining insight into the effects produced by copper and carbon black both on the kinetics and the geometry of PVDF crystal growth and on the compatibility of the initial polymer system. As is well known, fillers may act as true compatibilizing agents among incompatible systems[12] or as phase structure regulating components[13]. Thus the properties (including the electrical features) of filled polymers do not depend only on the filler content but also on its dispersion in the matrix.

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Table 1 Glass transition temperatures of PVDF/N and PVDF/PS/N systems at 10 Hz

	Composition			
Sample	PVDF/PS (% ϕ_v)	N (% ϕ_v)	T_g^{PS} (K)	T_g^{PVDF} (K)
F	100/0	0	–	239
FN0	100/0	2	–	241
FN1	100/0	10	–	239
FN3	100/0	30	–	234
FN4	100/0	35	–	238
FSN10	70/30	2	373	231
FSN11	70/30	10	378	233
FSN13	70/30	30	384	241
FSN14	70/30	33	384	242
FSN20	50/50	2	373	237
FSN21	50/50	10	377	236
FSN23	50/50	30	382	237
FSN24	50/50	38	–	–
FSN30	30/70	2	–	243
FSN31	30/70	10	377	242
FSN33	30/70	30	378	239
FSN34	30/70	38	–	–

Table 2 Glass transition temperatures of PVDF/Cu and PVDF/PS/Cu systems at 10 Hz

	Composition			
Sample	PVDF/PS (% ϕ_v)	Cu (% ϕ_v)	T_g^{PS} (K)	T_g^{PVDF} (K)
F	100/0	0	–	239
FC0	100/0	2	–	234
FC1	100/0	10	–	238
FC3	100/0	30	–	240
FC4	100/0	40	–	244
FSC10	70/30	2	373	238
FSC11	70/30	10	372	240
FSC13	70/30	30	373	245
FSC14	70/30	35	373	243
FSC20	50/50	2	374	237
FSC21	50/50	10	371	240
FSC23	50/50	30	374	242
FSC24	50/50	35	374	242
FSC30	30/70	2	374	236
FSC31	30/70	10	374	239
FSC33	30/70	30	377	239
FSC34	30/70	35	376	249

EXPERIMENTAL

The materials used were two commercial polymers, Solef 6010 (PVDF) from Solvay ($\bar{M}_w/\bar{M}_n=4.5$) and 143E (PS) from BASF ($\bar{M}_w/\bar{M}_n=2.5$). The conducting fillers used were carbon black (N) Isaf N200 in powder form (particle size 20 nm) and metallic copper (Cu) from Merck, also in powder form (particle size 63 μm).

The blends were obtained from the melt under an N_2 atmosphere in a Brabender torque rheometer using a thermoplastic mixing chamber (type W60) preheated to 473 K. The rotor speed was set at 55 rev min^{-1} and the materials remained in the chamber for about 10 min once the torque had stabilized, which ensured perfect homogenization.

The dynamic mechanical measurements were conducted in a dynamic mechanical thermal analyser MKII from Polymer Laboratories at 3, 10 and 30 Hz in the temperature range 133–413 K and at a rate of 2 K min^{-1}.

Thermal analysis was done by means of differential scanning calorimetry in a Perkin–Elmer DSC7. The samples were held at a temperature of 493 K for 5 min in order to destroy their thermal histories. Then they were quenched (350 K min^{-1}) down to their crystallization temperatures. For the dynamic test, cooling rates of 0.1, 0.5, 1, 2 and 5 K min^{-1} were applied.

For scanning electron microscopy (SEM), impact-fractured samples were used. The fracture surfaces were coated with an Au/Pd alloy and observed with a Hitachi 52100 microscope under an acceleration potential of 15 kV.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

Dynamic mechanical analysis is a fundamental tool for gaining insight into the effects exerted by the filler on the polymeric matrix. These effects are displayed as a modification of the peak position and width of the relaxation spectrum as a consequence of filler–polymer interaction.

Tables 1 and *2* show the variations in glass transition temperature for the different blends as a function of composition and filler content at a frequency of 10 Hz.

Figure 1 shows the glass transition temperatures of PVDF (T_g^{PVDF}) in PVDF/filler systems plotted against carbon black concentration and copper concentration for the three experimental frequencies. For both blends different behaviour was recorded. Whereas for the copper composites T_g^{PVDF} increases in proportion to the filler concentration, in the carbon black composites T_g^{PVDF} decreases until a filler concentration of 30% is reached, whereupon it increases considerably and in some cases surpasses the initial value.

In *Figure 2* T_g^{PS} and T_g^{PVDF} variations are represented as a function of carbon black concentration. It can be observed that T_g^{PS} increases in proportion to carbon black concentration, and the increase is larger for a smaller PS content in the blend. In contrast, T_g^{PVDF} behaves differently. Whereas for a low PS content the glass transition temperature increases markedly, for a medium or high PS content in the blend T_g^{PVDF} remains practically constant or diminishes with increasing carbon black content.

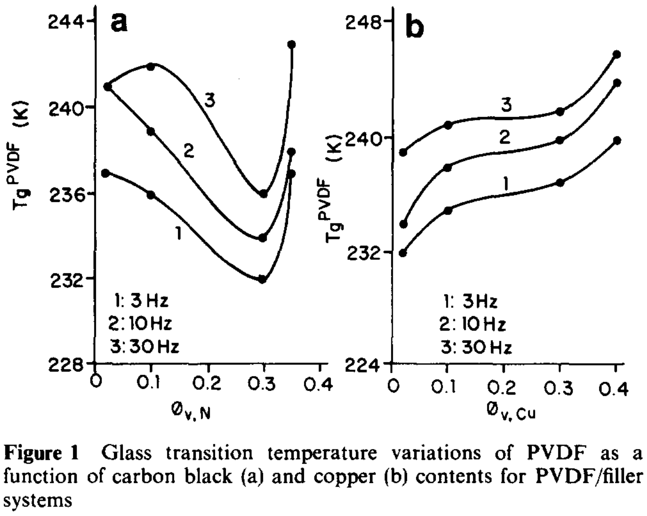

Figure 1 Glass transition temperature variations of PVDF as a function of carbon black (a) and copper (b) contents for PVDF/filler systems

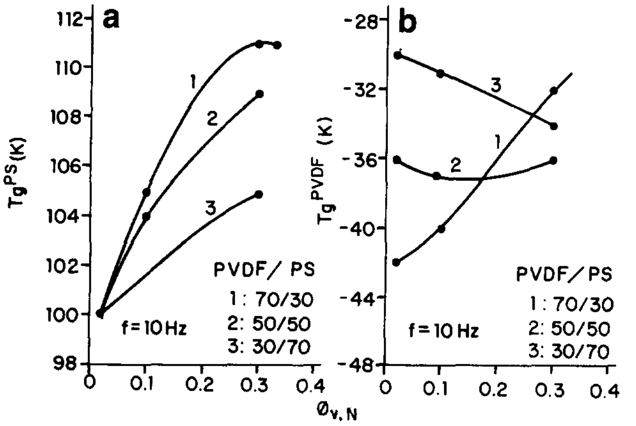

Figure 2 Glass transition temperature variations of PS (a) and PVDF (b) as a function of carbon black content for PVDF/PS/N systems

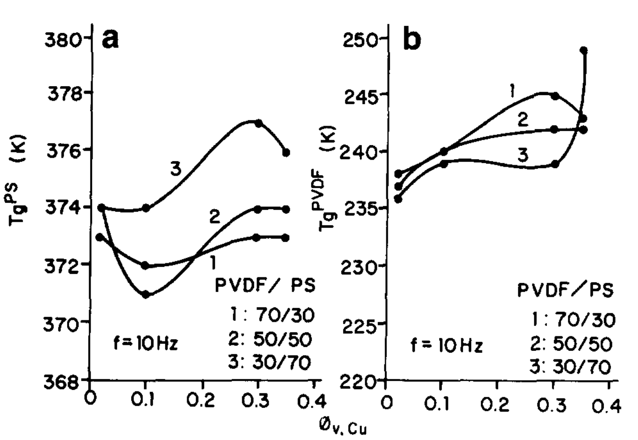

Figure 3 Glass transition temperature variations of PS (a) and PVDF (b) as a function of copper content for PVDF/PS/Cu systems

Figure 3 shows the T_g^{PS} and T_g^{PVDF} variations as a function of metallic copper content. It can be observed that T_g^{PVDF} undergoes a slight increase upon increasing the copper content, whereas T_g^{PS} remains practically constant in all instances, although the most noteworthy variations and the higher values occur for systems with a higher PS content, similar to the behaviour observed for T_g^{PVDF}.

The slight changes recorded for the glass transition temperatures of the components in the PVDF/PS blends when filled with metallic copper and the more prominent variations observed for the same systems in the presence of carbon black are, in principle, attributable to a partial compatibilization of the polymeric systems as a consequence of filler incorporation. This partial compatibilization is directly related both to the phenomenon of filler–matrix interaction and to a homogenization and micronization of the different polymer phases as a consequence of increasing filler content, as can be seen in the SEM micrographs in *Figure 4* showing the phase distribution of the PVDF/PS system in the absence and in the presence of carbon black.

Isothermal crystallization

The data relating to the isothermal crystallization kinetics of the binary and ternary composites were analysed on the basis of the Avrami equation[14], which gives the variation in crystalline content over time at a constant crystallization temperature for a molten sample

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

where $X(T)$ is the weight fraction of crystallized material at time t, K represents the rate constant of the crystallization process and n is the Avrami exponent, which depends on the type of nucleation taking place and the growth geometry. The n and K values were obtained from the slopes and intercepts, respectively, of plots of $\log\{-\ln[1-X(T)]\}$ against $\log t$ for degrees of crystallinity below 30% and for each crystallization temperature. Secondary crystallization processes were not observed in the isothermal crystallization of PVDF/N composites (*Figure 5*). Similar behaviour was shown by all the binary and ternary systems studied here.

In order to gain knowledge on the effect produced by each conducting filler on PVDF crystallization, the kinetic parameters T_m, $\log K$ and n are represented as functions of the carbon black and metallic copper contents for the systems PVDF/N and PVDF/Cu, respectively, in *Figures 6* and *7*. These figures show that neither copper nor carbon black affects the melting point of PVDF, regardless of the respective filler content (*Figures 6a* and *7a*). The crystallization rate of PVDF increases with increasing copper content over the whole range of experimental concentrations. The same finding applies to the carbon black composites, with the caveat

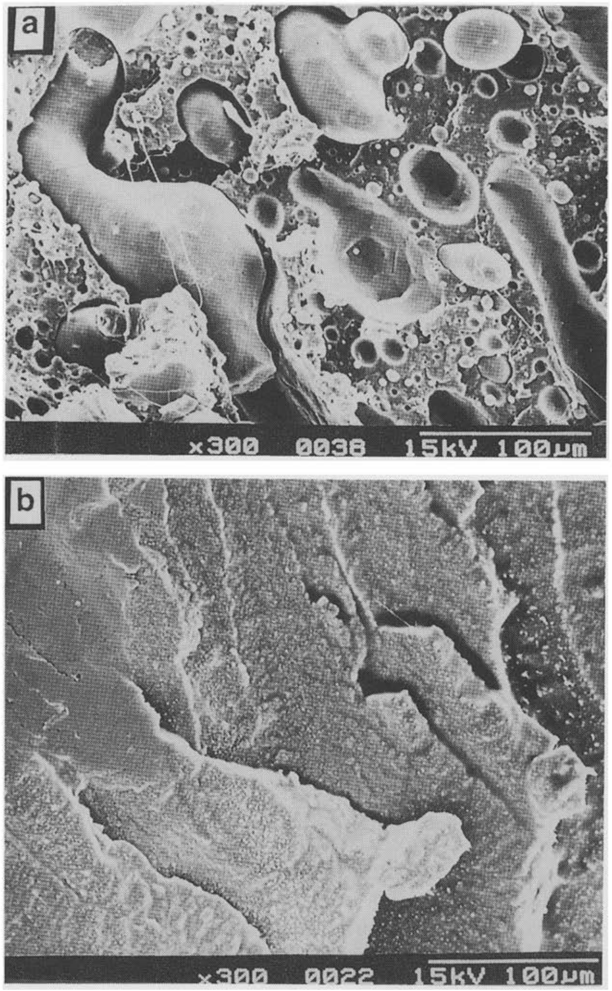

Figure 4 SEM micrographs of a PVDF/PS blend in the absence (a) and in the presence (b) of carbon black

that at a carbon black concentration of 30% the crystallization rate diminishes (*Figures 6b* and *7b*). The increase of the crystallization rate may be interpreted, in principle, as a consequence of the nucleating effect exerted by one or the other filler on PVDF; the decrease of K in the carbon black composites at a 30% filler content, which is not observed for the copper composites at that filler concentration, is related to other concurrent circumstances in the process: first, the large number of carbon black particles, larger than the number of copper particles at the same concentration, which may trigger an impediment to crystallization; and secondly, the different surface activities of copper and carbon black which may lead to interactions of quite different nature, such as those inhibiting the spherulite nucleation process. The latter would explain the decrease in PVDF crystallization rate at high carbon black concentrations. The crystal growth geometry as derived from the interpretation of the exponent n in the systems PVDF/N and PVDF/Cu (*Figures 6c* and *7c*) shows that n diminishes in inverse proportion to filler content from approximately 3.0 (for low filler contents) down to 2.3–2.4 (for higher filler contents), which in turn is indicative of the fact that PVDF crystallizes tridimensionally for a low filler content, whereas it shows a medley of bidimensional and tridimensional crystallizations at higher filler contents. In both cases the nucleation mechanism is heterogeneous.

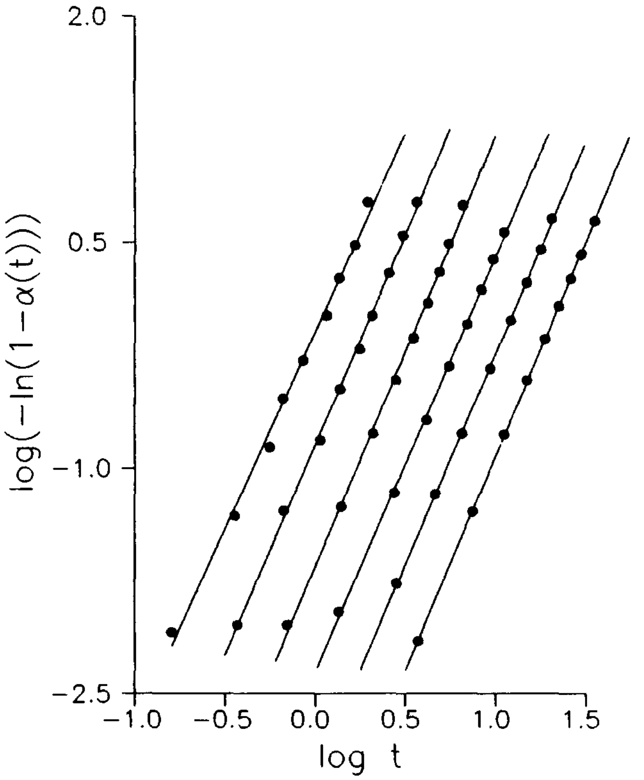

Figure 5 Avrami plots for the isothermal crystallization of PVDF/N systems

Figures 8 and *9* are based on PVDF/PS/N and PVDF/PS/Cu systems and show plots of T_m, log K and n against the respective filler percentages. These figures allow us to draw the following conclusions. The melting temperature of PVDF in the blends with PS is a function not only of blend composition but also of the relevant filler content. For carbon black (*Figure 8a*), T_m^{PVDF} diminishes for medium filler contents and increases at higher filler levels, whereas the copper-filled blends behave exactly in the opposite way. It should be noted that the temperature variations do not exceed 4 K even in the extreme cases. Hence the changes recorded cannot be attributed to a compatibilizing effect of copper or carbon black.

Moreover, the results point towards a phase-homogenizing process within the PVDF/PS system,

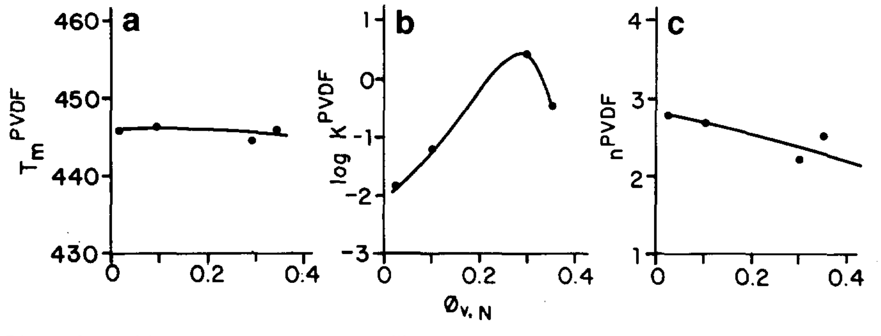

Figure 6 Melting temperature (a), crystallization rate (b) and Avrami exponent (c) of PVDF as a function of carbon black content for PVDF/N systems

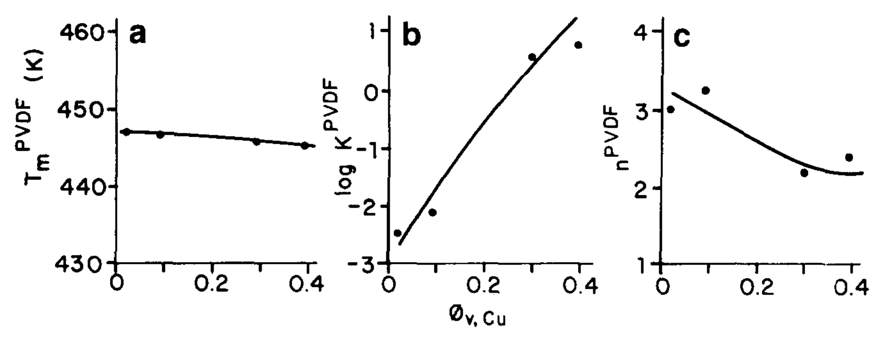

Figure 7 Melting temperature (a), crystallization rate (b) and Avrami exponent (c) of PVDF as a function of copper content for PVDF/Cu systems

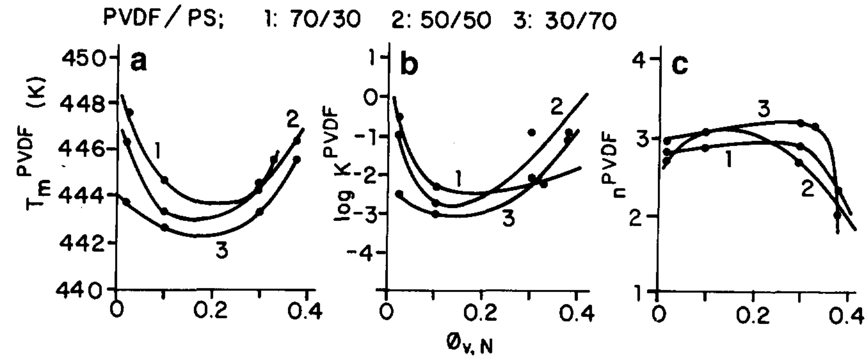

Figure 8 Melting temperature (a), crystallization rate (b) and Avrami exponent (c) of PVDF as a function of carbon black content for PVDF/PS/N systems

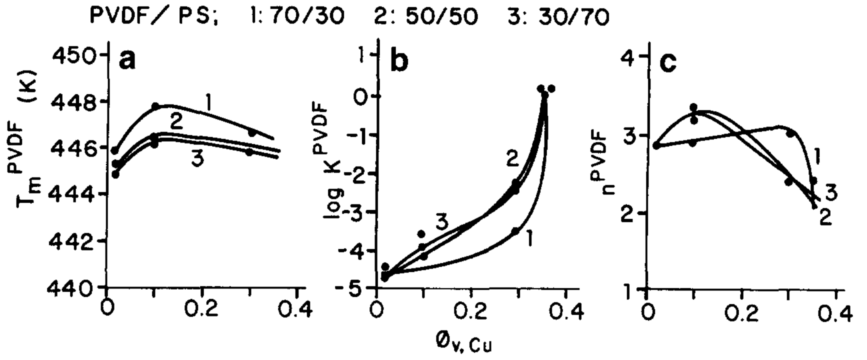

Figure 9 Melting temperature (a), crystallization rate (b) and Avrami exponent (c) of PVDF as a function of copper content for PVDF/PS/Cu systems

although partial compatibilization owing to the presence of carbon black is not to be discarded since carbon black consistently coincides with a decrease of the melting point of the crystalline polymer, in full agreement with Nishi–Wang theory. In the case of copper, however, the existence of partial compatibilization has to be discarded because a slight increase in T_m^{PVDF} for medium filler contents is followed by a decrease to the original melting temperature at higher filler contents.

The nucleating effect of copper in PVDF crystallization (*Figure 9b*) remains clearly visible in all blend varieties. The value of the rate constant increases with increasing copper concentration. In the case of blends containing carbon black (*Figure 8b*), however, K^{PVDF} diminishes in inverse proportion for low and medium carbon black contents and increases for the higher filler contents, yet does not exceed the values recorded for low carbon black systems. The explanation for this behaviour can be found in two opposing interactions: on the one hand, the nucleating nature of carbon black is responsible for such an effect on PVDF crystallization, as has been demonstrated elsewhere; and on the other hand, there is an inhibitory effect triggered by the presence of intermediate complexes as a result of carbon black–polystyrene interaction[15].

With regard to the PVDF geometry in the presence of PS and/or filler, *Figure 8c* shows *n* to reach a constant value of 3.0, independent of PS or carbon black content, whilst the carbon black concentration remains below the volume fraction of 30%. As soon as the filler volume fraction exceeds 30%, *n* drops to approximately 2.3, which is indicative of tridimensional and bidimensional co-crystallization taking place.

PVDF growth geometry in the presence of PS and copper shows different features from those described for the carbon black based system, as it is influenced by both the PS and the copper content. Thus, for a low PS content (*Figure 9c*) and with increasing copper concentration *n* remains constant, only to diminish with higher copper contents in a similar way to the system containing carbon black. For a medium or high PS content, however, an increase in the copper content causes *n* to increase, but thereafter it drops drastically to 2.3 at medium and high copper levels, which in turn give rise to the aforementioned co-crystallization of bidimensional and tridimensional systems as a consequence of the presence of high copper concentrations.

Non-isothermal crystallization

The data referring to non-isothermal crystallization of the binary and ternary systems were also analysed using the Avrami equation, yielding straight lines when plotting $\log\{-\ln[1-X(T)]\}$ against $\log t$ for each cooling rate β. The kinetic data were collected below conversions of 30% by weight. As to the binary PVDF/N and PVDF/Cu systems, *Figures 10a* and *10b*, respectively, show the rate constant of the non-isothermal crystallization process as a function of the carbon black and copper concentrations for the different experimental cooling rates. In both systems no important variations were observed, *K* remaining practically constant over the whole compositional range.

In order to elucidate the effect of polystyrene and/or the filler on the non-isothermal crystallization rate of PVDF for each cooling rate, the value of $\log K^{PVDF}$ was

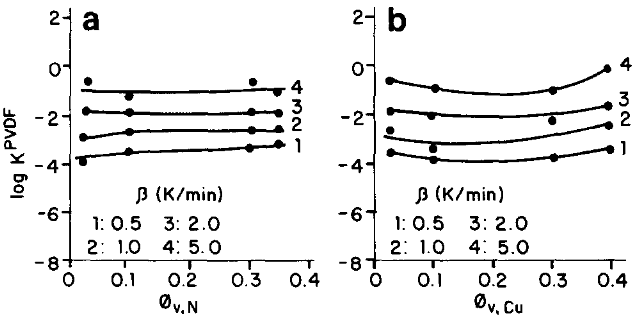

Figure 10 Non-isothermal crystallization rate of PVDF as a function of carbon black (a) and copper (b) contents for PVDF/filler systems

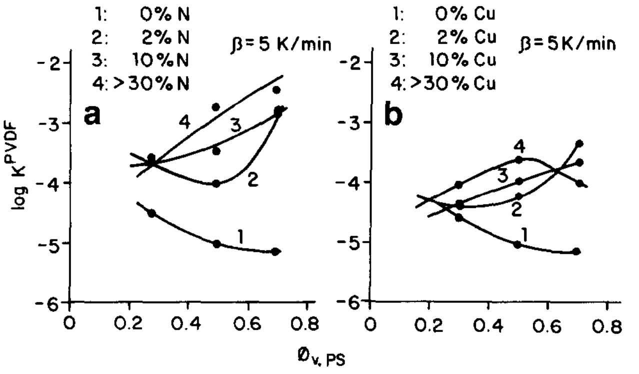

Figure 11 Non-isothermal crystallization rate of PVDF as a function of PS content for PVDF/PS/N (a) and PVDF/PS/Cu (b) systems

Table 3 Non-isothermal crystallization parameters of PVDF/N systems

	Composition		Non-isothermal parameters		
Sample	PVDF/PS (% ϕ_v)	N (% ϕ_v)	β (K min^{-1})	n	log$K$
FN0	100/0	2	0.1	3.4	−5.555
			0.5	3.8	−3.930
			1.0	4.0	−2.941
			2.0	3.9	−1.685
			5.0	4.0	−0.707
FN1	100/0	10	0.1	3.5	−4.881
			0.5	3.8	−3.452
			1.0	3.9	−2.634
			2.0	4.1	−1.907
			5.0	5.0	−1.227
FN3	100/0	30	0.3	3.6	−3.881
			0.5	3.9	−3.357
			1.0	3.8	−2.599
			2.0	4.3	−1.916
			5.0	3.7	−0.567
FN4	100/0	35	0.1	3.2	−4.902
			0.5	3.0	−2.950
			1.0	3.4	−2.587
			2.0	3.6	−1.887
			5.0	4.4	−1.068

plotted against PS content for the different carbon black and copper concentrations used. *Figure 11* shows the results obtained when conducting the test at a cooling rate of 5 K min^{-1}.

Figure 11 allows us to conclude that, independent of filler content, the PVDF crystallization rate increases with increasing PS content in the blend, except for the filler-free samples which contain neither carbon black nor copper. With regard to the effect of either filler on K^{PVDF}, it is safe to state that for carbon black containing systems K^{PVDF} increases in proportion to carbon black content, independent of blend composition, whereas for the copper-filled systems this is not the case. Thus, for low and medium concentrations, when increasing the copper content, K^{PVDF} tends to increase. In contrast, for increasingly higher PS contents this value decreases.

Table 3 lists some experimental results derived from the non-isothermal crystallization. The Avrami exponent n, as a general rule, experiences a significant increase when increasing the cooling rate at which non-isothermal crystallization was studied. This finding, which has been reported by several authors[16–18], can be explained in terms of the conditioning factors inherent in non-isothermal crystallization[19].

The results described above allow us to draw the following conclusions. Copper and carbon black modify the microstructure and morphology of the basic system formed by PVDF and PS in three ways: (i) the crystalline geometry of PVDF changes as a function of filler content; (ii) the phase morphology is modified by the presence of polystyrene in such a way that with increasing carbon black or copper content the incompatible phases are micronized or homogenized; and (iii) it is essentially the carbon black filler which partially compatibilizes the original blend, as demonstrated by the shifts in the glass transition temperatures of PVDF and PS and the decrease in melting point of PVDF as a consequence of the presence of the filler.

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