

# Effect of compatibility on dielectric relaxation and on the microstructure of semicrystalline polymer blends

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Polyvinylidene fluoride, polystyrene, polyvinyl acetate and their blends were investigated using dielectric measurements at different temperatures and frequencies in order to study the effect of compatibility on the glass transition temperature of these polymer systems. Isothermal crystallization kinetic studies were performed in order to determine the microstructure and the morphology of the samples.

## 1. Introduction

The current importance of the use of polymer blends as an alternative means to chemical synthesis for the production of novel and advanced polymeric materials [1,2] need not be emphasized here. One of the most important properties that needs to be considered when examining polymer blends is the compatibility between the components, since the state of compatibility will condi-

tion all of the physical properties in the final system. One of the most commonly used routes in the study of the compatibility of polymeric systems is based on the interpretation of shifts in the glass transitions of the components due to the effect of blending [3–5].

Table 1  
Isothermal crystallization: melting behaviour and kinetic parameters of the PVF<sub>2</sub>/PS systems

Sample	Composition PVF <sub>2</sub> /PS (% $\phi_v$ )	$T_c$ (K)	$T_m$ (K)	$K$ ( $\times 10^3$ $\text{min}^{-n}$ )	$n$
PVF <sub>2</sub>	100/0	421	442.9	446.68	2.90
		423	443.1	53.70	2.78
		425	443.5	7.08	2.96
		427	445.3	1.86	2.75
FS1	70/30	421	441.8	284.45	3.07
		423	442.2	43.65	3.01
		425	442.8	6.59	2.97
		427	—	0.74	3.06
FS3	30/70	421	441.2	467.50	2.73
		423	441.7	59.94	2.74
		425	442.1	11.62	2.70
		427	442.7	2.73	2.60

Table 2  
Isothermal crystallization: melting behaviour and kinetic parameters of the PVF<sub>2</sub>/PVA systems

Sample	Composition PVF <sub>2</sub> /PVA (% $\phi_v$ )	$T_c$ (K)	$T_m$ (K)	$K$ ( $\times 10^3$ $\text{min}^{-n}$ )	$n$
PVF <sub>2</sub>	100/0	407	447.5		
		421	442.9	446.68	2.90
		423	443.1	53.70	2.78
		425	443.5	7.08	2.96
FA1	70/30	427	445.3	1.86	2.75
		407	441.3		
		413	444.2	9.58	2.89
		415	444.4	6.12	2.78
FA3	30/70	417	444.8	2.57	2.57
		419	445.1	1.39	2.74
		407	433.4		
		397	429.0	812.09	2.84
		399	429.0	412.20	2.61
		401	431.0	140.01	2.69
		403	432.0	20.61	2.59

The present work studies the structure of two polymeric systems based on polyvinylidene fluoride, one compatible (polyvinylidene fluoride/polyvinyl acetate) and the other incompatible (polyvinylidene fluoride/polystyrene) via the kinetics of the isothermal crystallization of the samples. Moreover, the differences in the values of  $T_g$  in the blends with respect to those of the pure components are analyzed by a dielectric relaxation spectroscopy technique developed by the present authors.

## 2. Experimental

### 2.1. Materials

The polyvinylidene fluoride (PVF<sub>2</sub>) used was Solef 6010 supplied by Solvay; the polyvinyl acetate (PVA) was Mowilith 50 supplied by Hoechst; and the polystyrene (PS) was BASF product 143E.

Blends were prepared in a Brabender plastimeter using a type W60 thermoplastic mixing chamber preheated to a temperature of 468 K.

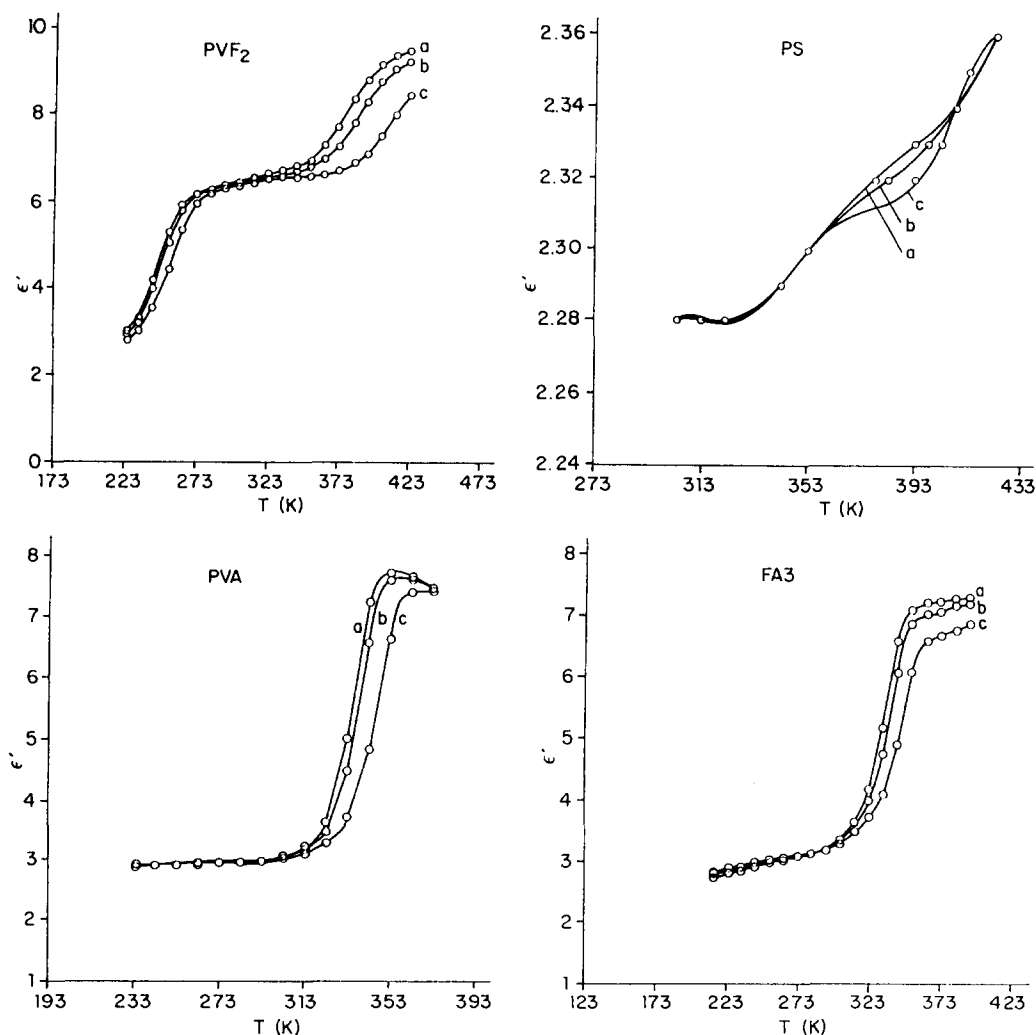


Fig. 1. Variation in the dielectric constant with temperature at different frequencies. a, 1 kHz; b, 2 kHz; c, 10 kHz.

## 2.2. Isothermal crystallization

Isothermal crystallization from the melt was studied using a Perkin-Elmer model DSC 7 differential scanning calorimeter operating in a  $N_2$  atmosphere.

## 2.3. Dielectric measurements

Measurements of the capacitance and dielectric dissipation factor was taken with a GenRad model 1620A capacitor bridge using a three-terminal connection for the sample cell. Frequencies chosen were 1, 2 and 10 kHz and the temperature range

was between 213 and 433 K. Samples were in the form of discs 7.2 cm in diameter and 0.1 cm thick. Since moisture increases the degree of polarization of the samples, precautions were taken to minimize the effect of absorption of water.

## 3. Results

The kinetics of the isothermal crystallization from the melts of  $PVF_2/PVA$  and  $PVF_2/PS$  blends were analyzed using Avrami's equation [6]:

$$\chi_T = 1 - \exp(-Kt^n), \quad (1)$$

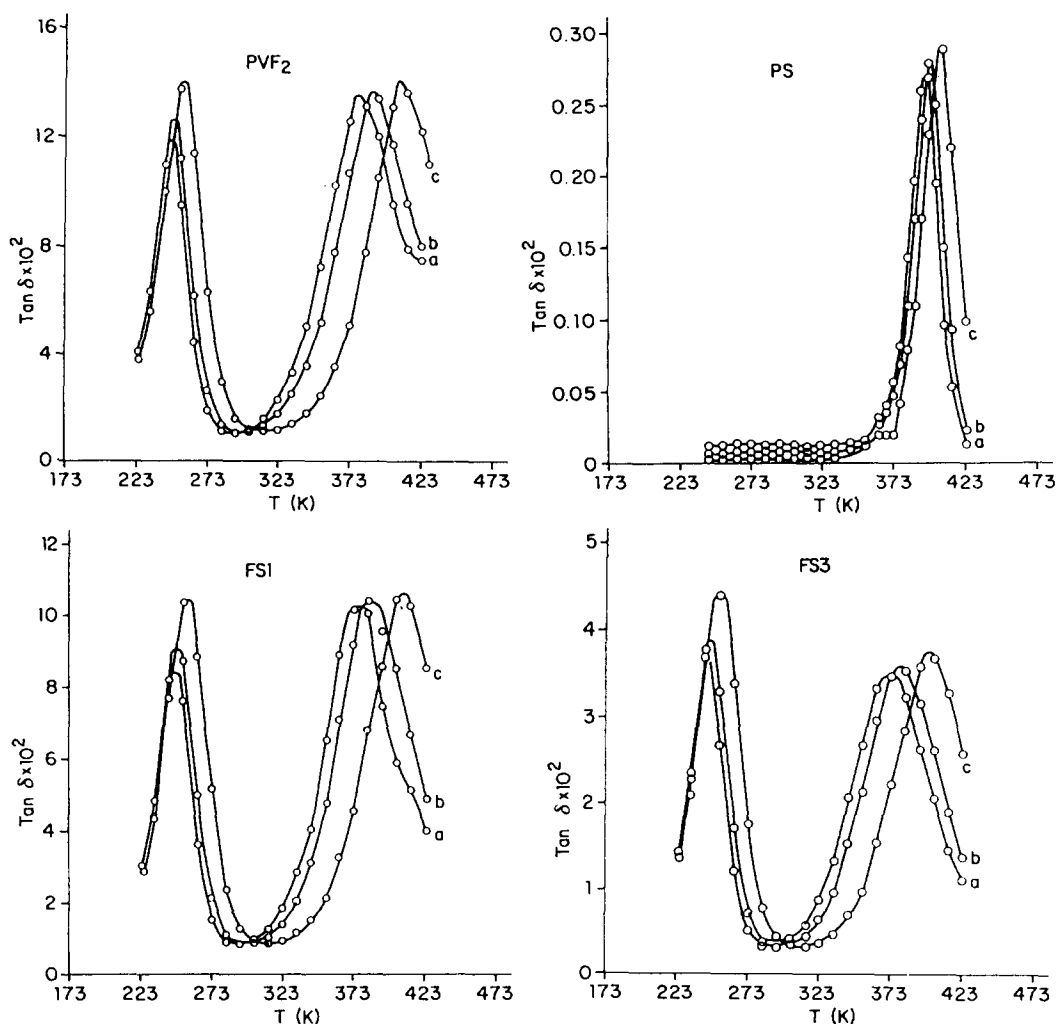


Fig. 2. Variation in the dielectric dissipation factor with temperature at different frequencies. a, 1 kHz; b, 2 kHz; and c, 10 kHz.

where  $\chi_T$  is the fraction in weight of the material crystallized at time  $t$ ,  $K$  is the overall kinetic rate constant, and  $n$  is Avrami's exponent, which depends on the type of nucleation and on the geometry of the growing crystals.

Values for  $K$  and  $n$  were calculated for each  $T_c$  from the slope and the  $y$ -intercept of the lines obtained by plotting  $\log(-\ln(1 - T))$  vs.  $\log t$ .

Tables 1 and 2 present samples compositions, the starting conditions, and the results of the kinetic study of the isothermal crystallization process for the systems based on PVF<sub>2</sub>/PS and PVF<sub>2</sub>/PVA, respectively.

Figure 1 shows the variations in the dielectric constant,  $\epsilon'$ , with temperature,  $T$ , at the studied frequencies for the different homopolymers and, as an example, for the FA3 blend. Figures 2 and 3 show the behaviour of  $\tan \delta$  with temperature at the three frequencies employed.

#### 4. Discussion

With relation to the results of the isothermal crystallization, we can observe that the overall kinetic rate constant decreases at low concentra-

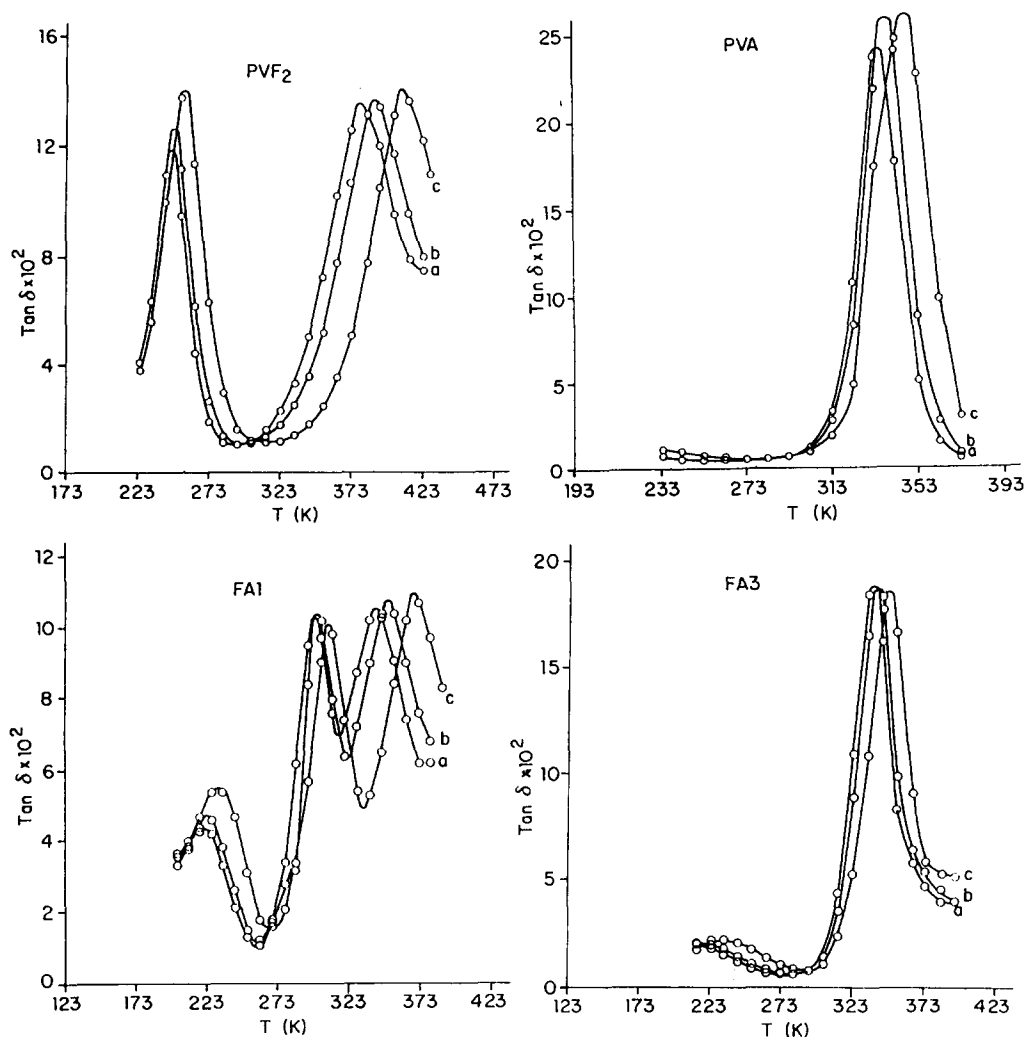


Fig. 3. Variation in the dielectric dissipation factor with temperature at different frequencies. a, 1 kHz; b, 2 kHz; c, 10 kHz.

tion of PS and increases subsequently. This effect is more pronounced at lower crystallization temperatures. However, in the PVF<sub>2</sub>/PVA systems,  $K$  decreases significantly when the concentration of PVA rises. This suggests that PVA is acting as a nucleating agent for PVF<sub>2</sub> crystallization.

Although Avrami's exponent,  $n$ , decreases slightly in both the PVF<sub>2</sub>/PS and the PVF<sub>2</sub>/PVA systems when the content of the PS or PVA component in the mixture increases, the values are very similar to those for the homopolymer PVF<sub>2</sub> alone, which suggests that the PVF<sub>2</sub> takes on the same geometry of growth independently of the value of  $T_c$  and the composition of the blend.

Both PS and PVA lower the melting point, but this effect is more pronounced in the PVF<sub>2</sub>/PVA system (about 14 K) than in the PVF<sub>2</sub>/PS systems, as would be expected for a compatible and an incompatible blend respectively [7]. With regard to the dielectric measurements, in all cases  $\epsilon'$  decreases with frequency and increases with temperature (fig. 1). This agrees with the dielectric response of a polar dielectric [8].

For the polyvinylidene fluoride, two regions of dielectric relaxation appear. The low-temperature loss peak has been studied by several researchers [9,10], and it is probably associated with the glass transitions. Most workers have suggested that this process is caused by the cooperative rotational motions of dipolar groups within the main chain in the amorphous parts of the polymer. The high-temperature peak,  $\alpha_c$ , has been associated with the annealing process and may involve the crystalline phase [11–13]. Both processes are dielectrically active and they involve re-orientation of the dipole-moment vector. The other homopolymers studied, polystyrene and polyvinyl acetate, display only one peak for the glass transition temperature.

The results for the different binary blends indicate that two dielectric relaxations occur in the PVF<sub>2</sub>/PS systems. One (the low-temperature peak) corresponds to the glass transition temperature of the polyvinylidene fluoride, but the other is difficult to assign, because of overlap between the processes of relaxation,  $\alpha_c$ , of PVF<sub>2</sub>, and the glass transition of PS. There is a slight displacement in the  $T_{g,PVF_2}$  which becomes more evident when the frequency employed increases.

In the binary systems composed of PVF<sub>2</sub> and

PVA, up to three transitions can be seen at the lowest concentration of polyvinyl acetate (fig. 3), which can be assigned to  $T_{g,PVF_2}$ ,  $T_{g,PVA}$  and  $\alpha_{c,PVF_2}$  with increasing temperature. In this case there is significant displacement of the glass transition temperature values, particularly for the polyvinylidene fluoride at high frequencies. When the concentration of polyvinyl acetate increases,  $T_{g,PVF_2}$  shifts towards still lower temperatures, below 216 K, depending on the frequency. This could be ascribed to the enhanced chain mobility arising from the decrease in the intermolecular interactions, which is indicative of a certain degree of compatibility in the PVF<sub>2</sub>/PVA blends.

## 5. Conclusions

(1) The microstructure of poly(vinylidene fluoride), studied using Avrami's exponent,  $n$ , does not change significantly with the presence of PS or PVA.

(2) The PVF<sub>2</sub>/PVA binary systems demonstrate a higher level of compatibility than the PVF<sub>2</sub>/PS blends as shown by the depression of  $T_m$  determined by DSC, and displacements in the values of  $T_g$  observed by dielectric relaxation.

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