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Electron spin resonance, electrical and magnetic properties of polyvinylidene fluoride films filled with equal amounts of $FeCl_3$ and $CuCl_2$

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Polyvinylidene fluoride (PVDF) films, filled with equal mass fractions ($\leqslant 0.175$) of $FeCl_3$ and $CuCl_2$ were prepared. An X-ray diffraction analysis revealed that the prepared films were partially crystalline in the form of the β phase PVDF. The measured electron spin resonance spectra were characterized by a main signal (arising from the filler ions) and a superimposed hyperfine pattern (due to free radicals). The temperature (T) dependence of the d.c. magnetic susceptibility exhibited a Curie–Weiss behaviour, in the range of 95–250 K, indicating localized energy states. The detected positive values of the paramagnetic Curie points suggest a ferromagnetic interaction between the magnetic ions at low temperatures. A Pauli paramagnetic temperature independent susceptibility was observed at $250\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$, implying a role for itinerant energy states. The d.c. electrical resistivity was measured in the temperature range of 300–420 K. The electrical conduction had an interpolaron hopping mechanism. The calculated hopping distance was formulated numerically to be a linear function of the temperature and filling level and found to have a value of $\leqslant 0.62$ nm.

1. Introduction

Polyvinylidene fluoride (PVDF) is an important ferroelectric polymer due to its high piezo- [1] and pyro-electric activity [2]. Four crystalline forms of PVDF are known to exist in addition to an amorphous phase. The β-phase and the polarized α-phase are the only polarized phases in PVDF. Such phases are needed for piezo- and pyro-electric applications. The currently used preparation methods of PVDF containing β- and α-polarized phases tend to include some sort of external treatment such as: (a) stretching the polymeric film [3], (b) heat treatment [4] and (c) poling i.e., charging the films with high electric fields [5]. Such techniques may induce undesired structural deformations. Therefore we have prepared PVDF films containing a suitable fraction of β-phase by filling the PVDF matrix with metal halides. In our previous publications we have investigated the effect of filling PVDF with the chlorides of Zn, Al, Co [6], Ni [7], Fe and Cu [8] has on its physical properties.

The present work is devoted to the investigation of the effect of filling PVDF films with a mixture of equal fractions of $FeCl_3$ and $CuCl_2$ on their electrical and magnetic properties.

2. Experimental procedures

Samples were made from an α-PVDF resin provided by Solvay (Belgium) and referenced as: SOLEF 1008. Dimethylformamide (DMF) was used as the solvent for the resin, and equal mass fractions of $FeCl_3$ and $CuCl_2$ were used as fillers. Films were prepared by casting enough of the desired solution onto glass, so that the films were approximately 0.2–0.5 mm thick after the solvent was removed at 343 K. X-ray diffraction scans were obtained using a Seimens type F diffractometer with CuK_α radiation and a LiF monochromator. The electron spin resonance (ESR) spectra were recorded on a Jeol spectrophotometer (type JES-FE2XG) at a frequency of 9.45 GHz, using 1,1-diphenyl-2-pierylhydrazyl (DPPH) as a calibrant. The magnetic susceptibility was measured using a Faraday pendulum balance technique, which provides an accuracy better than ±3% provided that dimagnetic corrections are performed. The electrical resistivity was measured by a standard technique [9] using an autorange multimeter (Philips 175) with an accuracy of ±0.2%. The films were in the form of circular discs, of 1.6 ± 0.001 cm diameter. Contacts were of highly conductive silver paste, with an area of 1 cm^2. A guard ring was used. The sample was short-circuited for

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about two days, at a constant temperature of 300 K, before the d.c. voltage was applied. The resistivity was measured in the steady-state to avoid errors due to relaxation phenomena.

3. Results and discussion
3.1. X-ray diffractions

Fig. 1 depicts the X-ray diffraction scans of PVDF films filled with various fractions of $FeCl_3$ and $CuCl_2$. The observed spectra exhibit a partially-crystalline feature. The diffraction peaks are listed in Table I and they are assigned to the β-PVDF crystalline form [10].

3.2. Electron spin resonance

Fig. 2 shows the ESR spectrum of a PVDF pellet (as fabricated) that is characterized by complex hyperfine interaction (HI) peaks due to free radicals. This figure also shows the ESR spectrum of a PVDF film, prepared by casting using DMF as the solvent. A two fold effect on the ESR spectrum produced by the DMF are suggested, (a) a reduction of the HI peak values and (b) the appearance of a sharp negative peak.

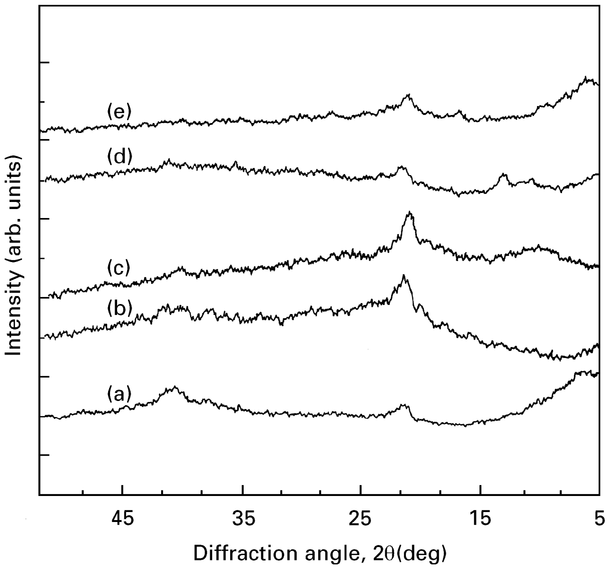

Figure 1 X-ray diffraction scans of PVDF filled with mass fractions of $CuCl_2 + FeCl_3$ of (a) 10 wt %; (b) 15 wt %; (c) 20 wt %; (d) 30 wt % and (e) 35 wt %.

TABLE I X-ray diffraction peaks and their assigned planes

W (wt %)				
10	2θ (deg)	21	40	
	(*h k l*)	(021)	(004)	
15	2θ (deg)	20.9	39.4	
	(*hkl*)	(021)	(004)	
20	2θ (deg)	20.3	39	
	(*h k l*)	(110)	(004)	
30	2θ (deg)	21	34.6	40.2
	(*h k l*)	(021)	(131)	(004)
35	2θ (deg)	20.6	26.8	34.2
	(*h k l*)	(021)	(022)	(131)

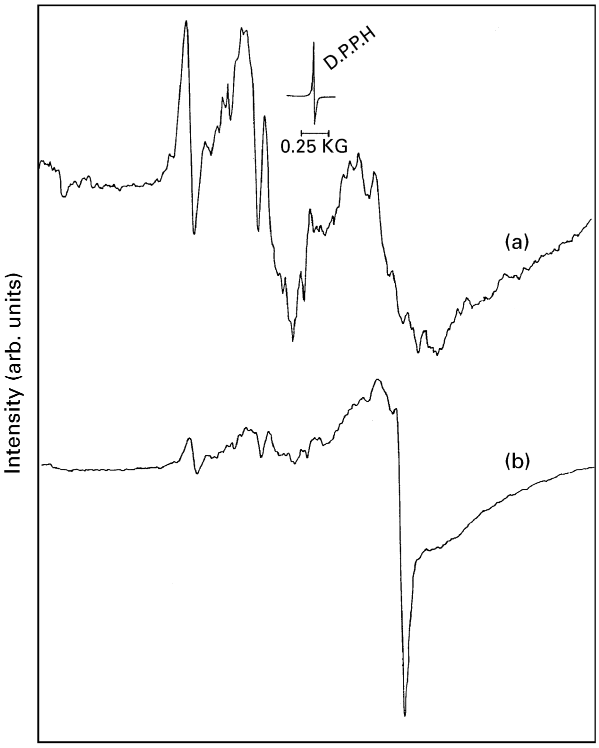

Figure 2 ESR spectra of PVDF: (a) pellets (as obtained from the synthesis procedure), and (b) films (prepared using DMF as a solvent).

Fig. 3 shows the ESR spectra of the filled films. The spectrum of the 5 wt % filling level is of an almost symmetrical Lorentzian signal, located around a Lande factor (g) equal to 1.942. This is similar to the spectra previously obtained [8] for PVDF filled solely with $FeCl_3$ in the filling range (w) of 5 wt % $\leqslant W \leqslant$ 40 wt %, indicating an octahedral distribution (OD) of Fe^{3+} ions in the PVDF matrix. The ESR spectra of samples with 10 wt % $\leqslant W \leqslant$ 25 wt % filling levels, shown in Fig. 3, exhibit complex forms, having for its main shape that of the spectrum of the unfilled PVDF pellets (free from DMF). The disappearance of the Lorentzian signal indicates that there is no Fe^{3+} OD in the PVDF matrix. This may be attributed to the effect of the $CuCl_2$ filler. In the case of the 35 wt % filling level the observed ESR spectrum exhibits a main broad Lorentzian shape, due to Fe^{3+} OD, with a superimposed sharp signal , due to the Cu^{2+} ions. It is believed that the Fe^{3+} and Cu^{2+} ions, which are responsible for this spectrum, belong to the $FeCl_3$ and $CuCl_2$ crystallites that are separated and exist as microphases due to the over saturation filling level (35 wt %). This suggestion can be supported by noting that for such a polymer the saturation filling level is around 30 wt % [11]. The content of these microcrystallites is too small to be detected by X-ray diffraction techniques.

The observed trends can be explained as follows: at low filling levels ($W <$ 10 wt %) there is a relative high content of filling sites in the polymeric matrix allowing the Fe^{3+} OD. Noting that the $CuCl_2$ molecule has a lower volume than $FeCl_3$, the $CuCl_2$ has priority in

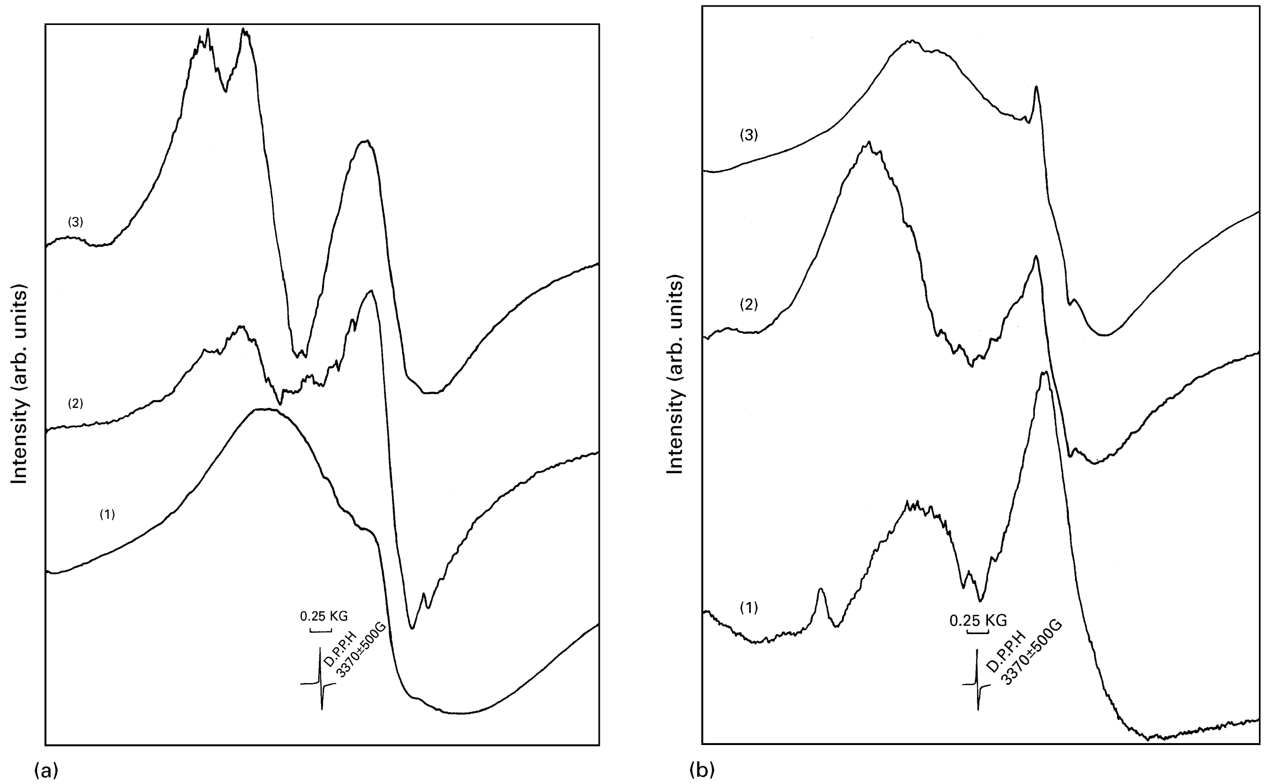

Figure 3 ESR spectra of PVDF films filled with various mass fractions of $CuCl_2 + FeCl_3$; (a) (1)5 wt %; (2) 10 wt % and (3) 15 wt %; (b) (1) 20 wt %; (2) 25 wt % and (3) 35 wt %.

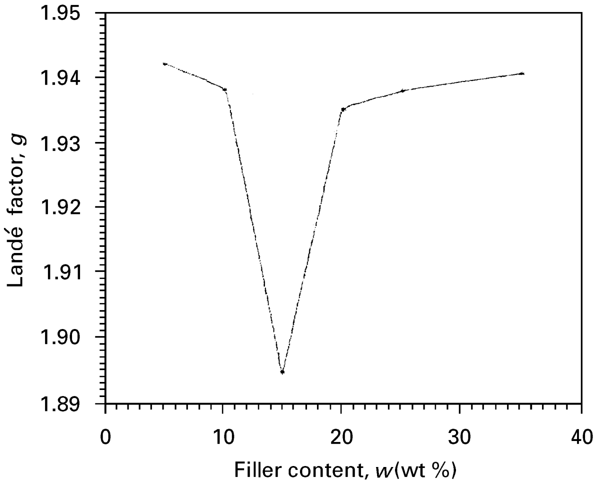

Figure 4 The average value of g-factor at various filling levels.

occupying the allowed filling sites. Thus as W increases the content of the suitable sites for Fe^{3+} OD decreases.

The average values of the g-factor, calculated from the ESR spectra, are plotted as a function of W, in Fig. 4. The minimum value of g ($= 1.895$) is obtained for the case of $W = 15$ wt %, indicating a maximum influence of the electronic orbital angular momentum on the ESR spectra. The variance of the g-values shows the variation of the mode of filling at various filling levels.

3.3. D.c. magnetic susceptibility

The temperature dependence of the reciprocal values of the d.c. magnetic susceptibility (χ), measured in the temperature (T) range of 95–285 K, for various filling levels is shown in Fig. 5(a and b). A temperature independent Pauli paramagnetic (TIPP) behaviour is observed, indicating the presence of itinerant electronic states, this is followed by a Curie–Weiss region of positive paramagnetic Curie points, (θ_p), indicating the presence of localized energy states allowing for a ferromagnetic interaction between the unpaired electrons at lower temperatures. It is remarkable that the temperature at which the TIPP behaviour changes to the Curie–Weiss behaviour is of the order of magnitude of the glass transition temperature ($T_g \approx 322$ K [12]) of PVDF. The filling level dependence of θ_p is shown in Fig. 6. It is found that θ_p can be formulated numerically as:

$$\theta_p = 100 \exp(-0.057\,W) \qquad (1)$$

The Curie–Weiss plots were used, together with the equation:

$$\mu = 2.839\,(\chi M T)^{\frac{1}{2}} \qquad (2)$$

to calculate the effective magnetic moment (μ), where M is a molecular weight of the used sample. The filling level dependence of μ is shown in Fig. 6, and it can be expressed numerically as:

$$\mu = 0.936 \exp(0.05W) \qquad (3)$$

The present magnetic behaviour is revealed to be that there are two types (localized and itinerant) of induced energy states due to the mixed filling with equal amounts of $FeCl_3$ and $CuCl_2$. These localized and itinerant induced energy states may affect the

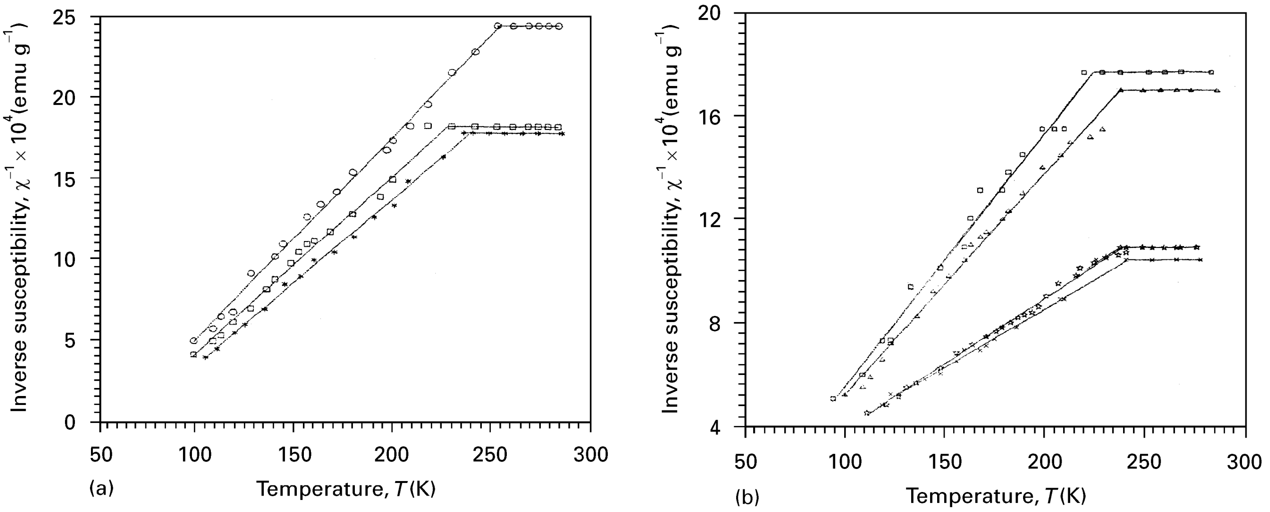

Figure 5 The temperature dependence of the d.c. magnetic susceptibility reciprocal, for $FeCl_3 + CuCl_2$ filling levels of (a); (○) 5 wt %; (□) 10 wt % and (∗) 15 wt % and (b); (□) 20 wt %; (△) 25 wt % (a); (b) (☆) 30 wt % and (×) 35 wt %.

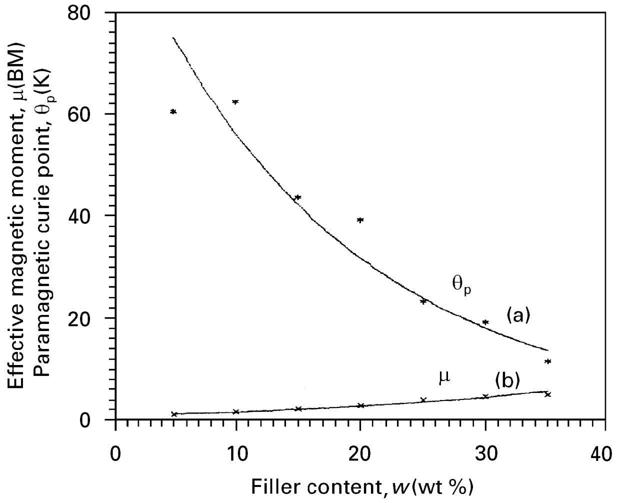

Figure 6 The filling level dependence of θ_p and μ.

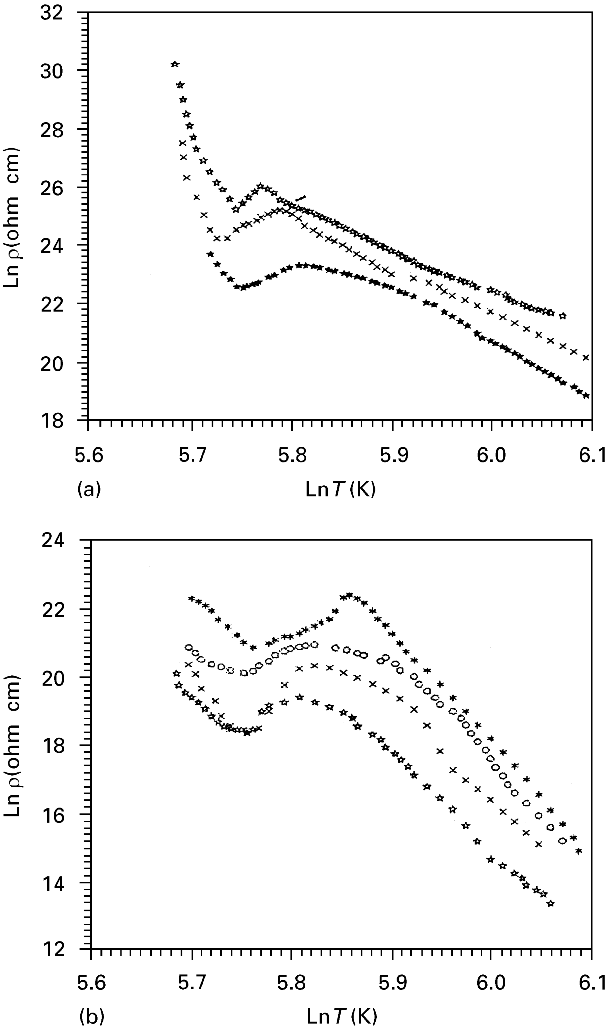

Figure 7 The dependence of the logarithm of the d.c. electrical resistivity on the logarithm of the temperature, for $FeCl_3 + CuCl_2$ filling levels of: (a); (☆) 5 wt %; (×) 10 wt % and (★) 15 wt %; (b); (☆) 20 wt %; (×) 25 wt%; (○) 30 wt% and (∗) 35 wt %.

electronic conduction as will be investigated in the next section.

3.4. D.c. electrical resistivity

The d.c. electrical resistivity, (ρ), of the present system was measured in the temperature range of 300–420 K, and the results are plotted in Fig. 7(a and b). Significant polaron and bipolaron contents were observed in PVDF filled with $FeCl_3$ [13] and $CuCl_2$ [8] using infrared absorption techniques. Accordingly the d.c. conduction of these systems was attributed to a quasi one-dimensional process between polaron and bipolaron states according to a model proposed by Kivelson [14] and then modified by Kuivalainen *et al.* [15], in which the resistivity is expressed as:

$$\rho = [KT/Ae^2\gamma(T)(R_0^2/\xi)\,\mathrm{I}(y_p y_{bp})^2/(y_p y_{bp})]\exp(2BR_0/\xi) \tag{4}$$

where $A = 0.45$, $B = 1.39$, y_p, y_{bp} are the concentrations of polarons and bipolarons respectively, and $R_0 = (3/4\pi C_{imp})^{1/3}$ is the typical separation between impurities whose concentration is C_{imp}. Also ξ is the average decay length of a polaron or bipolaron wave function (≈0.378 nm [16]). The transition rate of an electron between polaron and bipolaron states is [14]:

$$\gamma(T) = 1.2 \times 10^{17} \left(\frac{T}{300} \right)^{11} \qquad (5)$$

In the present work adjusting the values of ρ with the impurity concentration, C_{imp}, as the fitting parameter, taking $y_{\text{p}} = y_{\text{bp}}$, as a reasonable approximation and using Equations 4 and 5, one can obtain the values of the hopping distance, R_0. The linear parts of Fig. 7(a and b) correspond to the temperature ranges in which the interpolaron hopping occurs. A linear temperature dependence of R_0, at various filling levels, can be observed in Fig. 8. The filling level dependence of R_0, calculated at $T = 380$ K, is shown in Fig. 9. Thus a general formula for $R_0(W,T)$ can be found numerically as:

$$R_0(W,T) = (M_1 W + M_2)T + M_3 \qquad (6)$$

where $M_1 = -9.46 \times 10^{-5}\ \text{nm}\,\text{K}^{-1}$, $M_2 = -3.64 \times 10^{-4}\ \text{nm}\,\text{K}^{-1}$, and the values of M_3 are 0.939, 1.007, 1.273, 0.855, 1.369, 1.505 and 1.737 nm corresponding to W values of 5, 10, 15, 20, 25, 30 and 35 wt % respectively.

It was previously reported that for PVDF systems singly filled with $FeCl_3$ [13] or $CuCl_2$ [8] the dependence of R_0 on temperature and filling level was of the form:

$$R_0(W,T)\ \alpha\ \exp\,(D_1 W + D_2 T) \qquad (7)$$

where D_1 and D_2 are constants. In Equations 6 and 7 it is implied that $R_0(W, T)$ may be considered as an indicator for the change of filling modes.

The nonmonotonic dependence of R_0 on W, presented in Fig. 9 is nearly compatible with the dependence of the g-factor on W, shown in Fig. 4. This behaviour supports the suggestion that the mode of filling changes significantly around $W = 15$ wt %. Moreover the value of $R_0 \leqslant 0.62$ nm, is less than the separation between two successive head-to-head sites (~1.25 nm) [13]. Accordingly the head-to-head sites may not be the only hopping sites of the charge carriers but also additional virtual sites (of different type) may act as hopping sites. Such sites are induced due to the local fields produced by the free radicals and/or the filler segments distributed in the polymeric matrix.

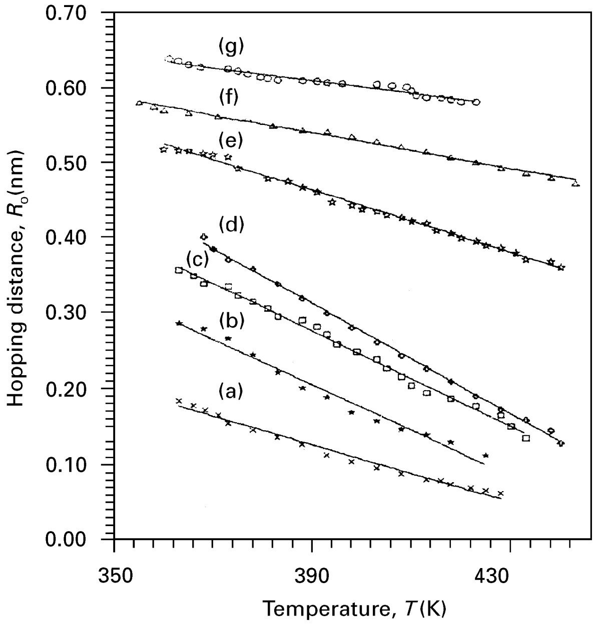

Figure 8 The temperature dependence of the hopping distance (R_0) for filling levels of (a) 20 wt %; (b) 25 wt %; (c) 30 wt %; (d) 35 wt %; (e) 15 wt %; (f) 10 wt % and (g) 5 wt %.

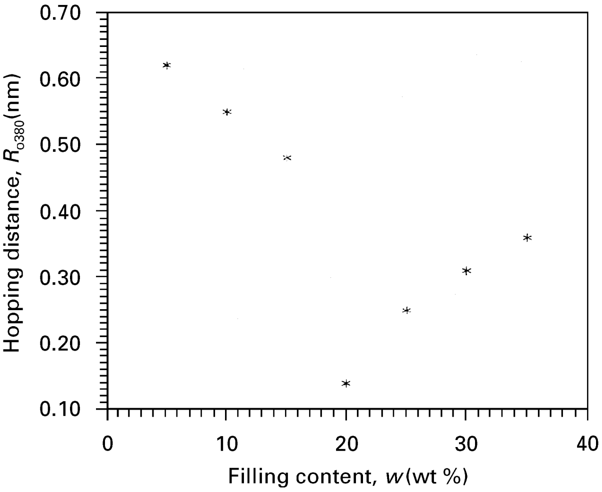

Figure 9 The filling level dependence of (R_0), calculated at (T = 380 K).

4. Conclusion

It can be concluded that the partially crystalline PVDF β-phase can be obtained by filling PVDF with equal mass fractions of $FeCl_3$ and $CuCl_2$. The priority for filling the available sites is $CuCl_2$ and then $FeCl_3$. This sequence may result in the non OD of Fe^{3+} ions in the filling range of 10 wt % $\leqslant W \leqslant$ 25 wt %. The postsaturation filling levels give rise to $FeCl_3$ microcrystallites, with Fe^{3+} OD, separated as a secondary phase. The induced localized and itinerant energy states, affect the conduction mechanism. The electrical conduction proceeds by electronic interpolaron hopping. An increased magnetoactivity for the present system, coupled to a reasonable β-phase fraction, may enhance its response to electromagnetic waves and make it more efficient as a microwave phase modulator [11].

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