JOURNAL OF MATERIALS SCIENCE 22 (1987) 2006–2010

Dielectric properties of solution-cast poly(vinylidene fluoride) films

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Dielectric parameters have been measured for solution-cast films of poly(vinylidene fluoride) (PVDF) in the temperature range 40 to 120° C and frequency range 50 Hz to 1 MHz. The infrared absorption spectrum shows these films to be predominantly of Phase III crystal structure. The α_c relaxation, which has generally been reported in the literature for Phase II PVDF, does not appear in the dielectric loss spectra. A small loss peak is observed which could probably be assigned to α' relaxation arising from molecular motions in the folds on the surface of the crystallites. Only a part of the α_a relaxation is observed due to the limitations of our experimental range of temperature and frequency. Trapped charge carriers make a large contribution to the dielectric parameters at lower frequencies.

1. Introduction

The dielectric properties of poly(vinylidene fluoride) (PVDF) polymer films are strongly dependent on the fabrication process. This is due to the fact that PVDF exists in several crystalline phases and the predominance of the individual phases can be controlled by the film fabrication process [1, 2]. For example, melt-quenching results in samples of Phase II with a TG^+TG^- conformation and polymer chains packed in a non-polar fashion. The stretching of Phase II films results in strain-induced recrystallization with the formation of Phase I with an all-*trans* conformation. This is the most highly polar phase of PVDF. Phase III has a $TTTG^+TTTG^-$ conformation, is polar, and may be obtained by casting hot solution in dimethyl acetamide (DMA). The polar counterpart of Phase II, also called Phase IV, can be obtained by subjecting the Phase II films to a high electric field. A non-polar analogue of Phase III also exists.

Dielectric relaxations of PVDF have been investigated by several researchers and summarized by Lovinger [1]. The polymer exhibits three main dielectric relaxations designated as α_c, α_a and β in order of decreasing temperature at a constant frequency. The β and α_a relaxations are considered to occur in the amorphous regions and the molecular motions involved are local mode molecular motion and micro-Brownian motion of main chain segments, respectively. The α_c relaxation is considered to arise from molecular motions in the crystalline regions of PVDF.

Several investigations have shown that the α_c relaxation disappears when a sample with Phase II structure is subjected to mechanical/electrical stress leading to a modification of Phase II structure to Phase I/Phase IV [3–9]. However, some researchers have observed the α_c relaxation for Phase I samples also [10, 11].

Although most of the investigators have associated the α_a relaxation with the glass transition of the polymer, Hahn *et al.* [12] have recently proposed that this relaxation is not related to the liquid-like amorphous phase but arises from the crystal–amorphous interphase.

It is evident that the relaxation behaviour of PVDF is strongly dependent on its crystalline morphology. In this paper the results of dielectric studies on solution-cast films of PVDF are reported. These films are predominantly of Phase III structure. A survey of the published literature shows that very little work has been done on the dielectric properties of this particular phase [2, 13], although a considerable amount of work has been done to understand its structure [1].

2. Experimental details

PVDF material used in the experiments was obtained from Janssen Chimica, Beerse, Belgium. The polymer, which was in powder form, was dissolved in DMA at 60° C. Films were prepared by casting this solution on to glass substrates at 60° C. Films could be detached from the substrates upon evaporation of the solvent.

The DSC thermogram was recorded at a heating rate of 10° C min^{-1} on a DuPont thermal analyser. An endothermic peak was observed at about 165° C which could be assigned to crystalline melting.

The infrared absorption spectrum recorded on a Perkin Elmer Model 580B spectrophotometer showed that the samples were predominantly of Phase III structure [14].

For electrical measurements, aluminium electrodes (area 1 cm^2) were deposited on both sides of the films by vacuum evaporation. Capacitance and dielectric loss tangent of 125 μm thick films were measured by a Hewlett Packard Model 4192A impedance analyser in the frequency range 50 Hz to 1 MHz and temperature range 40 to 120° C. Conductivity was measured using a Keithley Model 610C electrometer and an Aplab Model 7332 stabilized d.c. power supply for samples of 65 and 150 μm thickness.

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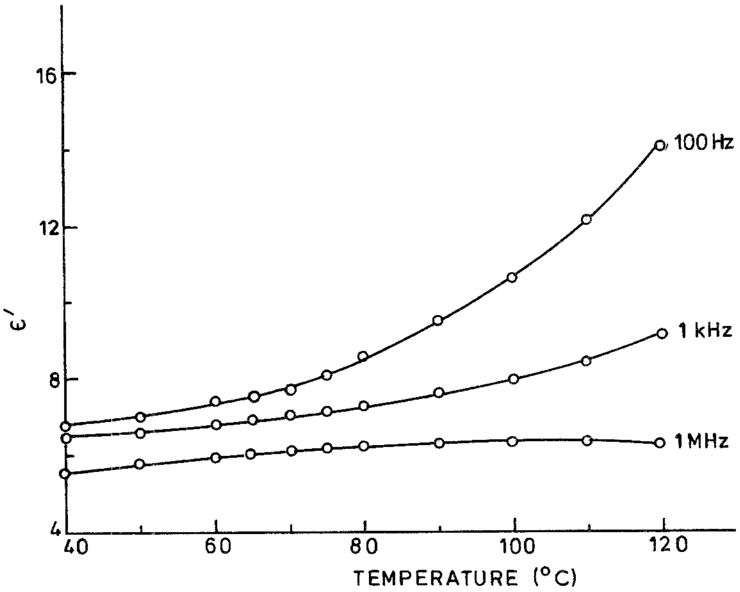

Figure 1 Temperature dependence of the dielectric constant of PVDF at various frequencies.

3. Results

Figs 1 and 2 show the temperature dependence and Figs 3 and 4 show the frequency dependence of the dielectric parameters measured for a 125 μm thick PVDF film. The dielectric constant (ε′) is observed to increase with temperature (Fig. 1) and this increase is more appreciable at lower frequencies (Fig. 3). Fig. 2 shows that the dielectric loss (ε″) increases with temperature for lower frequencies. At higher frequencies, ε″ initially decreases with temperature, shows a small peak which occurs at about 75° C for 100 kHz, and then begins to increase with temperature. Fig. 4 shows that ε″ decreases with an increase in the frequency until at high frequencies where it begins to increase.

Fig. 5 shows the temperature dependence of the conductivity measured at 1.2×10^3 sec after application of the electric field. The electric field across the sample was $2 \times 10^5 \mathrm{V\,m^{-1}}$ and no appreciable difference in the conductivity was observed for samples of thickness 65 and 150 μm. The measured conductivity is quasi-steady state (q.s.s.) conductivity rather than steady-state conductivity.

4. Discussion

The increase of ε′ with temperature (Fig. 1) is due to an increase of the total polarization, and is in agreement with the temperature dependence of polar dielectrics in general.

The initial decrease of ε″ with temperature at higher frequencies (Fig. 2) could be the post-peak portion of the α_a relaxation. The loss maximum would occur at still lower temperatures. This dielectric absorption is,

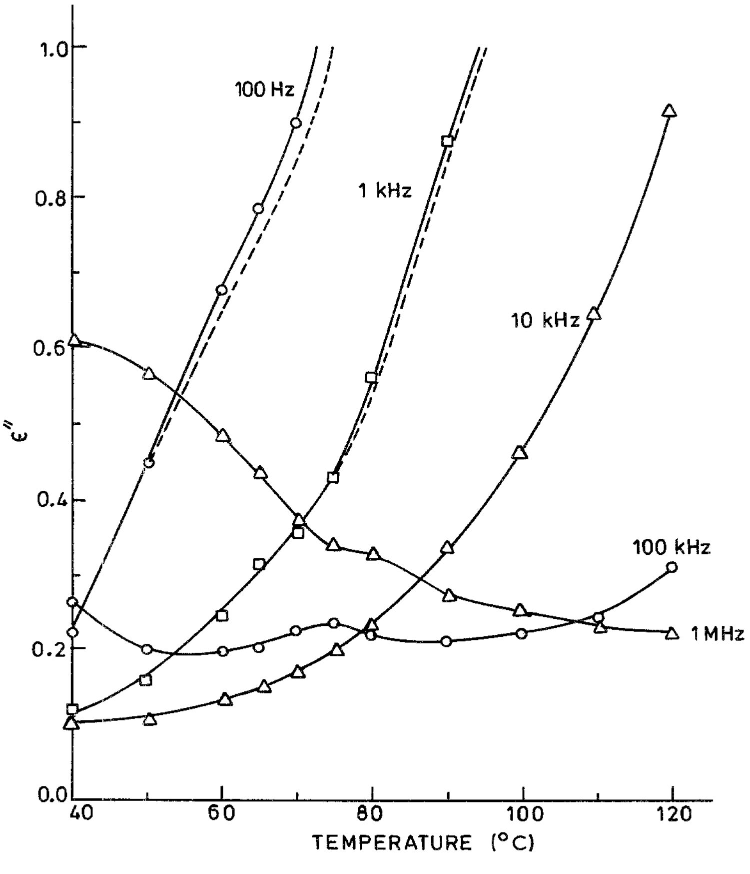

Figure 2 Temperature dependence of the dielectric loss of PVDF at various frequencies. The dashed curves show the dielectric loss from which conduction losses have been subtracted.

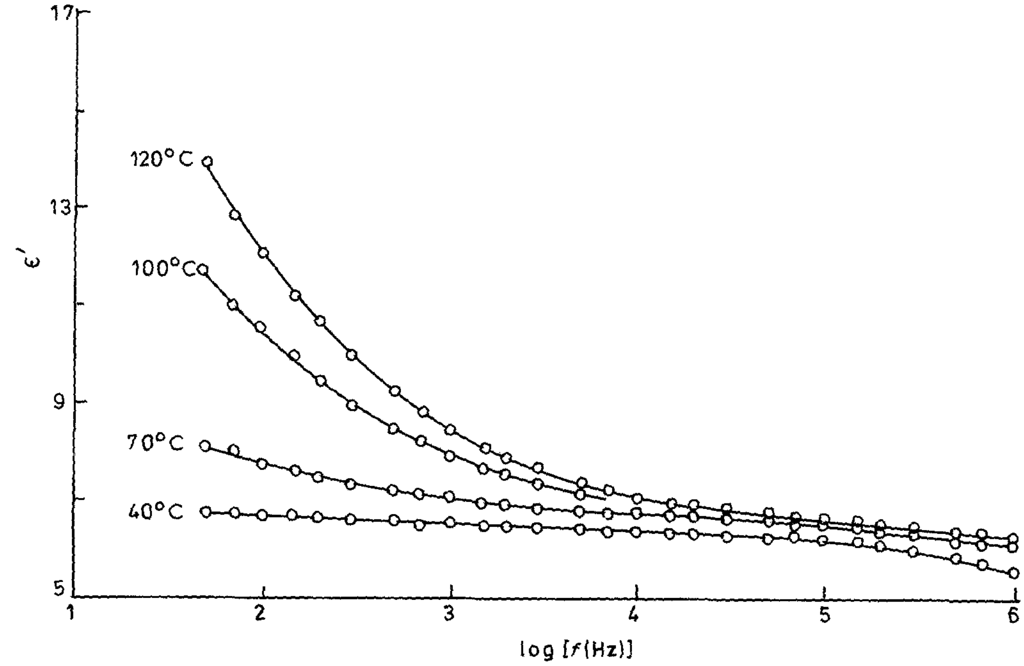

Figure 3 Frequency dependence of the dielectric constant of PVDF at various temperatures.

broadly, in the region of α_a relaxation of Phase II PVDF samples [15]. If the α_a relaxation corresponds to the glass-transition of the polymer, the relaxation parameters would probably not depend on the crystal structure. Nakagawa and Ishida [15] found that the crystal structure of Phase II holds locally even in the amorphous regions. A decrease in the relaxation amplitude and an increase in the relaxation temperature of the α_a relaxation have been observed on stretching Phase II samples [9]. This was explained on the basis that stretching affects the dielectric properties more through structural changes in the amorphous–crystalline boundaries than through an increase in the fraction of Phase I crystallites. From the behaviour of α_a relaxation in a compatible blend of PVDF with poly(methyl methacrylate), it has been proposed that this relaxation arises from molecular motions in the crystal–amorphous interphase region [12]. It appears that the α_a relaxation of PVDF may depend on its crystal structure. However, due to the limitations of our experimental range of temperature and frequency, complete α_a relaxation has not been observed, prohibiting any further analysis.

The small loss peak in Fig. 2 could be due to a relaxation process. Considering the relative position of this peak on the temperature scale among other relaxations of PVDF [1], it could be the relaxation (α') arising from molecular motions in the folds on the surface of the crystallites. This relaxation was first observed by Kakutani [10] in the dynamic mechanical relaxation spectra of Phase I and Phase II samples, but not in the dielectric relaxation spectra. The relaxation

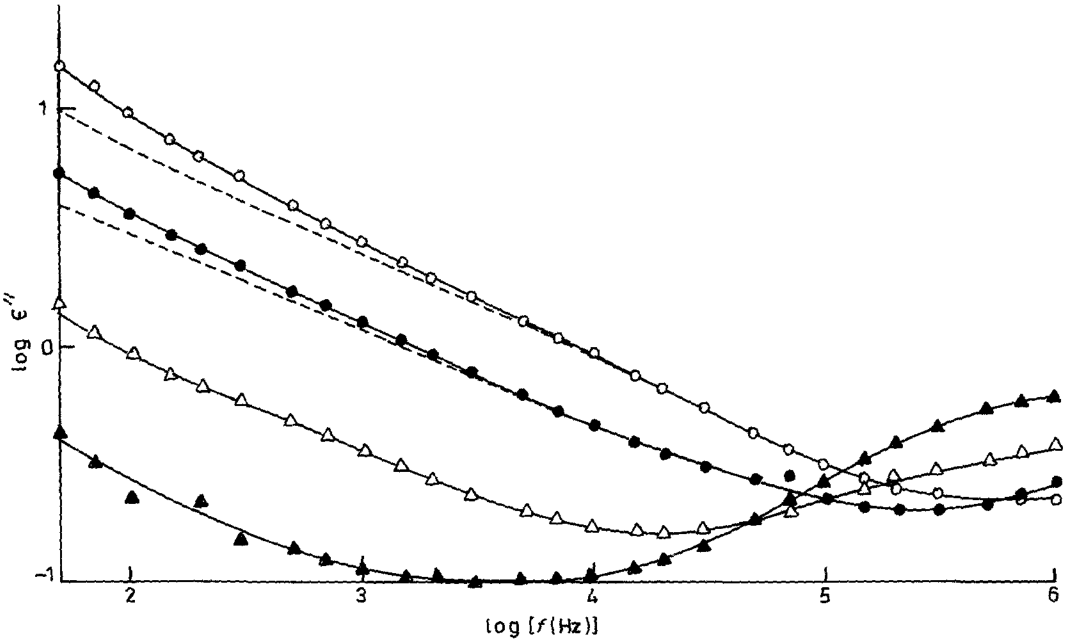

Figure 4 Frequency dependence of the dielectric loss of PVDF at various temperatures. The dashed curves show the dielectric loss from which conduction losses have been subtracted. (▲) 40° C, (△) 70° C, (●) 100° C, (○) 120° C.

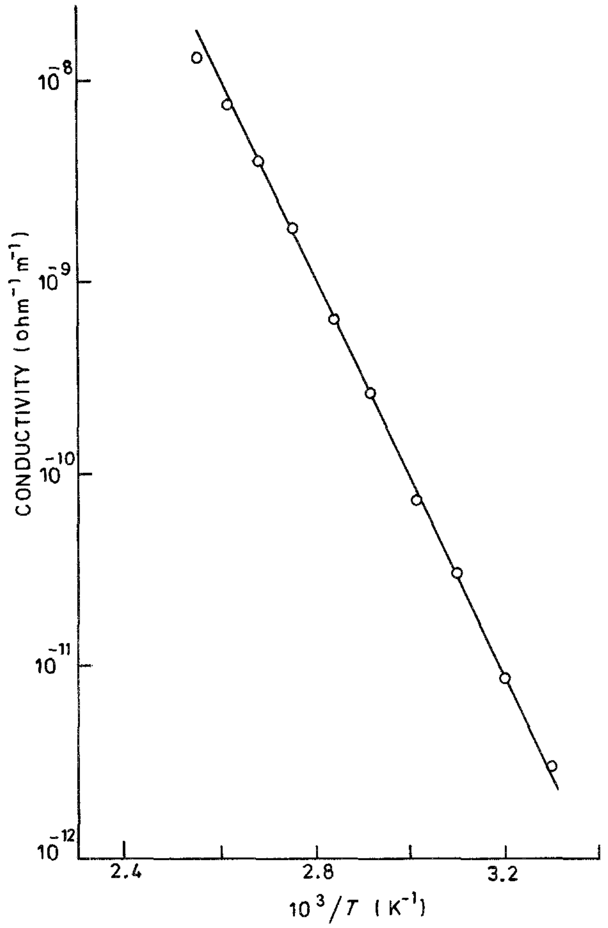

Figure 5 Temperature dependence of the conductivity of PVDF measured at 1.2×10^3 sec after the application of an electric field of strength $2 \times 10^5\,\mathrm{V\,m^{-1}}$.

was confirmed later by McBrierty *et al.* [16] from NMR studies on Phase II samples and also by Lovinger and Wang [17] from dynamic mechanical studies.

The dielectric loss spectra of Fig. 4 do not show the α_c relaxation. It has been observed by several researchers in the present range of temperature and frequency (e.g. [15]) for Phase II samples. The α_c relaxation has been observed to be dependent on the crystal structure also. It has generally been observed for Phase II samples and found to disappear as the Phase II crystallites were transformed to Phase I/Phase IV [3–9]. It is quite likely that the α_c relaxation does not appear in our dielectric spectra due to the Phase III structure of our samples. This result is in agreement with the findings of Klasse and Turnhout [13].

Fig. 4 shows increasing dielectric losses with decrease in frequency. The strong low-frequency dispersion of ε'' is generally assigned to d.c. conduction losses and/or trapped charge carriers. The contribution of d.c. conduction to the dielectric loss ($\varepsilon''_{\mathrm{d.c.}} = \sigma_{\mathrm{d.c.}}/\omega\varepsilon_0$) is estimated using the conductivity data shown in Fig. 5. Using the q.s.s. values of conductivity, an overestimated contribution of conduction losses would be obtained. The dashed curves in Figs 2 and 4 show the dielectric losses which have been corrected for q.s.s. conduction losses. The overestimated conduction losses are still small as compared to the total dielectric losses, and therefore, are not expected to be deleterious in further analysis.

The low-frequency dispersion of ε'' could now be attributed to trapped charge carriers. Ionic impurities have been observed to get deposited near the electrodes (at very high temperatures) or trapped at the crystalline–amorphous interfaces, leading to large losses at low frequencies in PVDF samples [18–22, 27–30].

Investigations on charge-carrier trapping in PVDF have also been done by the thermally stimulated discharge current measurement (TSC) technique [8, 9, 23–25]. TSC peaks were observed corresponding to the release of charge carriers trapped in the crystalline–amorphous interface regions. The peak temperature and the activation energy for the release of trapped charge carriers were found to differ for the Phase I, II, and IV samples [8, 9].

Very low frequency dielectric loss has often been obtained by Fourier transformation of the absorption currents from the time to the frequency domain using Hamon's approximation [26]. Using this technique, loss peaks have been observed due to interfacial polarization at the crystalline–amorphous boundaries in PVDF [9, 27]. The loss peaks showed an Arrhenius type of temperature dependence and were designated as α_i relaxation [27].

Trapped charge carriers make an important contribution to the dielectric properties of PVDF. Further work is, therefore, necessary to gain insight into the charge carrier trapping processes at the crystalline–amorphous interfaces, particularly in the case of Phase III PVDF.

5. Summary

The dielectric properties of solution-cast PVDF films have been studied. The α_c relaxation does not appear in the dielectric loss spectra due to the Phase III crystal structure of the samples. A small loss peak is observed which could probably be assigned to α' relaxation arising from molecular motions in the folds on the surface of the crystallites. Charge carriers trapped at the crystalline–amorphous interfaces make a large contribution to the dielectric parameters at lower frequencies.

Acknowledgements

This work was supported in part by the Council of Scientific and Industrial Research (Government of India).

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Received 30 May
and accepted 31 October 1986