11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Influence of the amorphous-crystalline interface on the dielectric and ferroelectric polarization of α- PVDF

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Abstract –The influence of uniaxial stretching on the dielectric properties and remanent polarization of α-PVDF was determined. Commercial films supplied by Bemberg Folien GmbH were used. Some films were uniaxialy stretched at 140ºC and with draw ratio (R) of 4, resulting in α-phase oriented films. Morphological effects of orientation were investigated by differential scanning calorimetry (DSC) and infrared spectroscopy (FTIR). It was verified that the orientation increases the crystallinity by the reduction of the amorphous-crystalline interface and, consequently, increase the stable remanent polarization. It was verified also a strong reduction of the metastable polarization and of the permittivity at $5x10^{-5}$ Hz and an increase on the the permittivity at 1 kHz. These results allow supposing that the amorphous-crystalline interface is the responsible by the origin of the metastable polarization and the dielectric α_c-relaxation.

Poly(vinylidene fluoride) (PVDF) has remarkable properties leading to electro-optics, electro-mechanical and biomedical applications. In particular, its piezo- and pyroelectric properties provide possibilities for many technological applications. The crystalline phase in PVDF contains at least four polymorphic modifications (α, β, γ, and δ) [1,2]. The apolar α-phase, is the most common, being easily obtained by melt crystallization or from dimethylformamide or dimethylacetamide solutions at temperatures above 120º C.

In this study, changing of morphological, dielectric and ferroelectric properties with the drawing in α-PVDF was investigated. The samples were stretched at 140ºC and R=4, obtained oriented α-PVDF films. The crystalline phase, degree of crystallinity and dielectric properties of the samples, oriented and unoriented, were determined by Fourier transformed infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and dielectric spectroscopy (DS), respectively. The hysteresis loops of these films were determined by the ramp voltage technique [3,4]. In this method the linear ramp voltage is applied in a PVDF sample. The ramps are applied in discontinuous cycles and with the short-circuit time between the consecutive cycles. The number of the ramps voltage, of same polarity or reverse, it is controlled, allowing the application of an arbitrary sequence of ramps. In this way the stable and metastable remanent polarization can be determined separately.

The correlation between structural, dielectric and ferroelectric characteristics of the oriented and unoriented samples shows that the stretching increases the stable polarization due the increase of the degree crystallinity and chains orientation. An increase of the permittivity at 1kHz was observed, probably caused by the better molecular ordination and consequent larger dipoles density in the amorphous phase. A decrease of the permittivity at $5x10^{-5}$ Hz and a strong decrease in the metastable polarization were also observed and it can be relationship with the reduction of the amorphous-crystalline interface. The existence of this interface between the crystalline and amorphous phases was shown firstly by Flory [5]. Recently Ozkazanc et al [6] verified that the dielectric loss maxima, corresponding to the α_c-relaxation transition in α-PVDF films, decrease and still disappears with the draw ratio. Our results, supported by the work of Ozkazanc et al, allow us to infer that the dielectric relaxation is also associated to the amorphous-crystalline interface.

References

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