Influence of Morphology on Electric Conductance in Poly(ethylene naphthalene-2,6-dicarboxylate)

Jose Fidel Chavez, Juan Jorge Martinez-Vega, Noureddine Zouzou, Jean Guastavino*

Laboratoire de Génie Electrique de Toulouse (UMR-CNRS 5003), Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France.

Summary: Polymers find an important field of application in the electrical industry because of their utilization as insulators and dielectrics. The challenge over the last several years has been to make electrical compounds smaller in size. In that way the material morphology is of strategic importance in the performance of new components in relation to their geometry. Therefore, it is important to know the influence of different types of stress on electric properties of the materials.
We have studied the influence of the crystallinity on electric conductance of poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN), which is increasingly replacing some dielectrics (polypropylene and PET) in certain electric applications.
Starting from an amorphous PEN, samples with various crystallinities were obtained and analyzed using DSC in order to determine their thermal characteristics.
Moreover, measurements of charge and discharge currents were carried out on PEN samples to characterize their electric properties. The steady state current observed after 120 min, in response to the electric field, shows an increase in the insulator resistivity with the crystallinity. The increase in the crystallinity favors a decrease in the free volume, so the movement of charges is restricted especially by the species of large sizes.

Keywords: crystallization; electric conductance; insulator resistivity; morphology; PEN films

Introduction

Poly (ethylenenaphthalene-2,6-dicarboxylate) (PEN) is a polymer obtained by polycondensation of naphthalene-2,6-dicarboxylic acid and ethylene glycol.[1]

PEN competes with PET (poly(ethylene terephthalate)) in engineering applications that require high performance in terms of dielectric properties, thermal stability and physical and chemical properties.[2] The rigid aromatic ring system of naphthalene explains a better performance of this polyester. Indeed, the naphthalene moiety in PEN provides stiffness of the linear backbone,

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leading to improved characteristics fitting its applications, such as thermal resistance, excellent mechanical properties like tensile properties and dimensional stability, and outstanding gas barrier characteristics.[3] Due to all these advantages, the interest of the market in PEN growing also due to the study of its electric and mechanical behavior, and of other prominent electronic characteristics (such as an increase in the product of capacitance and voltage per unit of volume and its application in the technology of surface mounted technology (SMT) insulator).[4]

The electric conductance across the surfaces of insulating polymers is an aspect of considerable technical and commercial interest but poorly understood (as regards the mechanisms involved), despite the effort made by several authors of theoretical end experimental studies. [5] With PEN, the problem is even greater due to its recent appearance on the market and obviously due to little experimental and theoretical study, especially at high electric fields. In particular, the clear and transparent viewpoint of the charge injection and carrier migration processes will be essential in the future of these materials. Our paper contributes to explanation of the behavior of PEN, in electric fields from 7 MV/m to 120 MV/m using amorphous and semicrystalline PEN with crystallinity of 40 % .

Experimental

The PEN films used in this work were kindly provided by DuPont de Nemours Luxembourg. The films were obtained by biaxial orientation. The samples contain additives, which allow the rolling up of films. Two types of PEN were characterized: films of 70 μm thickness of very low crystallinity (amorphous films) and films of the same thickness with a partly crystalline structure (40 %).

The stages of sample preparation were metallization and annealing followed by secondary vacuum processing. The sample used was metallized on its two faces, yielding a metal-insulator-metal structure. Thus two zones were formed: the first, the interface between the material and metal, and the other was the bulk. With the aim to study the influence of morphology and of the mode of preparation of the samples on their electric behavior, three studies were carried out:

(a) Initially, we studied an amorphous sample of metallized PEN.

(b) Next, a sample of amorphous PEN was metallized and then annealed (PEN-SC1)

(c) A sample of amorphous PEN was annealed and then metallized (PEN-SC2)

In the cases b and c, the samples were placed in vacuum ($\approx 10^{-6}$ mbar) for 8 h before experiment. The objective was to remove traces of moisture and air bubbles formed sometimes in the sample. In Fig. 1, we show thermal characteristics and crystallinities of the samples. Crystallinity was calculated using the relation:

$$\chi(\%) = 100 \times \frac{\Delta H_f - \Delta H_c}{\Delta H_\infty}$$

Where ΔH_f is the enthalpy of fusion, ΔH_c the enthalpy of crystallization and $\Delta H_\infty = 103.4$ J/g the enthalpy of fusion of fully crystalline PEN. [6]

With PEN-SC1 and PEN-SC2, we did not find any important difference with respect to semicrystallinity and other thermal characteristics like glass transition.

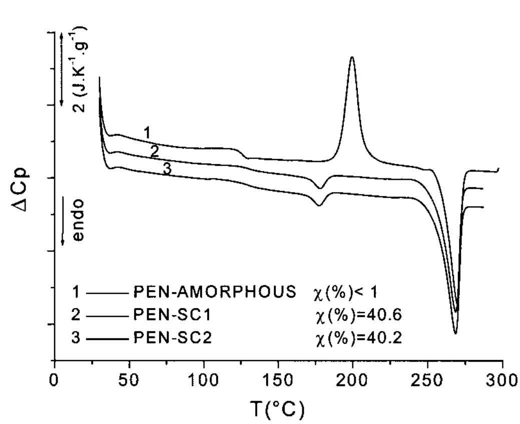

Figure 1. Comparison of thermal characteristics. ΔC_P is the specific heat and $\chi(\%)$ the crystallinity.

The measurements proceed in vacuum ($\approx 10^{-6}$ mbar) to avoid the problems of contour discharges. The characteristics current/voltage, *I/E*, were obtained at ambient temperature by application of a continuous voltage.

The samples were metallized with evaporated gold under vacuum. This technique makes it possible to obtain gold electrodes of 20 mm diameter and 30 nm thickness. The process of metallization is carried out in vacuum (1 mbar) to keep the purity of gold.

On annealing, the material was heated from room temperature to 160 °C at a heating rate of 10

°C/min. The temperature remained constant for 180 min to obtain the desired semicrystalline morphology. The sample was then cooled down to room temperature at the same rate. The heat treatment was carried out in a Mettler FP82HT device; the temperature control was performed with a regulator of Eurotherm-2404 type.

With regard to the instrumentation, we used a controlled feeding, Fug Electronik GmbH HCN 35-20000. Its use eliminated current disturbances due to the oscillations of excitation. Its operation was 0-20 kV with a maximum current of 5 mA. We used a vibrating read electrometer (Cary 401), which allows a reliable measurement of current from 5×10^{-15} A to 10^{-11} A. The principle of operation is the collection of charges by a vibrating capacity. The voltage which appears at the terminals of the capacitor is converted to an alternating signal by the vibrating electrode. By combining a synchronous detection with this alternating signal, the current is obtained. In order to perform acquisition of the data by this analog device, we used a numerical multimeter and a numerical and controllable (bus IEEE 488) picoammeter Keithley 617.[7]

Results and Discussion

We can approach the discussion of the influence of the morphology of the samples on their electric behavior.

In Fig. 2, we traced *I/E* characteristics of the three studied samples. In particular one of them shows that the insulator resistivity (the ratio of the direct voltage to the total current which crosses the electrodes and the sample for 120 min) depends at the same time on the bulk resistivity and the sheet resistivity of the sample (IEC standard resistivity 167).[8] The resistivities of the samples were found as: amorphous PEN is $\rho = 2.93 \times 10^{16}$ Ωm, for the PEN-SC1 $\rho = 5.73 \times 10^{16}$ Ωm, and finally for the PEN-SC2 $\rho = 3.76 \times 10^{16}$ Ωm .

In the region of weak fields, the rise in voltage induces an increase in current; for this linear behavior the resistivity is independent of the applied electric field.[9] The displacement of the charge carriers between the two electrodes is the source of conductivity in the material.

An increase in the crystallinity causes a decrease in the conductivity of PEN, since an increase in crystallinity favors a decrease in free volume making thus difficult the charge movement. The difference in the conduction levels of the two morphologies of PEN, i.e., amorphous and partly crystalline, depends on the quality of this course. Indeed, assuming a constant number of carriers, we can observe a strong reduction in mobility associated with the semicrystalline samples. We point out that this semicrystalline structure is heterogeneous because it contains amorphous parts, amorphous parts under constraint (thus more rigid) and crystalline parts. Probably, this heterogeneous nature of the structure causes the reduction in the conduction level.

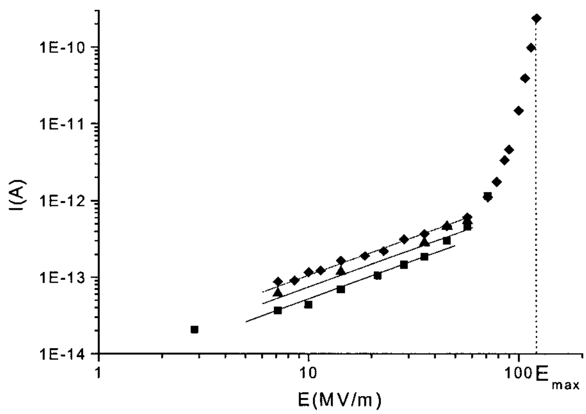

Figure 2. Comparison of *I/E* characteristics: ♦ PENam (amorphous PEN); ■ PEN-SC1. ▲ PEN-SC2 . (E_{max} is the maximum field applied to amorphous PEN, 120 MV/m).

The ionic conductance phenomenon is very sensitive to a reduction in the free volume associated with the formation of new intermolecular connections of the van-der-Waals type as well as to the proportion of the amorphous region more susceptible to lodge this type of transport.[10] However, the presence of the ionic conduction phenomenon due to the presence of impurities remains hypothetical.

Even though the difference in resistivity between the amorphous PEN and semicrystalline PEN is obvious, that which differentiates the PEN-SC1 and PEN-SC2 is less clear from the electric point of view. The measurement is qualitative in terms of the proportion of the ordered phases but not quantitative in terms of the nature, size and concentration of crystallites. On the other hand, a relation between the adhesion strength of the metal and the film resistance, particularly the sheet resistance, may exist. The latter is due to a combination of surface roughness and interfacial reactivity, which is very low for evaporated gold films; so a contribution to sheet resistance can be entirely attributed to surface roughness.[11] Another aspect of *I/E* characteristic is the value of the threshold field from which the number of the injected carriers is significant compared with that of intrinsic carriers.

A phenomenon of demetallization was found with the semicrystalline samples, PEN-SC1 and PEN-SC2, when getting into the region of 70 MV/m fields. This phenomenon forced us to stop the experiment due to great variation of the measurements. However, it is important to remark that it is not a predisruptive phenomenon. In amorphous samples, such phenomena do not occur.

Conclusion

The objective of this paper and its originality consists in making a comparison of the electric response of two different structures of PEN. The first was characterized by a homogeneous amorphous phase and the other by a heterogeneous morphology, corresponding to a crystallinity of 40 %. The heterogeneous PEN was prepared by two methods, which had an influence on the its properties.

The experimental results revealed an increase in the insulator resistivity with increasing crystallinity. The increase in crystallinity supports the reduction in free volume; thus, the displacements of the charge carriers are limited in particular to the species whose size is significant. The reduction in mobility is significant also for crystalline morphology characterized by a more compact and heterogeneous structure.

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