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The Influence of Crystallization and Morphology on the Field Mechanical Induced Strain of Poly (Ethylene 2, 6-Naphthalene Dicarboxylate) Thin Films

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Abstract: Measurements are reported on the influence of crystallinity on the field induced strain response of Poly (ethylene 2, 6-naphthalene dicarboxylate) PEN thin films using an optical non contact measurement technique based on the tracking of successive positions of computerized markers. Markers move when the sample is subjected to the application of a dc high voltage and a computerized tracking of the successive positions of the four markers permit us to quantify the induced mechanical strain using Lagrangean formalism. The observed strain levels varied from $\sim 10^{-3}$ to 10^{-2} . The results revealed higher deformation levels in case of amorphous compared to similar partially crystallized samples. The field induced strain characteristics indicate three zones. Indeed, initially there is a region of very low deformation until an electrical field threshold is attained after which an increasing induced strain level is observed. Finally, there is a diminution of the strain that could be produced by a local densification of the material. This behaviour suggests the presence of a thermally dominated mechanism attributed to the propagation of local breakdowns caused by large local fields in micro-voids.

Key words: Field induced strain, dielectric properties, thin PEN films, optical non contact measurement, breakdown, ageing

INTRODUCTION

Poly (ethylene 2,6-naphthalene dicarboxylate) (PEN), a high-performance thermoplastic polyester, has attracted considerable attention for many years due to its superior thermal, mechanical, barrier and chemical resistance properties, which make PEN useful in a wide range applications, such as films, magnetic tapes and packaging (Ford, 1996). This aromatic polyester used recently in electrical engineering presents praiseworthy physical performances which make it an interesting material to investigate and may be considered as a serious competitor of polyethylene terephthalate (PET) for manufacture of capacitors. PEN is a polymer obtained by dicarboxylic polycondensation of the naphthalene-2,6 and ethylene glycol acid. The process used for the manufacture of films calls upon the dicarboxylic cross esterification of the dimethyl ester of the naphthalene-2, 6 acid with the ethylene glycol (Buchner *et al.*, 1989).

This material is often subjected to higher electric fields which can induce mechanical stress within the insulator structure surface producing a local mechanical

strain. In previous experimental investigations (Mamy *et al.*, 2004; Chavez-Lara and Martinez-Vega, 2004) an attempt was made to assess the mechanical response of PET under gradually increasing electrical fields. It was suggested that these electrical stresses were responsible for localized mechanical strains.

The aim of this study is the quantification of the mechanical strain induced by a high dc electric field in Poly (Ethylene-2, 6-Naphthalene dicarboxylate) PEN films by using an optical measurement method (tracking). The tracking method allowed measuring induced mechanical strains on the flat gold-metallized surfaces of amorphous and semi-crystalline PEN thin films. Several PEN samples with different crystallinity rates and thickness have been considered. The kinetics of crystallization and melting of PEN have been investigated by using Differential Scanning Calorimeter (DSC) to ensure the morphology status of the samples provided. DSC was performed using a TA Instruments device of type DSC 2010. The DSC cell was calibrated using pure indium. This technique allows us to determine the glass transition (T_g) and the melting point temperature (T_m) of the sample. The knowledge of

crystallization (ΔH_c) and melting (ΔH_m) enthalpies of the samples allows for the calculation of the crystallinity rate ($\chi(\%)$), as mentioned in (Martinez-Vega *et al.*, 2001). Based on experimental considerations by using DSC, a thermal cycle of crystallization was carried out. Different specimens were obtained in this way, starting with as-received amorphous polymers. However, in order to improve the comprehension of phenomena that might lead to the electrical breakdown and ageing mechanism, a quantitative study by a non destructive optical technique without involving any physical contact, based on the follow up of four computerized markers on the sample surface was used to investigate the effect of the thermal treatment on the induced mechanical strain of partially crystallized PEN films. Both amorphous and semi-crystalline PEN samples were subjected to dc electric fields for different durations up to their electrical breakdown, with or without depolarization. In the present work we compare the level and the evolution of electrical field induced strain in amorphous and partially crystallized PEN samples; emphasizing the quantification of field induced strain occurring before the electrical breakdown, as function of crystallinity and the electrical field. Interpretation of the morphological changes and the levels of the field-induced mechanical deformation corresponding to various measurement protocols are discussed subsequently.

MATERIALS AND METHODS

The experimental measurement method is based on the follow-up of four markers on the sample surface. This

technique makes it possible to follow in real time the mechanical behavior of PEN thin films under high electrical fields.

Material: Commercial PEN (Teonex TM) provided by Teijin DuPont Films (Luxembourg), in A4 sheet format were employed for experiments. The as-received samples were PEN films, partially crystallized Teonex Q51 12 and 25 μm thick, as well as amorphous 14, 25 and 70 μm thick.

Experimental device and samples preparation: Figure 1 shows the schematic diagram of the experimental apparatus developed to conduct the electrical field induced strain measurement by using an optical technique based on the tracking of successive position displacement of four computerized markers by DEFTAC software (associated with an optical system formed by an optical microscope connected to a Charge Coupled Device (CCD) camera (resolution = 768 pixels. 576 pixels with 256 gray levels) provided by MATROX -METEOR II, image processing card permitted the observation of the sample surface in reflected light (Dupré *et al.*, 2005). To guarantee a better electrode/polymer contact, the test samples were metalized by gold coating using a S150B plasma sputter coater. To determine the morphology of the samples under study and the impact of gold metallization on the initial PEN morphology, we analyzed two samples with Differential Scanning Calorimetry (DSC): one was as-received (for the morphological study) and the other was gold-metallized (for the study of the effect of the metallization on the thermal properties of the material). The analyses were carried out under liquid nitrogen with

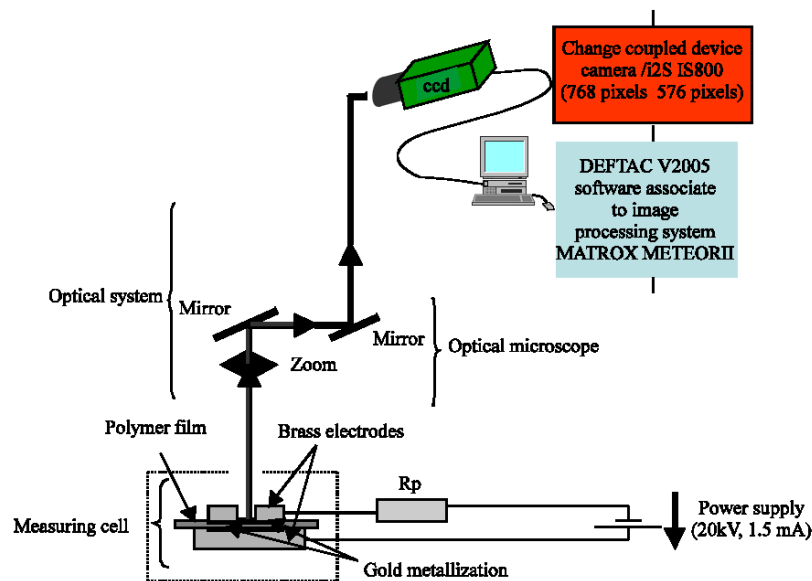


Fig. 1: The schematic diagram of the experimental setup

specimens of about 11 mg; each sample was subjected to a rise in temperature from ambient temperature to 290°C at 10°C min⁻¹. The DSC thermograms show practically no difference between the as-received and metalized samples indicating no appreciable effect of gold metallization on the morphological properties of the PEN.

Electrodes of 20 mm diameter and 30 nm thickness were thus obtained on both sides. The prepared sample was placed between two external brass electrodes. The upper one, the negative, was constructed as a hollow cylinder of 12 mm diameter. This permitted the use of a flexible light source to illuminate the upper face of the sample. The lower electrode, the positive, was connected to a high dc voltage source (HCN 35-20000; 20 kV and 1.5 mA limited current) with controllable output. The samples were placed between electrodes in the measuring cell; the electrodes were short-circuited a few hours before the testing in order to eliminate the initial charges existing on the sample faces before applying the electric field.

Figure 2 shows the obtained image of the gold-metalized surface of a sample using. This image reveals small, contrasting spots, which represent the microscopic light contrast of traditional metallization. To manipulate the test sample as little as possible, we identified four of these spots with computerized marking. The four markers thus obtained allowed us to quantify the electric field induced strain in real time.

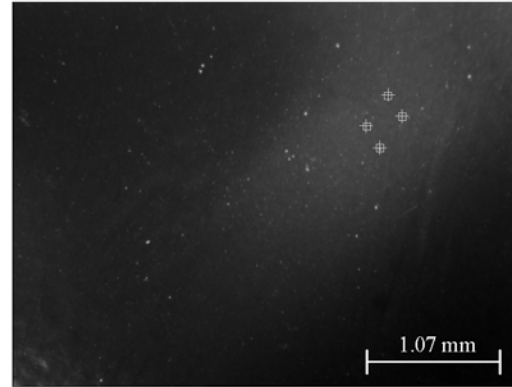


Fig. 2: Disposition of four markers on gold-metalized amorphous PEN sample

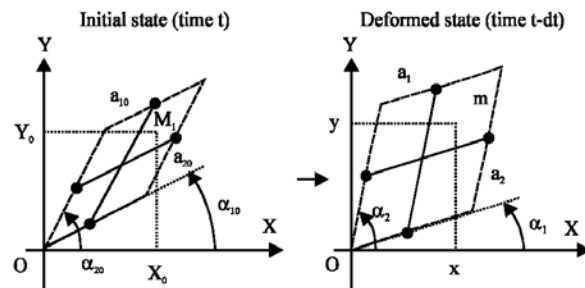


Fig. 3: Diagram of the follow-up of four markers

Principle of strain measurement: The principle of strain measurement consists of four markers (Fig. 3), forming a cross, positioned on the sides of a parallelogram.

Knowing the coordinates of these spots, at each state of loading, we can use the calculation of the lengths (a_1 and a_2) and orientations (α_1 and α_2) to determine, into a large deformation formulation, the Green-Lagrange strain tensor ($\bar{\bar{E}}$) (Nadai, 1950):

$$\bar{\bar{E}} = \frac{1}{2} (\bar{\bar{F}}^M \cdot \bar{\bar{F}}^M - \bar{\bar{I}}) \quad (1)$$

where, $\bar{\bar{F}}^M$ the gradient tensor function of the following components:

$$\bar{\bar{F}}^M = \begin{pmatrix} \left(\frac{a_1 \cos \alpha_1 \sin \alpha_{20} + a_2 \cos \alpha_2 \sin \alpha_{10}}{a_{10} \sin(\alpha_{20} - \alpha_{10})} + \frac{a_2 \cos \alpha_2 \sin \alpha_{10}}{a_{20} \sin(\alpha_{10} - \alpha_{20})} \right) & - \left(\frac{a_2 \cos \alpha_2 \cos \alpha_{10}}{a_{20} \sin(\alpha_{10} - \alpha_{20})} + \frac{a_1 \cos \alpha_1 \cos \alpha_{20}}{a_{10} \sin(\alpha_{20} - \alpha_{10})} \right) \\ \left(\frac{a_1 \sin \alpha_1 \sin \alpha_{20}}{a_{10} \sin(\alpha_{20} - \alpha_{10})} + \frac{a_2 \sin \alpha_2 \sin \alpha_{10}}{a_{20} \sin(\alpha_{10} - \alpha_{20})} \right) & - \left(\frac{a_2 \sin \alpha_2 \cos \alpha_{10}}{a_{20} \sin(\alpha_{10} - \alpha_{20})} + \frac{a_1 \sin \alpha_1 \cos \alpha_{20}}{a_{10} \sin(\alpha_{20} - \alpha_{10})} \right) \end{pmatrix} \quad (2)$$

The experimental technique makes it possible to measure the induced mechanical deformation components associated with the plane surface of a film. We label these components ϵ_x , ϵ_y and γ_{xy} , which are associated with the

directions parallel to the x -, y - and xy -shearing axes, respectively. The ϵ_1 and ϵ_2 components are associated with the principal a direction at which γ_{xy} is null. We have assumed the homogeneity of the deformation on the measurement base and as a result, the reported values are averages.

The principle of mark tracking is to calculate the geometric center of the spot from a rectangular zone (the research zone), defined at the beginning of the computation, around each spot by its upper left coordinates (x_z , y_z) and size (N_x , N_y). For large deformations and movements, this research zone is automatically moved at each step of time, with consideration given to the measured displacement, to keep the spot inside. Then, the coordinates (x_g and y_g) of each marker are derived with the following equations:

$$\begin{cases} x_g = \frac{\sum_{x=0}^{N_x} \sum_{y=0}^{N_y} x [I(x,y) - I_z]}{\sum_{x=0}^{N_x} \sum_{y=0}^{N_y} [I(x,y) - I_z]} + x_z \\ y_g = \frac{\sum_{x=0}^{N_x} \sum_{y=0}^{N_y} y [I(x,y) - I_z]}{\sum_{x=0}^{N_x} \sum_{y=0}^{N_y} [I(x,y) - I_z]} + y_z \end{cases} \quad (3)$$

$I(x, y)$ is the light intensity of the pixel with coordinates x and y .

where, I_0 is the lower limit of the light intensity (beyond this limit, the pixel is not discriminated) and $I(x,y)$ is the light intensity of the pixel with coordinates x and y .

Procedure: Measurements were carried out at the room temperature at atmospheric pressure and for very short durations (less than 30 min), in order to minimize the influence of the environmental conditions. Several protocols of dc electric stress application were adopted (Zegnini *et al.*, 2006); the differences consisted in the duration of dc voltage application and/or the existence of a depolarization period. To assess the level of deformation resulting from high dc voltage application, PEN samples were stressed for periods of 5, 10, 15 and 30 min followed by a similar depolarization period at every voltage level with different CCD camera sampling rates (one photo per three seconds and six seconds, respectively). After the test, we removed the electric stress to study the return of the material to its original state. To obtain measurement reproducibility, we carried out measurements of the noise levels before the application of the electric field for a certain period.

RESULTS AND DISCUSSION

Differential scanning calorimetry: The thermal analysis DSC was successfully performed in order to obtain significant degrees of crystallinity. The as-received amorphous PEN samples were first maintained at 170°C for different annealing times 5, 10, 15, 30, 45, 60, 90, 120, 180 min; the protocol of isothermal crystallization of as-received amorphous PEN is given in Fig. 4.

DSC measurements have been carried out from 30 to 300°C, in order to characterize the glass transition, the melting point and the crystallization degree of the material. The results obtained with as-received material as well as with the amorphous one. The glass transition, clearly observable in the scan corresponding to the amorphous sample, lies at approximately $T_g = 123^\circ\text{C}$: obviously the change of baseline becomes less pronounced when the isothermal annealing time increases. This amorphous sample crystallizes between 160 and 220°C, preceding the fusion of the material at 268°C. The scan corresponding peak, which indicates a high degree of crystallinity in the material. The main endothermic peak, located at 268°C, corresponds to the fusion of the crystalline phase and is preceded by a small endothermic peak probably associated with a solid state transition in the material (Fig. 5). According to the extrapolated heat of fusion for

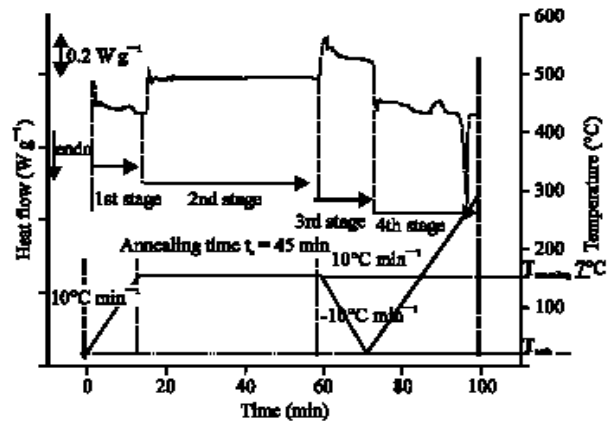


Fig. 4: Protocol of isothermal crystallization

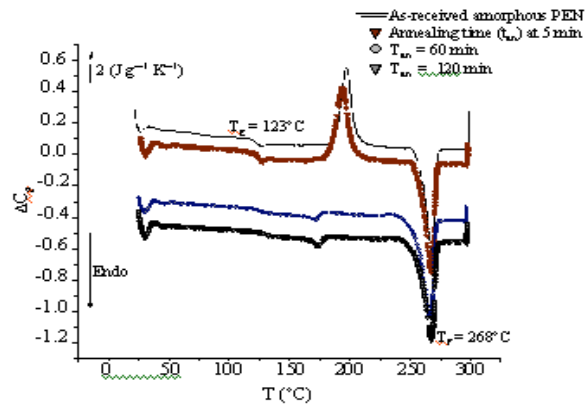


Fig. 5: DSC thermograms of PEN samples annealed at 170°C

a pure PEN crystal (103.3 J g^{-1}) and the total heat flow involved in the endothermic peaks, a crystallinity degree of about 4.17% is estimated for the as-received amorphous sample.

Table 1 shows an augmentation in the amount of crystalline phase as isothermal annealing duration increases. Three stages of evolution are observed, the first one corresponds to annealing times lower than 15 min, where the material remains almost, amorphous. Subsequently, a fast crystallization rate is observed, between 15 and 45 min. As result the peak of the cold crystallization disappeared then a small pre-melting peak is observed instead. Finally, a constant percentage of crystallinity about 42% is obtained for the longest periods. In addition it was observed at higher temperatures, the melting peak is around 268°C and it does not be affected by this thermal treatment. The obtained results are explored to analyze the dependence of the rate of crystallinity on the mechanical response of PEN thin films.

Table 1: Annealed as-received amorphous PEN 70 μm samples

t_a (min)	T_a (min)	T_m (°C)	Δh_c (J g ⁻¹)	Δh_m (J g ⁻¹)	γ (%)
As-received	123	268.20	-33.02	37.31	4.17
5	122	267.68	-32.72	39.71	6.76
10	125	267.67	-33.07	40.18	6.87
15	125	267.89	-29.12	37.59	8.19
30	125	267.38	-15.21	40.74	24.69
45	126	266.51	-4.64	42.94	37.11
60	128	266.57	+1.64	43.15	43.31
90	127	268.11	+2.623	41.39	42.56
120	129	267.52	+3.055	42.80	44.34
180	130	267.97	+3.488	39.99	42.04

Performance of the strain measurement: The accuracy of the strain measurement is a function of the marker position and the distance between the spots. The measurements of the noise level were carried out for an as-received PEN sample 70 μm thick on a mechanical deformation without an electric field. The measurements of the noise level were carried out for an as-received PEN sample on a mechanical deformation without an electric field. Figures 6a and b show the measured components of the noise levels corresponding to the distant markers.

Figure 6a and b show that in the case the noise levels were very small and corresponded to the predicted error (2×10^{-4}). For This result we could neglect the effect of the weight of the higher electrode. Moreover the measured mechanical strain deformations in this study corresponded only to the strain induced by the electric field application.

Field induced strain measurements: During the present study, we highlighted the optical observation of the surface of PEN thin films for the analysis field induced strain. To perform this investigation PEN films were subjected for periods of 300 sec at gradually increasing 0.5 kV constant step of high applied voltage. It is important to mention that the maximum applied voltage that we have imposed was 7 kV; the deformation of the film was recorded with constant CDD camera using a sampling rate (one image per three seconds). An attempt was made to compare the level and the evolution of field induced strain in the as-received amorphous and partially crystallized PEN samples (Zegnini *et al.*, 2007). Two different samples with different degrees of crystallinity were chosen to study the breakdown phenomena. Figure 7 shows the sample with a crystallinity of ($\chi = 17, 41\%$), which broke down at electric field of 6.21 kV. The figure shows the moment of spark due to its electrical breakdown. The geometry of the arc due to breakdown is very well sparking defined in Fig. 7.

Figure 8 shows the induced strain produced during the test. Figure 8a shows the principal strain components of the film deformation as function of time. It is interesting to note that ϵ_1 is positive and ϵ_2 is negative (even through it is close to zero). This anisotropy is probably to the biaxial orientation of the film micro-morphology produced

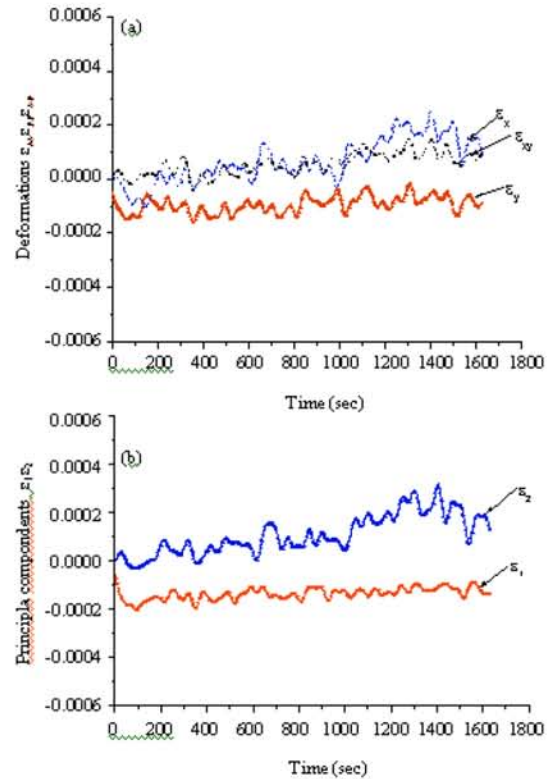


Fig. 6: Strain components of the noise levels (electric field = 0)

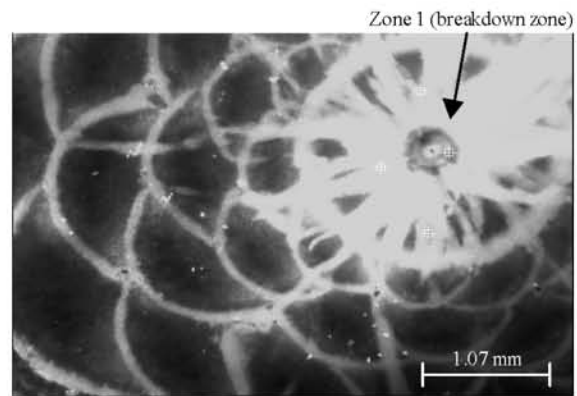


Fig. 7: Final captured image after breakdown the PEN sample 25 μm thick with a crystallinity of ($\chi = 17, 41\%$)

during its manufacturing. Figure 8b shows the contributions of the average fitted values ϵ_1 and ϵ_2 to evaluate of the electric field induced strain ϵ as a function of the electrical field, until the electrical breakdown

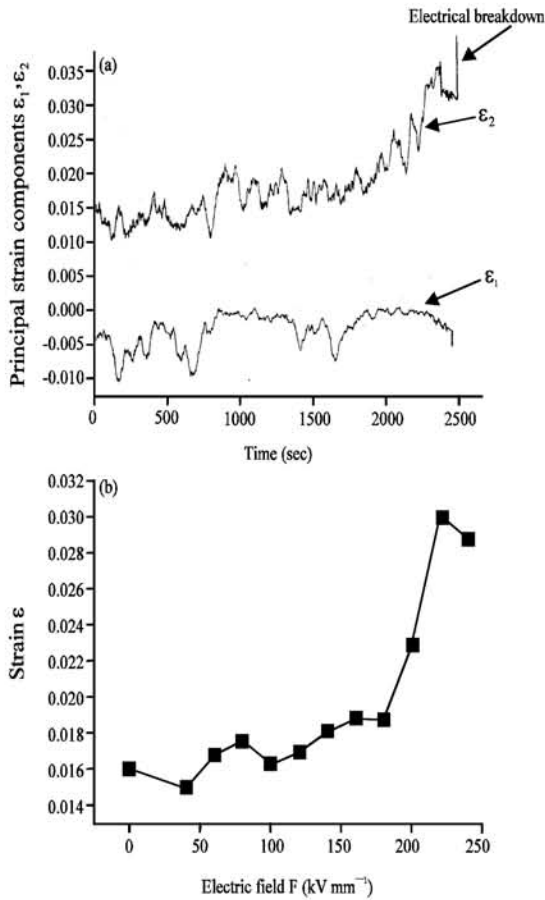


Fig. 8: Induced strain versus electrical field of PEN 25 μm thick sample partially crystallized ($\chi = 17.41\%$)

(Ford, 1963). The evolution of the electric field induced shows three zones. Indeed, initially there is a region of very low deformation until an electrical field threshold is attained after which an increasing induced strain level is observed. Finally, there is a diminution of the strain that could be produced by a local densification of the material. This behaviour suggests the presence of a thermally dominated mechanism attributed to the propagation of local breakdowns caused by large local fields in microvoids. It is rather a mechanism of electrical aging having a mechanical origin. Thus, on the basis of a previous image-acquisition program used to explore the influence of crystallinity on the mechanical response of the same sample, two distinct domains resulting from dielectric breakdown were investigated (Fig. 9). The first is with dielectric breakdown zone more vulnerable to the field-induced mechanical deformation as compared to the second which is situated outside this region. However, the level of the induced mechanical deformation seems to have similar evolution, in particular when the values of the

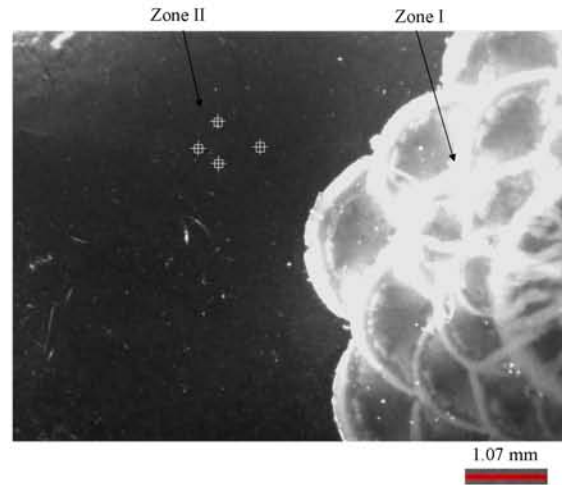


Fig. 9: Definition of two zones the PEN 25 μm thick sample with a crystallinity of ($\chi = 5.14\%$); the first one (zone 1) inside the damage area and the second one (zone 2) outside this area

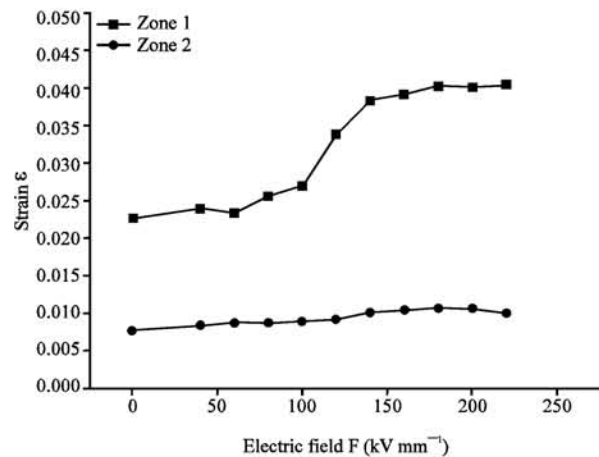


Fig. 10: Comparison of the induced strain at each zone

electric stress are relatively small (Fig. 10). This observation links in a straightforward way the local strain with the electrical breakdown phenomena. The possible explanation of this behavior is probably the diminution of the trapped charges mobility of responsible for the reorganization of macromolecular chains in zone I and the conformational changes probably vary the molecular inter-space. It is possible that the deformation at the breakdown area could be set up by pre-existent defects from the chemical or physical manufacturing processes, where the strain concentrated until the final electrical breakdown.

Figure 11a and b shows the influence of the crystallinity on the strain behaviour and the electrical

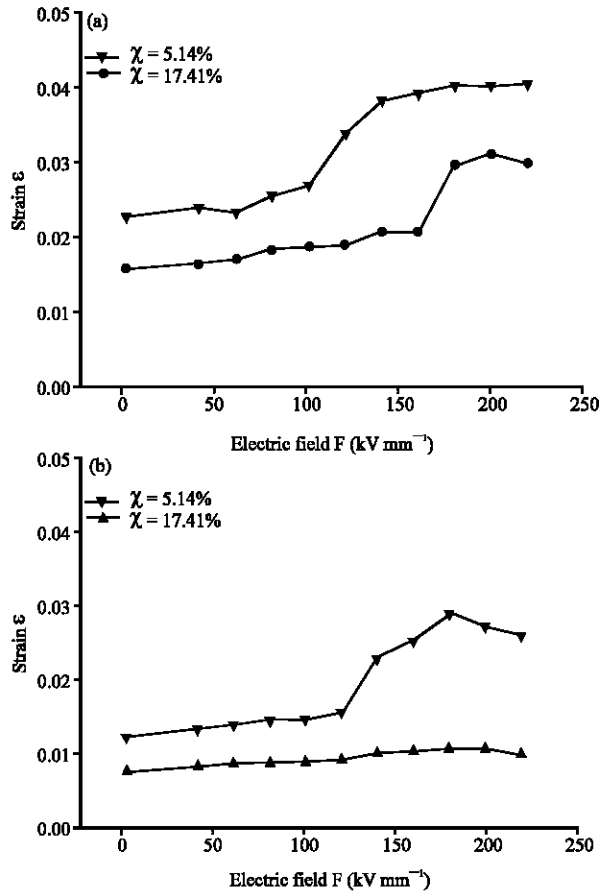


Fig. 11: Influence of the crystallinity on the strain behaviour and electrical breakdown (a) behaviour at zone I and (b) behaviour at zone II

breakdown field. It is observed that the lower crystallinity sample ($\chi = 5, 14\%$) presents a larger strain than the other one ($\chi = 17, 41\%$).

The previous observations are very interesting because it shows that the crystallinity produces an electrical weakness of the tested sample. It is important to indicate that the conductivity of the amorphous PEN is almost larger than the semi-crystalline PEN (Chavez-Lara *et al.*, 2004). Therefore, the higher crystalline sample is capable of accumulating a larger electrostatic energy, which seems to be the main factor that the electrical breakdown.

In addition, the influence of crystallinity on the induced strain in treated PEN 70 μm thick samples, the results given in Fig. 12 reveal higher deformation levels in case of amorphous samples. Furthermore, for annealing time 60 and 120 min, the crystallinity degree is constant respectively 43.31 and 44.34%. But the local strain observed for $t_a = 120$ min is lower compared to $t_a = 60$ min, at the high electric field range. This can be explained by a

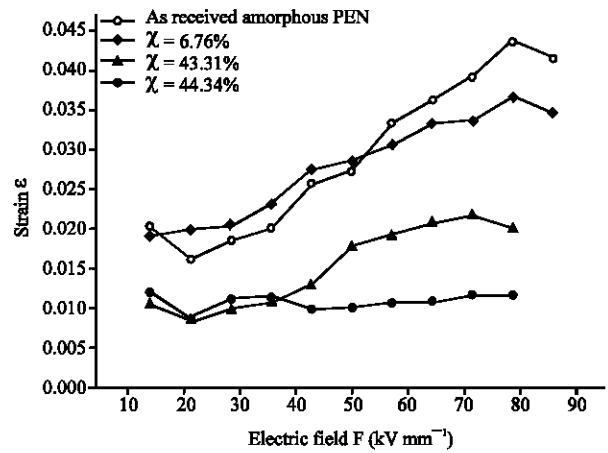


Fig. 12: Influence of crystallinity percentage on the field induced strain

more ordered microstructure that has higher mechanical strength. This morphology increases the stiffness of the polymer, hence its mechanical properties.

CONCLUSION

A non-destructive optical technique has been applied to the measurement of field-induced strain in PEN thin films in order to give a clear concept of ageing phenomenon and breakdown mechanism in a polymeric material. The resulting induced strain levels and patterns were dependent on the level, measurement protocols (ramp test, with depolarization test) and duration of electric stress application, thickness and morphologies of the samples. A thermal protocol of isothermal crystallization has been conducted to obtain PEN film crystallized samples with different crystallinity degrees, starting with as-received amorphous. The tracking method was employed to evaluate the local induced strain on the basis of a previous image-acquisition program at two different zones of the tested sample; breakdown zone (zone 1) inside the damage area and zone II outside this area. The results revealed higher deformation levels in zone I compared to the distant unaffected zones (ie zone 2). This difference in induced strain was observed even at very weak electrical fields. Moreover, plots of field-induced strain to analyze the influence of crystallization on the level of mechanical deformation and threshold field. It was observed that the field-induced strain was dependent on the crystallinity of the treated samples dependent on the crystallinity and the electrical breakdown of tested samples. The field-induced strain diminished when the crystallinity increased, as well as the maximum voltage supported by the film before electrical

breakdown. The obtained results implies further work to validate a clear concept of ageing phenomenon and breakdown mechanism in a polymeric material under operating conditions, in which several stresses are involved.

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