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On the cold drawing of poly-ether-ether-ketone (PEEK) tubes

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Abstract

The mechanical behaviour commonly referred as cold drawing (CD) is a phenomenon that occurs once the yield point is reached, in a thermoplastic material subjected to a uniaxial tensile test at constant strain rate. In effect, after yielding the sample undergoes a neck in its cross-sectional area, which then propagates along the entire useful length of the sample while the applied force remains constant. This phenomenon occurs in amorphous or semi-crystalline materials in a wide range of temperatures below the glass transition temperature. Understanding this phenomenon involves knowing what deformation mechanisms operate and how they are related to the morphology of the material. In this work, on one hand, the mechanical response of poly-ether-ether-ketone (PEEK) thermally aged at 25 and 135 °C for 30 day is measured. In previous researches PEEK aged at 130 and 135°C undergoes cold drawing when subjected to a tensile strain rate of $1,7 \cdot 10^{-3} \text{ s}^{-1}$ at 25 °C. In addition, the average stress and the ultimate elongation of the plateau depend on the temperature and the duration of the annealing. On the other hand, wide angle X ray diffraction, density measurements, differential thermal analysis, shape memory analysis and complex impedance measurement allow determine changes in the amorphous and crystalline phases due to thermal aging and cold drawing effects.

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1. Introduction

In order to study the aging of polymers for nuclear applications some aspects of Nuclear Energy Agency (AEN) (2010) were considered.

Nomenclature

LOCA	Loss-Of-Coolant Accident
CD	Cold drawing
T_g	Glass transition temperature
T_m	Melting temperature
T_{REC}	Recrystallization temperature
DSC	Differential Scanning Calorimetry
ASTM	American Society for Testing and Materials
M_n	Number average molecular weight

Accelerated thermal aging processes were performed on PEEK tubes in previous work during 30 days at different temperatures (25, 55, 90, 130 and $T_{LOCA} = 135$ °C). In the mechanical characterization for samples aged at 130 °C is visualized a plateau (constant engineering stress) in the tensile test curve (engineering stress vs strain) after yielding, this is known as CD. Experimentally, CD is visualized as a necking and the subsequent propagation of the neck along the specimen, Nuclear Energy Agency (1999) set in that this kind of phenomenon is important to study in order to improve the performance of nuclear power plant. Some researchers as Nitta, K-H and Motowo T. (2006) proposed models focused on understanding CD of semi-crystalline polymers and others as Leonov A.I. *et al* (2002) in its propagation too. This work focused on the second case, various techniques (characterization and functionalization) were applied to aged specimens at two temperatures (25 and 135 °C) for 30 days, such as:

- Mechanical characterization: uniaxial tensile test.
- Morphological characterization: X-ray diffractometry and densitometry, molecular weight (evaluating T_g according to Roovers J. *et al* (1991)).
- Thermal characterization: DSC.
- Electrical characterization: considering the use of dielectric PEEK tubes electrical characterization is performed by measuring complex impedance.
- Physical functionalization: PEEK presents shape memory. Controlled functionalization tests were conducted in order to evaluate the performance of the post-CD capacity of PEEK tubes. Subsequent uniaxial tensile tests showed the influence of the shape memory on the structure of the aged material.

Finally, the discussion of the interpretation of the experimental results is exposed.

2. Materials and methods

PEEK was purchased to GoodFellow company, its chemical structure is showed in Fig. 1. This semi-crystalline polymer ($T_g \approx 140$ °C and $T_m \approx 340$ °C) presents excellent mechanical, thermal and electrical properties as well as a good resistance to neutron radiation.

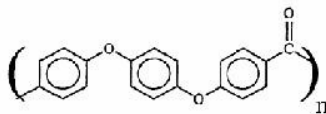


Fig. 1. Chemical structure of PEEK.

2.6. Accelerated thermal aging

Thermal (physical) treatments were performed considering some aspects mentioned by Ogale A.A. and McCullough R.L. (1987) according to ASTM D 573 (2004), in the Thermal Treatment of Materials Laboratory (CAC-CNEA), at 25 and 135 °C in an oven with forced air recirculation, Fig. 2. This consists of a heater, a air moderator circuit and a temperature controller that apply continuous or intermittent heating.



Fig. 2. Oven with air forced recirculation.

2.2. Mechanical characterization

INSTRON 5500R servo-mechanical test machine was used; test temperature was 25 °C and the strain rate was $1,7 \cdot 10^{-3} \text{ sec}^{-1}$. This was performed in the Mechanical Properties Laboratory of Advanced Materials Division of the Materials Management (CAC-CNEA). At a certain aging time (0, 3, 7, 15 and 30 days) five specimens were tested according to ASTM D 638 (1983). From PEEK tubes were cut samples with length of $100 \pm 1 \text{ mm}$ for uniaxial tensile test, arranging them in jaws designed *ad hoc* to clamp as shown in Fig. 3 (a)-(b).

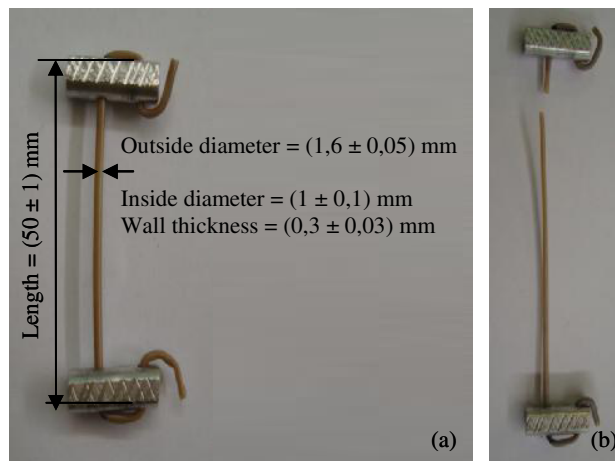


Fig. 3. PEEK tube specimen. (a) Before uniaxial tensile test; (b) after uniaxial tensile test.

From the engineering stress vs strain curve were determined: the tensile modulus, the yield stress, the stress of CD and its strain range.

2.3. Morphological characterization

Empyrean Detector PIXCEL3D diffractometer belonging to Laboratory X-ray Diffraction Department of Condensed Matter Physics Research Management and Applications (GAI & ANN-CAC-CNEA) was used. From diffractograms, considering an angle range (2θ) of 5-35°, percentage of crystallinity was obtained. Reproducibility was 6 %, so one diffractometry was performed to every experimental measurement.

Measurements of density were performed with a pycnometer in the Laboratory of Uranium Compounds (LADCU) Nuclear Fuel Cycle Management (CAC-CNEA). Due to low dispersion in preliminary values of density, one measurement was performed for each time of thermal aging at 135 °C, after and before of the CD.

M_n was estimated considering T_g following the empirical fitting according to Roovers, J. *et al* (1991).

2.4. Thermal characterization

A DSC TA Instruments, model 2000 Q belonging to Laboratory of Thermal Studies Department of Condensed Matter Physics (GAI & ANN-CAC-CNEA) was used. Thermograms were obtained from 25 to 360 °C at 20 °C/min, according to this, T_g , T_{REC} and T_m were evaluated. Preliminary reproducibility was 1 %, so one measurement to every sample was performed.

2.5. Electrical characterization

An impedance analyzer, model SI 1260 belonging to Department of Micro and Nanotechnology, Investigation and Non-Nuclear Applications Management (CAC-CNEA) was used. For this purpose, a cylindrical capacitor was constructed whose tubular dielectric was the PEEK tube. Complex impedance was measured considering a frequency range of 10 kHz -1 MHz and the potential difference ($\pm 1V$) applied, at different aging times and temperatures.

2.6. Physical functionalization

Shape memory tests under controlled conditions were performed, that is, at an average heating rate of 7 °C/min. Start temperature of the shape recovery and the recovery rate were measured.

3. Results and discussion

Fig. 4 shows the tensile tests curves for all days of aging at 135 °C upto complete CD; this phenomenon is not observed for the sample as received but in all aged samples from the third aging day.

Within thirty days of aging the tensile modulus increased by 8 % from baseline (unaged materials) of $1,3 \pm 0,2$ GPa; yield stress increased by 5 %, with an initial value of 77 ± 1 MPa, CD stress increased by 1 % with an initial value of 81 ± 1 MPa (third day) and CD strain range increased 11 %, with an initial value of $0,58 \pm 0,02$ mm/mm.

After CD, samples were subjected to a controlled heating to assess the shape memory in the conditions mentioned above. Indeed, it was possible to reverse the change in cross section as a consequence of CD. This dimensional change altered the mechanical behaviour of the material.

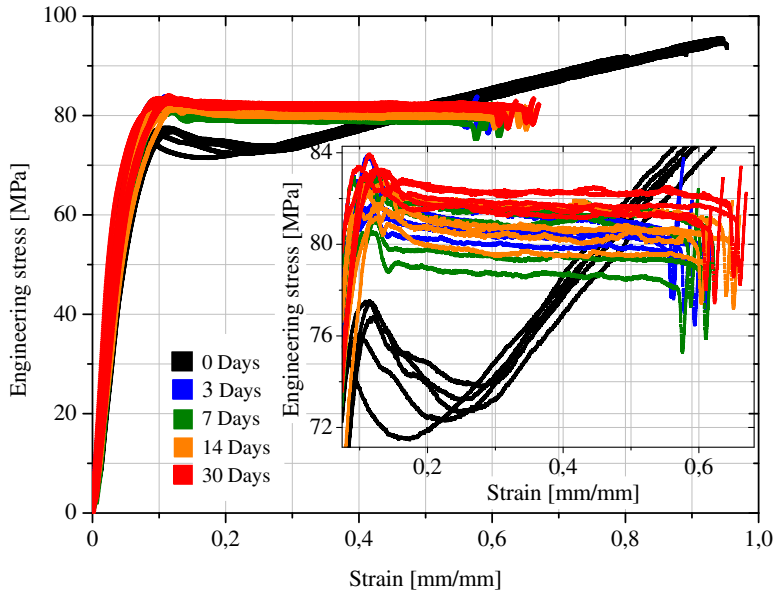


Fig. 4. Mechanical behaviour vs aging time (colours) for thermal aged PEEK at 135°C.

Uniaxial tensile test curves of the material that recover its shape are displayed in Fig. 5. There, the inactivation phenomenon of cold drawing is emphasized, resulting in a hardening post-yield behaviour.

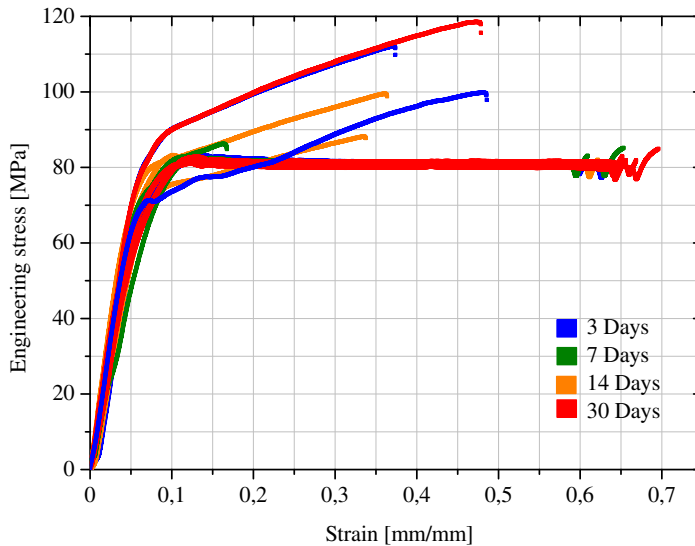


Fig. 5. Mechanical behaviour vs aging time (colours) for thermal aged PEEK tubes at 135 °C before shape memory tests (curves with CD) and after it (curves with hardening post-yielding).

To begin assessing the relationship between morphology and mechanical behaviour of the PEEK, percentage of crystallinity as a function of aging time was determined, shown in Fig. 6.

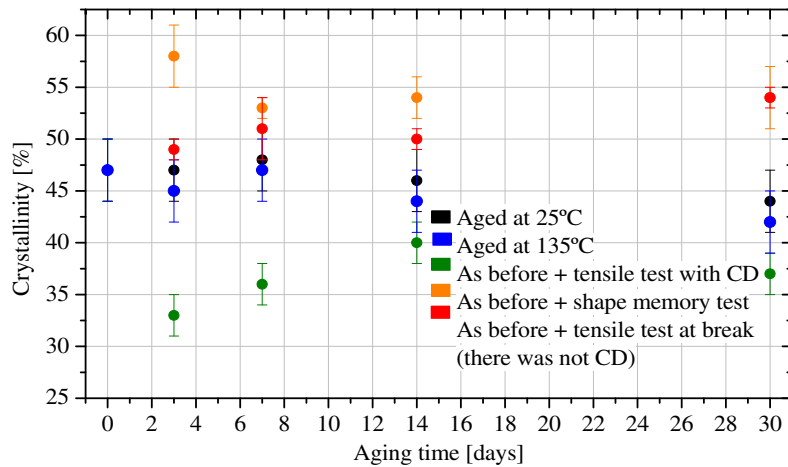


Fig. 6. Percentage of crystallinity vs aging time for all cases.

It is notable that the percentage of crystallinity decreases slightly after thirty days for both thermal aging treatments (25 and 135 °C). Increasing aging temperature (25 to 135 °C) is visualized a decrease in the percentage of crystallinity, *id est*, polymer is slightly more amorphous.

For all days of aging, percentage of crystallinity decreased after CD (green spots) and increased in time upto fourteenth day. This experimental result is consistent with a model proposed in the literature, as Leonov J. (2002) according to which CD reduces the crystallinity of the polymer, *id est*, crystalline lamellae provide macromolecules to the amorphous phase through loss of local order configuration set by crease with adjacent reentry.

As shown in Fig. 6, crystallinities of the post-shape memory tests increased (orange dots), even at values above the pristine sample; the enthalpy absorbed to recover the shape of the sample is used to recrystallize the material. Material has these high crystalline values prior to the uniaxial tensile test, after the shape memory test. After uniaxial tensile test, the crystallinity (red dots) decreased for all days of aging, except for the last day, for which values matched.

From above it follows that the decrease of crystallinity is necessary but insufficient condition for the manifestation of CD. The difference between these structural changes (cold drawing-hardening) clearly does not explain it only with crystallinity, this does not consider, for example, the level of mobility of the macromolecules of the amorphous phase, the most sensitive to it. To evaluate this factor, T_g is evaluated by DSC. In Fig. 7 the evolution of T_g is presented for all cases.

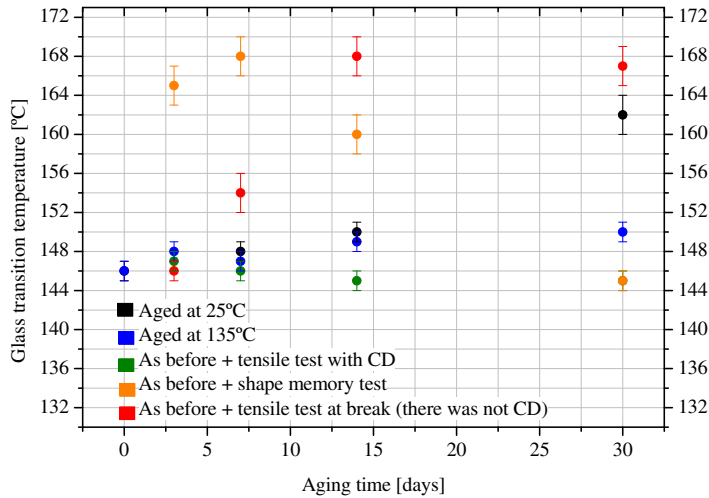


Fig. 7. Glass transition temperature vs aging time.

T_g increases slightly with aging time (for 25 and 135 °C thermal treatment), but a slight decrease for the same treatment at higher temperature is observed. After CD, T_g decreases for all days of aging (green dots), so there is more amorphous phase, as a consequence the mobility of the macromolecules are favored; these features were increased with aging time. Past shape memory test, T_g increased (orange dots). In contrast to the conditions set for the manifestation of CD, the hardening produced an increase of crystallinity and a decrease in T_g . After the second uniaxial tensile test, the tendency of the T_g (red dots) was not homogeneous.

The recrystallization temperature did not show notable changes. So far the mobility of the macromolecules of the amorphous phase was analyzed, which depends on its molecular weight. Indeed, the shortening or lengthening of the macromolecules could affect T_g . This change in length can be evaluated by M_n . For this, the empirical relationship between the T_g and M_n was evaluated according to Roovers J. *et al* (1991):

$$\frac{1}{T} = \frac{1}{T_g^\infty} + K \cdot \frac{1}{M_n} \quad (1)$$

Where T_g^∞ is the T_g to infinite molecular weight and K is an empirical constant. Roovers J. *et al* (1991) obtained thermograms by DSC at a heating rate of 10 °C/min. In the present work a heating rate of 20 °C/min was used, considering its dependence with T_g , to apply Eq. 1 to estimate M_n it is necessary to know the dependence between T_g and heating rate. Su-Don Hong *et al* (1986) found that the T_g of PEEK at 10 °C/min is 5 °C lower than that measured at a heating rate of 20 °C/min (used in this work), so at T_g measured were subtracted 5 °C. Following this treatment, the molecular weights were obtained, shown in the Fig. 8.

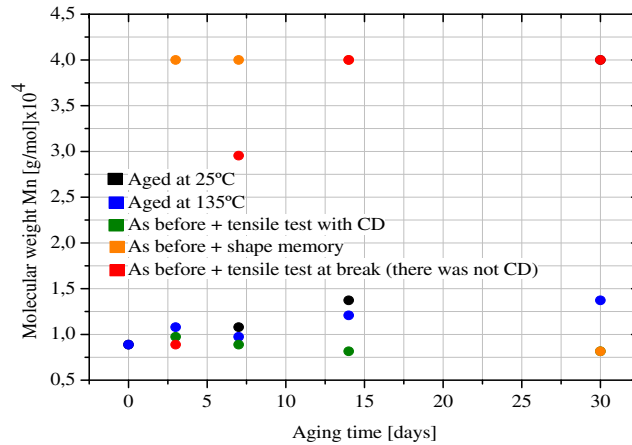


Fig. 8. Molecular weight of the PEEK — estimated by eq. (1) — vs. aging time.

So far the behaviour of the amorphous and crystalline phases separately were evaluated. However, some authors as Nitta K-H. and Motowo T. (2006) set that in semi-crystalline polymer there are three phases: crystalline, amorphous and third lamellae made up of clusters, the latter is attributed to the necking in the specimen during uniaxial tensile test. Therefore, it should be noted that all phases are structurally related, which promotes a synergy in the behaviour between all of them. In this sense, macroscopic density measurements were performed at pre-aged and post-aged samples at 135 °C thermal treatment and then uniaxial tensile tested them upto CD; Fig. 9 shows the values obtained.

It is notable that the major aging time passes, the higher density is (which decrease the overall free volume) upto a value close to the crystalline phase (1,32 g/cm³ according Jones D.P. *et al* (1985)) and then drastically fell in the thirtieth day. After CD, material (macroscopic density) is densified, which promotes higher presence of crystalline phase. This could be attributed to an increase in density of the amorphous phase (oriented chains).

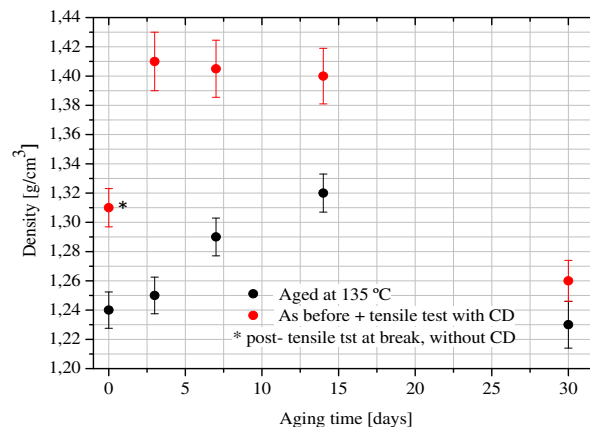


Fig. 9. Temporal evolution of the macroscopic density.

The above is related to the parameters obtained from the shape memory tests, performed with specimens aged at 135 °C that experimented CD. The start temperatures of the shape recovery of these samples are shown in Fig. 10, which do not practically depend of aging time (≈ 70 °C), while the shape recovery average rate and temperatures range used to activate this phenomenon decreased with time until the fourteenth day, probably due to reduced mobility of macromolecules.

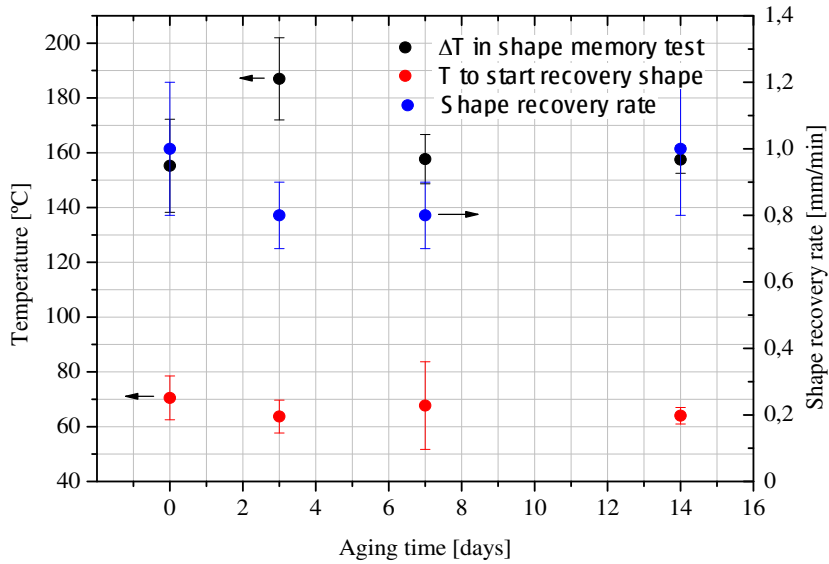


Figure 10: The onset temperature and the shape recovery temperature range involved in activate the capacity and average rate used to recover the initial shape vs aging time

Finally, by electrical characterization, the complex impedance (Z) was measured and its evolution with time was evaluated *versus* frequency and the applied potential difference. Both did not produce majors modifications on the value of Z , *id est*, the initial dielectric constant (3,2 at 1 kHz) did not practically change during thermal aging. In Fig. 11 the dielectric relaxation for specimens aged at 135 °C on days 0 and 7.

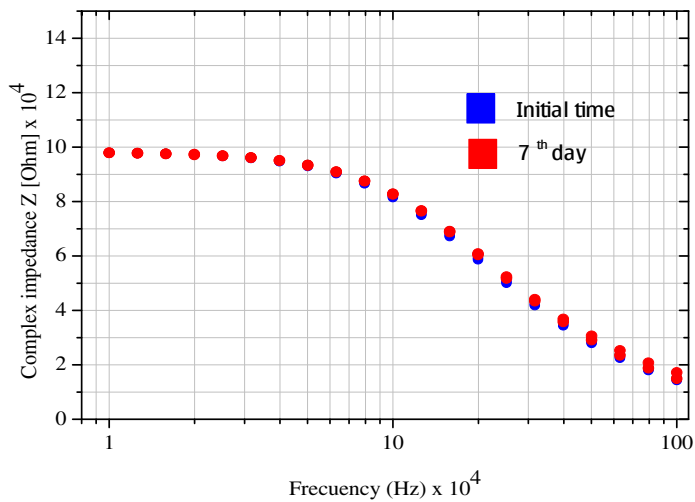


Fig. 11. Complex impedance vs applied frequency.

3. Conclusions

The central premise of the morphological model proposed in the literature, as Leonov A.I. (2002), to explain the phenomenon of cold drawing in semi-crystalline polymers, was empirically verified for PEEK. This phenomenon is favored as a consequence of decrease in the initial crystallinity and the free volume, both produced during thermal aging.

Acknowledgements

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