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Structural and Thermo-mechanical Evaluation of Two Engineering Thermoplastic Polymers in Contact with Ethanol Fuel from Sugarcane

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Special polymers have been used in the manufacture of storage structures and pipelines avoiding corrosive processes during ethanol fuel transport/storage. Therefore, this work investigated comparatively the effects of the ethanol on the physical-mechanical properties of poly (ether ether ketone) (PEEK) and polyamide 11 (PA-11) based on ageing tests. The WAXD and DSC results demonstrated slight reductions on the crystallinity degree of the aged PEEK, contrariwise to what happened with PA-11, where X_c increased after ageing. However, the results of thermal, thermomechanical and mechanical analysis (TGA, DMTA, tensile and micro-IITs) demonstrated that PEEK is stable and no significant changes were observed in its elastic modulus ($E_y \approx 3.4$ GPa, E' and $E_{it} \approx 3.7$ GPa) or glass transition temperature. PA-11, conversely, was sensitive to ethanol fuel and expressive changes of its physical-mechanical properties were verified. For both materials, a reasonable correlation between crystallinity and mechanical properties was established.

Keywords: *Ageing, Ethanol, Microindentation tests, Microhardness, Elastic modulus, Crystallinity*

1. Introduction

Biofuels have emerged, as an alternative for fossil fuels in several applications. In this context, the ethanol fuel transportation as well as its storage in tanks for marketing purposes, requires structures based on materials chemically compatible with the stored substance. Ethanol production systems and storage and distribution tanks have a series of gears, parts and components such as ethanol dispenser hoses, connectors, valves of submersible pumps, membrane filters, bushings and bearings that continually come into direct contact with the fluid during their service life and need keeps their structural integrity[1-6]. All are frequently made of carbon steel alloys, which usually need to be coated to avoid corrosion and oxidation problems[3-5]. Recent studies have reported that the worldwide existing infrastructure is not fully adequate to alternative fuels as ethanol or biodiesels[4,7]. Furthermore, the corrosive effects of alternative fuels are not well known for this existing transport and storage structures[4].

Steel tanks and dedicated pipelines offer significant advantages due to high structural resistance and low cost-effective relation if the corrosive aspects are included in the initial project. Therefore, avoiding corrosion or stress-corrosion cracking (SCC) on the metallic structures[3-5], annealing or other heat treatments can be applied. In some cases, chemical inhibitors can be added to the stored or transported fuels. Additionally, another promising alternative recommended in several cases where, for instance, inhibitors are not a good option, is the use of non-metallic pipes or internal polymeric coatings in dedicated pipes and storage tanks[7-9].

Engineering polymers are considered for this application due to their higher density what could reduce problems such as gas and fluid permeation. For this reason, there is currently and more than ever a great interest in developing and applying high performance polymeric materials as liners or in the manufacture of the parts themselves. Polymeric materials when employed as liners act as a protective barrier or chemical barrier. If the whole part is polymeric, its chemical inertness to the stored fluid is further intensified. In addition, high performance polymeric materials maintain a satisfactory performance in terms of key mechanical properties such as elastic modulus and yield stress over their entire service life[6,8-10]. However, long exposure times to the transported fluid may lead to the development of gradients of mechanical property reduction through the thickness, which may result in degradation and service failure[8-10]. This occurs due to the ageing of the polymer, leading to changes (increases or decreases) in its structural, mechanical and thermal properties such as tensile strength, elongation at break, hardness, elastic modulus, chemical resistance, glass transition temperature, and crystallinity[6,11]. The magnitude of the gradients that may appear depends mostly on the polymer, working temperature and the specific physical-chemical interactions between the polymer and the fluid. The diffusion processes and permeability may also affect the mechanical performance of the polymeric material employed[6,8,12], leading to ageing and degradation of the polymer or of some product that the polymer should protect.

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Poly (ether ether ketone) (PEEK) is a semi-crystalline thermoplastic high performance engineering polymer. It has high glass transition ($T_g \approx 145$ °C) and melting ($T_m = 340$ °C) temperatures and has been discussed in the literature since the 1980s[6,11-16]. It can be subjected to a variety of processing routes, has high chemical resistance to many solvents and is employed in a variety of engineering applications (e.g., aerospace, automotive and chemical industries)[17-22].

Polyamide 11 (or PA-11) is another high performance, thermoplastic and semi-crystalline engineering polymer that is widely used in industry and has a lower cost than PEEK. Its polymer chains are formed by amide and methylene groups with strong intermolecular attractions due to the hydrogen bonds that confer good mechanical, thermal and barrier properties. However, despite its versatility in terms of several technological applications, PA-11 is susceptible to chemical degradation in the presence of water (hydrolysis) and alcohols (alcoholysis), phenomena that are intensified by high temperatures (above 60 °C)[23,24]. Chaupart et al.,[24] explained that there are many possible causes for this behavior, among which the two simplest are the coexistence of a depolymerization process and random chain scission, or a localized fast hydrolysis process. Nevertheless, there are no systematic studies evaluating PA-11 behavior in ethanol fuel, since this material is employed in several oil and gas application, even in contact with water, at temperatures up to 60 °C, such in flexible lines for offshore oil exploration.

In this context, the present study sought to assess the comparative physical-mechanical behavior and chemical compatibility of the PEEK and PA-11, focusing the use of the PEEK in liners or in the manufacture of parts and small gears for ethanol fuel storage and transport. This is an important investigation due to increasing in the use of ethanol fuel worldwide and due to the current lack of thorough studies about the effects of the ethanol fuel on the structure of specialty polymers such as PEEK or PA-11.

To this end, PEEK and PA-11 were submitted to ageing tests in anhydrous and hydrated ethanol media at 60 °C, under atmospheric pressure. The choice of the PA-11 at comparison to PEEK was made purposely because of its known and related loss of chemical resistance in environments such as pure water[23,24] or oilfield water[25], under the effect of temperature. In addition, some samples were aged for the same time at 60 °C (annealing with no ethanol), whereas others were aged in ethanol at room temperature (23 °C) for comparison. The degree of crystallinity (X_c) of the polymers was evaluated before and after ageing, using wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was used to asses the thermal stability and the content of plasticizer in the materials, while dynamic mechanical thermal analysis (DMTA) was applied to study the dynamic storage modulus and glass transition temperature. The mechanical properties were evaluated by use of stress-strain curves and instrumented microindentation tests (referred here as micro-IITs), and the elastic modulus values were compared with those obtained from DMTA.

2. Experimental Methodology

2.1. Materials preparation

Commercial grade semi-crystalline PEEK (450G), manufactured by Victrex through standard injection molding according to ASTM D 638[26] (Type I dogbone-shaped) was used. Plasticized PA-11 (commercial grade produced by Arkema) was supplied in pellets and processed through compression molding (six tons of pressure at 220 °C for 5 min in the melting, following by a cooling at 80 °C for 10 min). Type I dogbone-shaped test specimens were also obtained. The same PEEK and PA-11 specimens were machined to prepare rectangular pieces (30 x 20 x 3 mm), which were used in the micro-IITs. Similarly, bars with dimensions of (50 x 10 x 3 mm) were produced to use in the DMTA analysis as per ASTM D 5023[27].

2.2. Ageing tests

PEEK and PA-11 ageing tests in anhydrous and hydrated ethanol were conducted over 1 and 3 months in thermal baths containing water at 60 °C and over 1 and 3 months at room temperature (23 °C), both situations under atmospheric pressure. The ageing tests were carried in accordance with the standard ISO 175[28]. The polymers were placed in cylindrical glass bottles of 1 L and with sealing caps to prevent the entry of liquids or exit of volatiles. The polymers were kept upright and separated inside the bottles. For the annealing experiments, the polymer samples were placed into a hot-air oven at 60 °C during the same ageing times. The specifications of the sugarcane ethanol are 94% v/v (hydrated ethanol) and 99.3% v/v (anhydrous ethanol), both acquired from CENPES/Petrobras.

2.3. Characterization methods

DMTA analysis was carried out for determination of the glass transition temperature (T_g) and dynamic storage modulus (E') of the PEEK and PA-11. The measurements were made in the three-point-bending mode in a dynamic mechanical analyzer (DMTA 242C, Netzsch Co.). The dynamic load and the amplitude were 4 N and 60 μm, respectively. The scanning range was from 0 to 250 °C for PEEK and -120 to 110 °C for PA-11 at a heating rate of 2 °C min^{-1} and a frequency of 1 Hz, under a nitrogen atmosphere.

The degree of crystallinity (X_c) of the polymers were assessed by X-ray diffraction using a Shimadzu diffractometer operated with CuKα radiation ($\lambda = 0.1542$ nm) for 2θ values from 5 to 80°. X_c integration and calculations were performed according to well-established procedures in the literature[13,29-31].

X_c was also calculated from DSC. The curves were obtained in a Q 8000 apparatus (Perkin Elmer) under a nitrogen atmosphere. The temperature range was from 25 to 400 °C for PEEK and 25 to 250°C for PA-11, both with a 10 °C min^{-1} heating rate. The degrees of crystallinity were obtained from DSC analyses according to literature procedures[32], using ΔH_f^0 (enthalpy of fusion of 100% crystalline polymer) tabulated as 130 and 226 J g^{-1} for PEEK[11,16] and PA-11[31], respectively.

The thermal stability of the PEEK and PA-11 was analyzed using TGA (Q500, TA Instruments). Approximately 15 mg of each sample was heated from 25 to 700 °C at a rate of 10 °C min^{-1}. The maximum temperature of the weight loss curves was taken as the decomposition temperature (T_d) of the samples.

Tensile tests were performed in an Instron model 5567 universal testing machine with a crosshead speed of 50 mm min^{-1} and using an optical extensometer (AVE) for measuring deformation. The elastic modulus (or Young's modulus, E_y) was obtained from linear regressions in low deformations in the stress-strain curves, and the yield stress (σ_y) was directly read from the curves.

Instrumented microindentation tests (micro-IITs) were carried out in a microindentation tester (MHT) from CSM Instruments using a three-side pyramidal Berkovich indenter tip and following the methodology described by Oliver and Pharr[33-35]. The contact load was defined as 10 mN, and maximum loads of 210, 310 and 410 mN, with a holding time of 200 seconds, were applied, scanning different regions of the sample surface. The holding time at the maximum loading is essential to ensure reduction of creep effects (the so called "nose effect")[33-35]. The loading and unloading rates were 200 mN min^{-1}. The micro-IITs produced mean values of µ-HB, E_{it} and maximum depth indentations (h_{max}) for the aged and unaged PEEK and PA-11 samples.

The mechanical properties obtained from stress-strain curves and micro-IITs were evaluated using statistical Student's t-tests with a confidence level (1 - α) of 95%, i.e., the differences were considered statistically significant for *p*-values below 0.05, as described by Montgomery et al.[36]. Furthermore, the mean results obtained were reported as mean followed by standard deviations and coefficients of variation, and presented as mean ± SD (CV). All statistical analyzes were performed using MS Excel (Microsoft).

3. Results and Discussion

3.1. Dynamic mechanical thermal properties

The curves of dynamic storage modulus for the unaged PEEK and PA-11 are shown in Figures 1 and 2, respectively. These curves clearly indicate the difference in the mechanical behavior of the two materials. PEEK is a much more rigid polymer over the whole temperature range evaluated. Figures 1 and 2 show that the *E'* values at 23 °C of the unaged materials are 3.7 GPa for PEEK and 472.7 MPa for PA-11, almost a degree of magnitude lower.

The main chain relaxation of the PEEK, taken at the maximum of tan δ, occurs at 165.5 °C, as shown in Figure 3, similar to values reported in the literature[6,11,16]. This high relaxation temperature for the PEEK polymeric structure is associated with the rigid segments of its backbone, as reported by Yuan et al.[16] and White et al.[20]. On the other hand, the flexible chains of the PA-11 can explain its T_g value of 13.6 °C (Figure 3), similar to values reported by Chaupart and Serpe[23], and is associated with the long segments between the amide groups and the significant amount of plasticizer present in this particular grade. It is well known that plasticizers increase the chain mobility by disrupting the H-bonding network present in polyamides[23]. PA-11 also has a secondary or β transition that can be seen in Figure 3 at approximately - 80 °C that has been associated with segmental motions involving adjacent nonbonded amide groups with other amide groups on nearby chains[23].

Figure 4 shows the T_g values of the PEEK and PA-11 as obtained from the maximum of the tan δ. It can be observed that PEEK's T_g is basically insensitive to fluid contact in the conditions evaluated (Figure 4b), as expected due to its chemical resistance, remaining around 165 °C before and after ageing. Furthermore, the low temperature employed (60 °C) was not sufficient to modify its crystallinity or favor ethanol diffusion. A more detailed analysis on the crystallinity degree as a function of the ageing time/fluid will be shown later on.

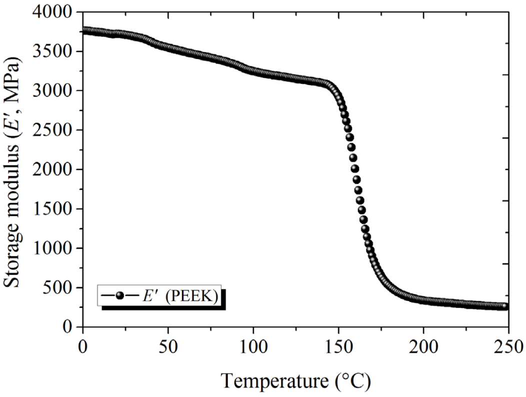

Figure 1. Storage modulus of the unaged PEEK at a frequency of 1 Hz.

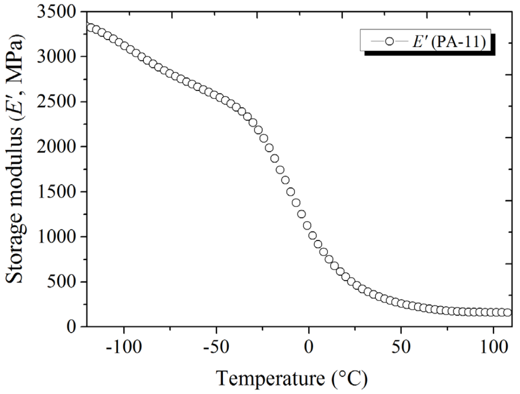

Figure 2. Storage modulus of the unaged PA-11 at a frequency of 1 Hz.

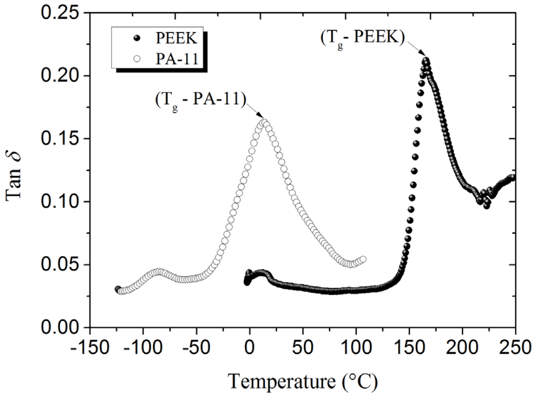

Figure 3. Tan δ values of the unaged PEEK and PA-11 at a frequency of 1 Hz.

On the other hand, the T_g values of the PA-11 considerably decreased as a function of the ageing time in anhydrous and hydrated ethanol, indicating a strong sensitivity of the PA-11 to both type of alcohols, as shown in Figure 4a. After 3 months ageing, the T_g was reduced from 13.6 °C to -28.7 °C and -16.5 °C for anhydrous and hydrated ethanol, respectively. The T_g reduction is attributed to the partial hydrolysis caused by the presence of water in the fluids, although this reaction is more drastic at temperatures higher than 80 °C[24], as well as a possible plasticizing effect exercised by ethanol absorbed and accommodated inside of the free volume of the polymeric chains of the PA-11 amorphous phase.

In Figures 5 and 6, the *E'* values of the PEEK and PA-11 are shown, respectively. The *E'* of the PEEK is basically constant as a function of the ageing time, ranging between 3.6 - 3.7 GPa. The PA-11, on the other hand, had a stronger reduction of its storage elastic modulus as a function of the ageing time, in both type of alcohols. At 60 °C, the *E*' of the PA-11 was reduced by 37.8% and 8.6% after ageing for 1 month, and after 3 months, the reductions were 50.1% and 43.2% for anhydrous and hydrated ethanol, respectively. It is interesting to note that, although the amount of water in the anhydrous ethanol was only 0.7%, this fluid was more aggressive to PA-11. Polyamides are known to suffer hydrolysis at critical temperatures[24], and this reaction happens even in the presence of very small amounts of water. Therefore, a similar behavior in both fluids was expected if hydrolysis was the main ageing mechanism. The results indicate that although hydrolysis may occur, the ethanol is also harmful to the material and contributes to the ageing mechanism. It is also believed that the plasticizer is extracted by a migration/diffusion process, and simultaneously, the material swells through the absorption of ethanol. This culminates in an increase in the total free volume, leading to an increase in the chain mobility, resulting in easier movement of the chains and lowering the T_g and storage modulus of the aged materials relative to the unaged. This hypothesis was well supported through of an evaluation of the degree of swelling of the PA-11, which can be found in subsection 3.4.

3.2. *Crystallinity*

The diffractograms of the PEEK and PA-11 unaged and aged in anhydrous and hydrated ethanol at temperature of 60 °C for 1 and 3 months are supplied as Supplementary material (Appendix A). In these diffractograms, PEEK presents four main crystalline peaks at 2θ = 18.7°, 20.8°, 22.5° and 28.7°, which, according to Nguyen and Ishida[11] and Lai et al.[37] correspond to the crystalline planes (110), (111), (200) and (211) of an orthorhombic unit cell. The PA-11 diffractogram presents major peaks at 2θ = 7.3°, 19.9° and 23.0°, characteristic of the (001), (100) and (010, 110) planes, respectively, of a triclinic unit cell, as proposed by Chaupart and Serpe[23], Jolly et al.[38] and Zhang et al.[39].

Table 1 shows the PEEK and PA-11 degrees of crystallinity for the unaged polymers, the polymers aged for 1 and 3 months in anhydrous and hydrated ethanol at 60 and 23 °C, and the polymers aged in hot-air (60 °C). X_c values obtained from the PEEK and PA-11 diffractograms were compared with the values obtained from DSC (thermograms not shown). The enthalpy of fusion (ΔH_f) of the first heating curve for each test conducted was considered.

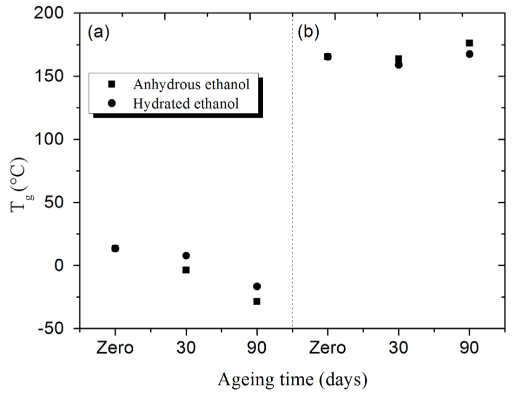

Figure 4. Variations of T_g of the PA-11 (a) and PEEK (b) unaged and aged in anhydrous and hydrated ethanol at 60 °C.

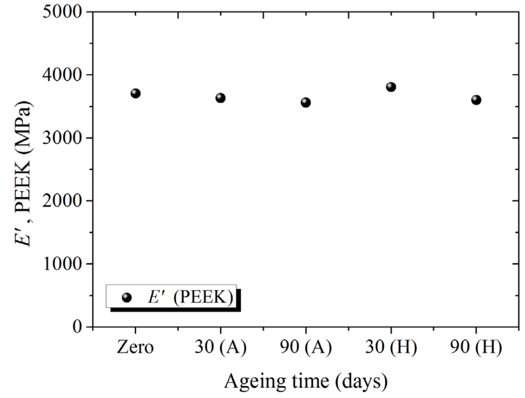

Figure 5. Variations of the storage modulus (*E'*) of the PEEK unaged and aged in anhydrous (A) and hydrated (H) ethanol at 60 °C.

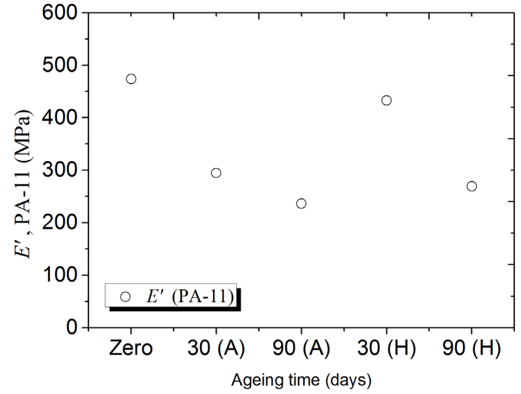

Figure 6. Variations of the storage modulus (*E'*) of the PA-11 unaged and aged in anhydrous (A) and hydrated (H) ethanol at 60 °C.

Although the results of WAXD were not conclusive about the changes in the degree of crystallinity of the aged PEEK (lack of a well-defined tendency of X_c), it can be noted that the mostly of the aged samples had a slight reduction in their X_c values relative to the unaged PEEK, in both temperatures evaluated, as shown in Table 1. Meanwhile, the DSC results for the unaged PEEK showed a crystallinity

Table 1. Degrees of crystallinity (X_c) of the PEEK and PA-11 obtained from X-ray diffractograms compared with X_c values obtained from DSC (curves of the 1st heating scan).

Material	Experimental conditions	Ageing time	X_c (%) - WAXD	ΔH_f (J/g^{-1})	X_c (%) - DSC
PEEK	Unaged	Zero	35.6	38.5	29.6
	Anhydrous	1 month	(32.2)$^{(a)}$(33.2)$^{(b)}$	(37.1)$^{(a)}$(34.2)$^{(b)}$	(28.5)$^{(a)}$(26.3)$^{(b)}$
	Anhydrous	3 months	(35.6)$^{(a)}$(33.6)$^{(b)}$	(35.9)$^{(a)}$(35.7)$^{(b)}$	(27.6)$^{(a)}$(27.0)$^{(b)}$
	Hydrated	1 month	(35.1)$^{(a)}$(34.7)$^{(b)}$	(35.8)$^{(a)}$(33.6)$^{(b)}$	(27.5)$^{(a)}$(26.0)$^{(b)}$
	Hydrated	3 months	(32.3)$^{(a)}$(33.9)$^{(b)}$	(34.7)$^{(a)}$(32.6)$^{(b)}$	(26.7)$^{(a)}$(25.0)$^{(b)}$
	Hot-air	1 month	(35.0)$^{(c)}$	(38.1)$^{(c)}$	(29.3)$^{(c)}$
	Hot-air	3 months	(35.3)$^{(c)}$	(37.5)$^{(c)}$	(28.8)$^{(c)}$
Material	**Experimental conditions**	**Ageing time**	**X_c (%) - WAXD**	**ΔH_f (J/g^{-1})**	**X_c (%) - DSC**
PA-11	Unaged	Zero	23.5	36.2	16.0
	Anhydrous	1 month	(24.3)$^{(a)}$(25.8)$^{(b)}$	(52.7)$^{(a)}$(47.2)$^{(b)}$	(23.3)$^{(a)}$(20.9)$^{(b)}$
	Anhydrous	3 months	(25.6)$^{(a)}$(26.8)$^{(b)}$	(49.5)$^{(a)}$(47.6)$^{(b)}$	(21.9)$^{(a)}$(21.1)$^{(b)}$
	Hydrated	1 month	(26.0)$^{(a)}$(25.7)$^{(b)}$	(48.2)$^{(a)}$(47.0)$^{(b)}$	(21.3)$^{(a)}$(20.8)$^{(b)}$
	Hydrated	3 months	(26.2)$^{(a)}$(24.7)$^{(b)}$	(48.1)$^{(a)}$(48.3)$^{(b)}$	(21.3)$^{(a)}$(21.4)$^{(b)}$
	Hot-air	1 month	(29.8)$^{(c)}$	(41.1)$^{(c)}$	(18.2)$^{(c)}$
	Hot-air	3 months	(29.1)$^{(c)}$	(49.7)$^{(c)}$	(21.9)$^{(c)}$

Materials ageing conditions: $^{(a)}$ Ethanol fuel at 60 °C. $^{(b)}$ Ethanol fuel at 23 °C. $^{(c)}$ Hot-air (60 °C).

of approximately 29% and a melting point (T_m) of 339.7 °C, whereas the materials aged at 60 °C presented crystallinity reductions of approximately 3.7% and 7.1% for PEEK aged over 1 month in anhydrous and hydrated ethanol, respectively. When PEEK was aged over 3 months in anhydrous and hydrated ethanol, the X_c reductions were 6.7% and 9.8%, respectively. Taken together, the DSC and WAXD results suggest a plasticizing effect of the ethanol on the PEEK, which might have been the cause of the crystallinity reduction in both types of ethanol. Nevertheless, only slight changes in the T_m values were observed, as they remained in the range of 338-340 °C. This apparent crystallinity reduction can explain an intensity reduction of the PEEK characteristic diffraction peaks that sometimes occurred (shown in the Supplementary material) (Appendix A), although it did not cause any position change or the emergence of new peaks, indicating that the orthorhombic unit cell was preserved. When PEEK was aged at 23 °C under the same conditions, similar reductions of X_c were obtained. On the other hand, samples aged purely in hot-air (60 °C) did not show significant changes in X_c and T_m, indicating that the changes observed are due to the ethanol and not to temperature alone.

Unaged PA-11 presented a low crystallinity value (approximately 16%, as measured by DSC) (Table 1), which is related to the presence of plasticizers in its polymer chain and the employed processing technique (compression molding)[23,25]. In the unaged condition, the complete fusion of the PA-11 occurred at T_m = 180.8 °C. The crystallinity modification observed for PA-11 caused by ageing was opposite to that of PEEK, i.e., PA-11 experienced an increase in the degree of crystallinity in the samples aged in anhydrous and hydrated ethanol at 60 and 23 °C compared to the unaged material (Table 1). The X_c increases in the materials aged for 1 month at 60 and 23 °C, as obtained from DSC, were approximately 45.6% and 30.6% (in anhydrous ethanol) and 33.1% and 30.0% (in hydrated ethanol), respectively. In the material aged over 3 months in anhydrous and hydrated ethanol, the X_c increases were 36.8% and 31.9% (in anhydrous ethanol) and 33.1% and 33.7% (in hydrated ethanol), at ageing temperatures of 60 and 23 °C, respectively. In these cases, the T_m values remained in the range of 184-188 °C. DSC results showed that the X_c increases caused by ageing in ethanol were usually more intense at 60 °C than at 23 °C, indicating that the temperature affects the ageing mechanism, although the fluid alone also changes the material crystallinity. For the thermal ageing experiments, it was also observed an X_c increase, as showed by results from DSC and WAXD. The PA-11 samples aged at 60 °C showed crystallinity increase from DSC of 13.7% and 36.9% after 1 and 3 months, respectively. Because the ageing temperature is higher than T_g (13.6 °C, as shown in Figure 3), the process was similar to an annealing treatment, favoring the rearrangement of the amorphous phase chains, thus contributing to crystal growth and additional crystallization. Therefore, the PA-11 is susceptible to both, fluid and temperature effects.

Because the grade of PA-11 used in the present study contains plasticizers[23,25], two simultaneous processes with different kinetics seem to be operating during ageing, the removal of the plasticizer to the environment and anhydrous and hydrated ethanol absorption by the polymer. The removal of the plasticizer was confirmed by thermogravimetric analyses, shown below, and the absorption of fluid was confirmed by a volume variation evaluation (see subsection 3.4). The swelling of the material by fluid absorption and its interaction with the polymer structure caused changes in the crystallinity even at room temperature because the T_g is below 23 °C. When the temperature was raised to 60 °C, the effect was even more accentuated, resulting in a material with greater crystallinity degree.

Hydrolysis could also cause an increase in crystallinity but was not considered the main cause in this process due to the low temperature employed and because the effect of the anhydrous ethanol was more drastic than that of the hydrated. Nevertheless, despite the low ageing temperature (60°C), even a minor percentage of hydrolysis occurred may have led to decreases in the molar mass of PA-11, and thus, contributing to X_c increases verified.

3.3. TGA measurements

The thermal scans of the PEEK and PA-11 were carried out to evaluate the thermal stability of the polymers. For PA-11, the goal was to analyze the main polymer chain degradation, as well as the loss of plasticizer. To this end, the initial plasticizer content and the remaining amount after ageing in anhydrous and hydrated ethanol at 1 and 3 months were quantified by TGA analysis.

As shown in Figure 7a, this grade of PEEK does not contain plasticizer and has a high thermal stability, which is attributed to the strong stability of the aromatic backbone, as discussed in the work of Patel et al.[15]. It can be seen in the thermograms of the Figure 7a that the main chain decomposition of the PEEK occurred in only one step, with maximum degradation temperature (T_d) of approximately 590 °C. A weight loss of 23% was observed at this temperature, resulting in the volatilization of approximately 45-50% of the polymer mass. The remaining polymer mass is supposed to be carbonaceous char. The behavior was similar in aged and unaged materials, suggesting no significant changes in thermal stability.

Figure 7b shows that the decomposition of the PA-11 occurred in two main steps, with important differences in the thermal stability of the aged and unaged materials. It can be noted that the first weight loss step of the unaged PA-11 occurred at approximately 232 °C with a 6.7% mass loss. Based on the literature[25,40,41], this decomposition temperature is compatible with the *N*-butyl-benzenesulfonamide (BBSA) plasticizer usually found in the composition of the PA-11. After the ageing in ethanol at 60 °C, the peaks decomposition temperature of the supposed plasticizer decreases to 182 °C (mass loss of 3.5% after 1 month in anhydrous ethanol), 189 °C (mass loss of 5.8% after 1 month in hydrated ethanol), 192 °C (mass loss of 5.3% after 3 months in anhydrous ethanol) and 189 °C (mass loss of 2.9% after 3 months in hydrated ethanol). This result confirmed the presence of the plasticizer in this PA-11 composition and its loss during the ageing process.

However, an opposite comportment occurred in the thermal stability of the second step degradation, corresponding to the degradation of the main chain of the PA-11, where the

Table 2. Elastic modulus (E_y) and yield stress (σ_y) of the PEEK and PA-11 obtained from tensile tests.

Sample	Ethanol (60 ºC)	Ageing time (days)	E_y (GPa)	Yield stress (σ_y) (MPa)
PEEK	Unaged	Zero	3.44 ± 0.17 (4.94)	97.55 ± 0.35 (0.36)
	Anhydrous	30	3.40 ± 0.07 (2.06)	97.94 ± 0.37 (0.38)
	Anhydrous	90	3.49 ± 0.08 (2.29)	97.41 ± 0.57 (0.58)
	Hydrated	30	3.35 ± 0.06 (1.79)	95.05 ± 0.75 (0.79)
	Hydrated	90	3.46 ± 0.07 (2.02)	95.27 ± 0.19 (0.20)
Sample	**Ethanol (60 ºC)**	**Ageing time (days)**	**E_y (MPa)**	**Yield stress (σ_y) (MPa)**
PA-11	Unaged	Zero	380.93 ± 2.44 (0.64)	10.79 ± 0.46 (4.30)
	Anhydrous	30	180.97 ± 2.31 (1.28)	8.44 ± 0.14 (1.66)
	Anhydrous	90	151.38 ± 0.77 (0.51)	8.30 ± 0.19 (2.29)
	Hydrated	30	193.78 ± 2.48 (1.28)	8.75 ± 0.56 (6.40)
	Hydrated	90	171.93 ± 3.06 (1.78)	8.04 ± 0.67 (8.33)

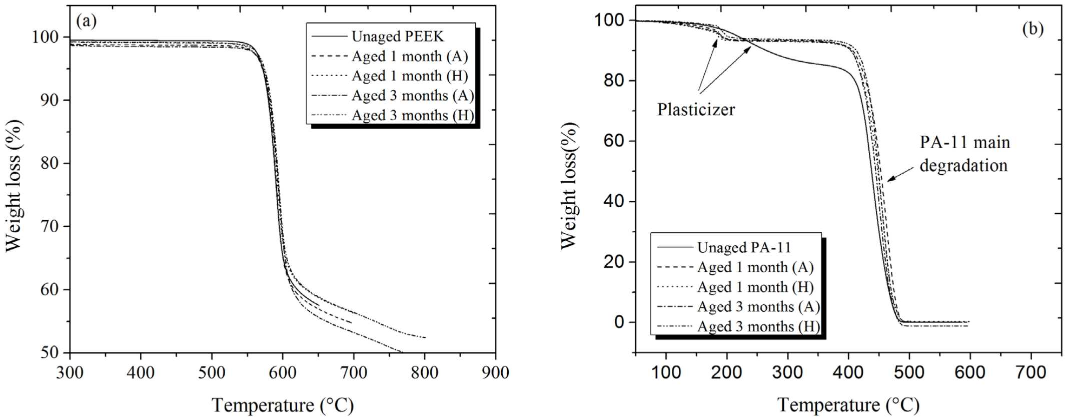

Figure 7. TGA thermograms of the PEEK (a) and PA-11 (b) unaged and aged in anhydrous (A) and hydrated (H) ethanol at 60 °C for 1 and 3 months.

degradation temperature at this step increased as a function of the ageing time in anhydrous and hydrated ethanol at 60 °C. This is associated with the additional crystallization caused by the ageing, as discussed earlier in the WAXD and DSC analyses. Hence, the degradation temperature of the unaged PA-11 chain was 439 °C, and this value was increased to the range of 449-461 °C, corresponding to an increase of approximately 2-5% in the decomposition temperature of the aged samples. These results confirm the increases in the thermal stability of the main chain of the aged PA-11 relative to the unaged samples.

3.4. Mechanical properties from tensile tests

The uniaxial tensile curves of the PEEK and PA-11 are available in the Supplementary material (Appendix A). The tensile curves reveal high elastic modulus (E_y) and yield stress (σ_y) values for PEEK and no changes in these properties as a function of the ageing time at the established conditions. The PEEK elastic modulus was approximately 3.4 GPa, and it did not significantly change upon ageing for 1 or 3 months (Table 2), as confirmed by Student's t-tests. The elastic modulus and yield stress results confirms the high chemical and structural resistance of the PEEK to the ageing conditions employed. For PEEK at room temperature, Nguyen and Ishida[11] reported an elastic modulus of 4 GPa and a yield stress of 100 MPa, and similar values also were reported in the works of Lai et al.[37] and Myllari et al.[42]. This elevated structural stiffness observed for PEEK is typical of polymeric materials of the poly (aryl ether ketone) class. From the molecular point of view, PEEK is a polymer composed of a series of aromatic rings interspersed with two ether bonds (C-O-C) and a ketone bond (C=O), both of which are naturally strong bonds[15]. Furthermore, each pair of aromatic rings forms a bond angle of approximately 125°[43], giving the chain a preferential planar zig-zag configuration, which allows a high packing degree and a good ordering of the aromatic rings, providing high thermal stability and structural stiffness to this material, as previously verified. This structure was apparently not affected by the ethanol, suggesting again that there was no effective physicochemical interaction of the PEEK polymeric chains with the ethanol. Therefore, no changes in E_y occurred at the established ageing conditions. These results corroborated the storage modulus values (E') obtained previously from the DMTA analyses.

On the other hand, the analysis of the tensile curves of the PA-11 indicates a low elastic modulus value of approximately 380 MPa (shown in Table 2), as was also reported by Chaupart and Serpe[23]. This low value may be partially explained by the presence of the plasticizer in PA-11, which facilitates flow and reduces the material stiffness. It is also due to its own chemical structure, basically constituted by methylene groups in a flexible chain. When unaged and aged PA-11 are compared, a significant reduction of the elastic modulus is observed, reaching levels of 52.5% and 60.3% for the material aged in anhydrous ethanol for 1 and 3 months, respectively. When the PA-11 was aged in hydrated ethanol for 1 and 3 months, the reductions were 49.1% and 54.9%, respectively. In both cases, all elastic modulus mean values were significantly different in the aged materials relative to unaged PA-11, according to Student's t-tests. However, the observed PA-11 modulus reductions were not compatible with the crystallinity increases observed by the other characterization techniques (Table 1). This is attributed to the effect of the domain of the amorphous phase on the PA-11 mechanical properties, as previously explained. Additionally, the effect of hydrolysis, even in low percentage, may have affected the mechanical properties due to chain scission and consequent reduction of molecular weight, leading to elastic modulus reduction of the material. These hypotheses were corroborated below by the results of the yield stress and instrumented microindentation (subsection 3.5).

Similarly to the occurred for the elastic modulus, PEEK did not present a statistically significant difference, according to Student's t-tests between the yield stress of the unaged samples and those aged for 1 or 3 months in anhydrous ethanol, reaching a value about 97 MPa (Table 2). However, the yield stress of the materials aged for 1 and 3 months in hydrated ethanol was slightly lower than that of the unaged sample (Table 2). The reductions observed were 2.6% and 2.3% for the materials aged for 1 and 3 months, respectively. In this case, despite the low reduction, the statistical tests indicated a significant difference, suggesting that hydrated alcohol might have a plasticizing effect on the PEEK surface, as previously detected from WAXD and DSC analyses.

On the other hand, similar to the elastic modulus, the PA-11 yield stress had a significant reduction from approximately 11 MPa to values close to 8 MPa after 1 and 3 months ageing in both types of ethanol (Table 2). The yield stress reductions were 21.8% and 23.1%, respectively, in the materials aged for 1 and 3 months in anhydrous ethanol at 60 °C, and 18.9% and 25.5%, respectively in the materials aged for 1 and 3 months in hydrated ethanol at 60 °C. As occurred with the elastic modulus, the behavior of the yield stress is not consistent with the degree of crystallinity observed from WAXD and DSC (see Table 1). The main justifications follow below.

Table 3 presents the values of the PA-11 volume increase caused by polymer swelling during the ageing in the different alcohols at different exposure times. These measures were obtained by Archimedes' method, as described in the literature[44]. The volume increments observed after 90 and 60 days were similar to those obtained after 30 and 15 days (Table 3), indicating that after a few days

Table 3. Volume increases of the PA-11 aged in ethanol at 60°C as a function of the ageing time: [(a)] PA-11 specimens aged in anhydrous ethanol. [(b)] PA-11 specimens aged in hydrated ethanol.

Sample	Ageing time (days)	Volume increase (%)[(a)]	Volume increase (%)[(b)]
PA-11	15	7.17 ± 0.04 (0.56)	6.61 ± 0.03 (0.45)
	30	5.95 ± 0.02 (0.34)	6.43 ± 0.04 (0.62)
	60	6.03 ± 0.01 (0.16)	6.45 ± 0.02 (0.31)
	90	6.13 ± 0.04 (0.65)	5.24 ± 0.03 (0.57)

of ageing, the polymer has already absorbed a substantial volume of anhydrous and hydrated ethanol, and this amount is maintained approximately constant for longer immersion times (saturation). The oscillations are attributed to the process of plasticizer extraction happening simultaneously with fluid absorption. Therefore, although the crystallinity increases upon ageing (Table 1), the percentage change was not significant, and the general behavior of the mechanical properties was governed by the material's amorphous phase and corresponding swelling.

In addition, it is possible that the absorbed ethanol can be associated to PA-11 chains by hydrogen bonds, exerting a plasticizer effect, thus contributing to the elastic modulus and yield stress reductions. The hypotheses proposed so far are well corroborated with the instrumented microindentation results presented below.

3.5. Mechanical properties from instrumented microindentation tests

Microhardness can be defined as a measure of the resistance of a material to plastic deformation. Its quantification by microindentation strongly depends on several test parameters such as the type of indenter and polymer, loading and unloading rate, holding time, and maximum test load, among others[33-35]. Thus, different polymer chemical structures will have different mechanical responses, which are governed by the viscoelasticity of these materials. The instrumented Berkovich microhardness (referred from now on as μ-HB) and instrumented elastic modulus (E_{it}) of the materials were the main properties assessed. The μ-HB depends on the projected contact area of the indented region (A_p), at a specified load, whereas E_{it} is obtained from the instantaneous unloading curve and depends of the relationship with A_p and the measured unloading stiffness[33-35].

In the supplementary material (Appendix A) is available a diagram of the complete loading-holding-unloading cycle used in each indentation performed at maximum loads of 210, 310 and 410 mN. This procedure allowed assessing different indentation depths on the surface of the aged and unaged PEEK and PA-11 samples.

Figure 8 presents two graphs of the typical curves of applied load as a function of the indentation depth (h_{max}) using a 310 mN maximum load for PEEK (Figure 8a) and PA-11 (Figure 8b), considering both materials in the conditions unaged and aged for 1 and 3 months in anhydrous and hydrated ethanol at 60 °C. The same behavior was observed when the 210 and 410 mN maximum loads were applied, and therefore, these curves are not presented. The loading and unloading profiles of the curves in Figure 8a show that aged PEEK did not suffer significant modifications in the maximum depth reached by the indenter, which was approximately 0.8 x 10^4 nm for both, the unaged and aged materials.

The E_{it} values of the PEEK obtained on the unloading were practically the same, approximately 3.7 GPa. These E_{it} values were in agreement with those found by Lai et al.[37] and Molazemhosseini et al.[45]. On the other hand, Figure 8b shows an increase in the maximum indentation depth obtained at PA-11 aged for 1 and 3 months, in both types of alcohol at 60 °C. In this case, due to the significant amount of fluid absorbed by PA-11, the unaged material presented a h_{max} value of approximately 2.4 x 10^4 nm, which was increased to approximately 2.6 x 10^4 nm (for the samples aged for 1 month in anhydrous and hydrated ethanol) and 2.8 x 10^4 nm (for the samples aged for 3 months in anhydrous and hydrated ethanol). These increases in penetration depth represent expressive μ-HB and E_{it} reductions at the PA-11 samples aged at 60 °C, differently from what occurred at PEEK.

The instrumented elastic modulus of the PEEK and PA-11 obtained from micro-IITs as a function of the maximum load, ageing time and type of alcohol are shown in Figure 9. The E_{it} values of the PEEK and PA-11 aged at 60 °C in an oven is also included. It can be observed that the elastic modulus of the PEEK before and after 1 and 3 months ageing in anhydrous and hydrated ethanol again shows a value of approximately 3.7 GPa. The E_{it} values of unaged/aged material are in good agreement with the literature[37,45,46]. The comparisons of the elastic modulus of unaged and aged PEEK were performed by Student's t-tests, and no significant differences were observed between the

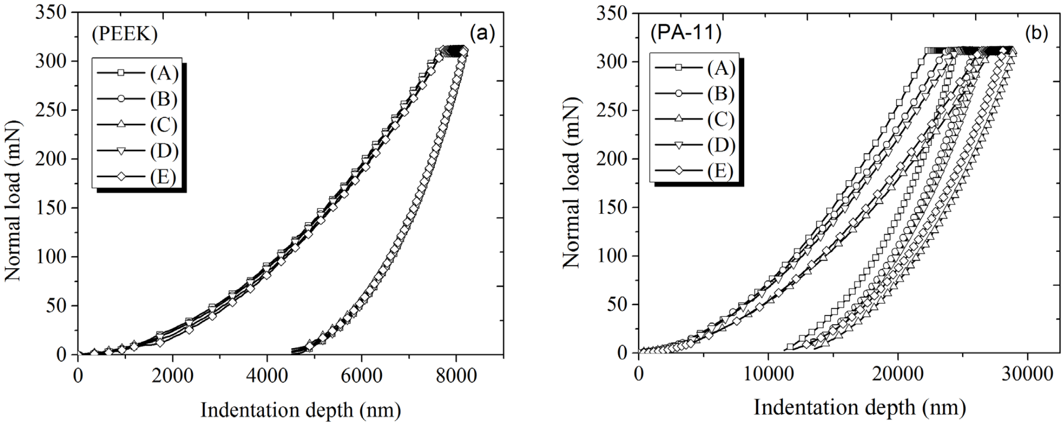

Figure 8. Loading-holding-unloading versus indentation depth at a load of 310 mN for PEEK (a) and PA-11 (b) as a function of the ageing time: unaged materials (A), and aged at 60 °C by 1 month in anhydrous ethanol (B), 3 months in anhydrous ethanol (C), 1 month in hydrated ethanol (D), and 3 months in hydrated ethanol (E).

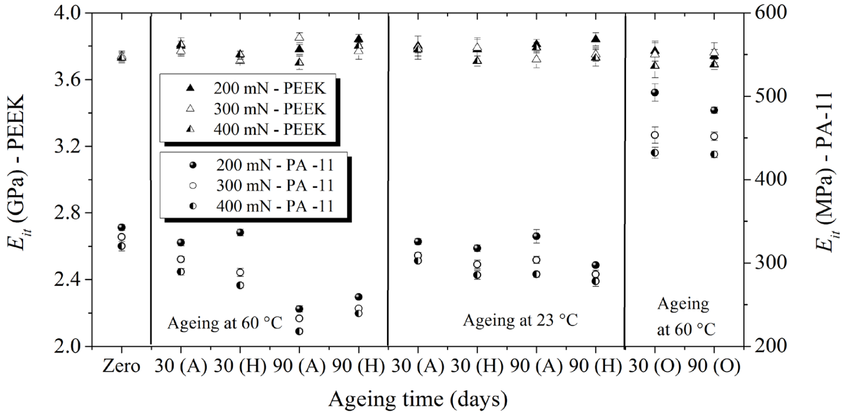

Figure 9. Behavior of the instrumented elastic modulus (E_{it}) from micro-IITs of the unaged and aged PEEK and PA-11 in anhydrous (A) and hydrated (H) ethanol, and post-annealing in oven with hot-air (O).

mean pairs compared. Similarly, the elastic modulus of the PEEK annealed at 60 °C showed a value of ~ 3.7 GPa. These results were very close to values of the modulus from DMTA and tensile tests, previously shown, again indicating the high chemical and structural resistance of the PEEK, as well as its excellent thermal stability. These results are also well correlated with the crystallinity values from Table 1 and proved that small changes in the X_c of the PEEK post-ageing in ethanol do not affect its mechanical properties.

On the other hand, the PA-11 E_{it} values presented significant reductions (as shown in Figure 9), which were confirmed by Student's t-tests. At 310 mN maximum load, the aged PA-11 at 60 °C shows E_{it} reductions from approximately 331 MPa to approximately 304 MPa (aged 1 month in anhydrous ethanol, equivalent to 8.1% reduction), 288 MPa (aged 1 month in hydrated ethanol, equivalent to 12.9% reduction), 233 MPa (aged 3 months in anhydrous ethanol, equivalent to 29.6% reduction) and 245 MPa (aged 3 months in hydrated ethanol, equivalent to 25.9% reduction). The modulus decrease was progressive with ageing time, which probably occurred because of the strong chemical interaction of the PA-11 with anhydrous and hydrated ethanol, leading to this polymer swelling (Table 3) and reduction of the mechanical properties caused by an increase of the total free volume of the polymer chains, as previously discussed. Additionally, some percentage of hydrolysis, related in subsections 3.1 and 3.2, may have occurred, thus contributing to this E_{it} reduction verified. These results of E_{it} also are in good agreement with the tensile and DMTA properties.

Figure 9 shows that such reduction gradients after 1 month ageing of the PA-11 in anhydrous and hydrated ethanol became yet more accentuated after 3 months ageing. For PA-11 aged in anhydrous and hydrated ethanol at 23 °C, there was also an elastic modulus reduction as a function of time, as shown in Figure 9, although not so marked as for ageing at 60 °C. It can be observed that the E_{it} values obtained from PA-11 ageing at 23 °C are located in a range intermediate between those obtained from unaged PA-11 and that aged in ethanol at 60 °C (see Figure 9). Hence, it can be perceived that the ageing temperature of 60 °C associated with ethanol directly influences the PA-11 ageing mechanism, strongly affecting its mechanical properties.

The effect of the fluid on the material can be perceived by comparing the modulus for the materials aged at 60 °C in ethanol and the material aged in the oven at the same temperature (Figure 9). After annealing, the PA-11 E_{it} value reached 453.3 MPa (increase of 36.9%) and 451.8 MPa (increase of 36.5%) for 1 and 3 months ageing, respectively, which can be attributed to the X_c increases (shown in Table 1), which are associated with crystal growth and additional amorphous phase crystallization. On the other hand, the PA-11 samples aged for 1 and 3 months in the fluid experienced significant E_{it} reductions, which are correlated with chain scion and swelling effects, previously explained.

The micro-IITs of the PA-11 with maximum loads of 210 and 410 mN showed the same tendency of reduction of the elastic modulus occurred in evaluation with 310 mN (Figure 9). In addition, it can be noted that the mechanical properties (E_{it} and μ-HB) were reduced with the maximum depth reached through the loads used in this test. This decay is due to the increase in the activation volume under the indenter. As reported by Oliveira et al.[47], the magnitude of the volume under the indenter is crucial on the measured values of the modulus. In a viscoelastic material, the beginning of the plastic deformation is the result of chain movements located in the amorphous region (higher free volume) and is constrained by the crystalline phase, which acts as the elastic part of the system. The amorphous phase is sensitive to localized shear stresses, and as suggested by Eyring theory[48], an increase in the applied stress causes a localized temperature built up reducing the local viscosity. The closer to the surface, the higher is the effect of constriction by the crystalline phase due to the smaller volume assessed.

The micro-IITs of the PEEK showed that the μ-HB values had only minor variations (similarly to occurred to E_{it}) remaining approximately 265 MPa before and after ageing (Figure 10). In this case, the Student's t-tests did not indicate significant variations. In few cases, the small differences observed were attributed to the plasticizing effect that ethanol might have caused on the PEEK surface layers, but without

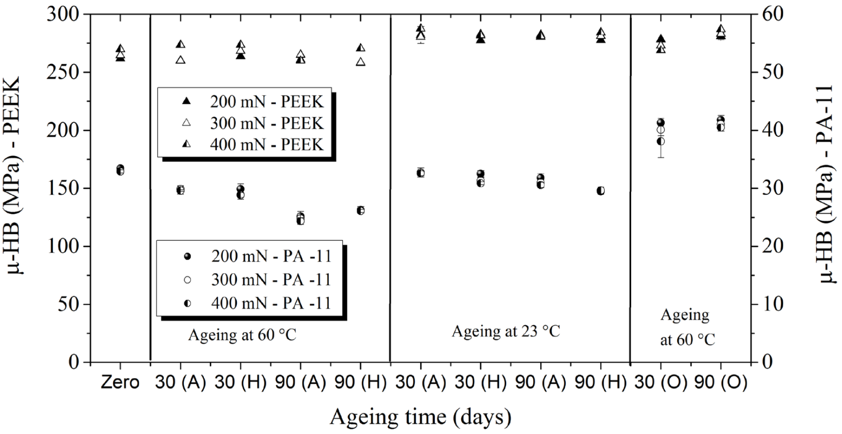

Figure 10. Behavior of the instrumented Berkovich microhardness (µ-HB) from micro-IITs of the unaged and aged PEEK and PA-11 in anhydrous (A) and hydrated (H) ethanol, and post-annealing in oven with hot-air (O).

a significant effect on the PEEK volumetric mechanical behavior as showed by tensile results. Comparative to the literature, the µ-HB values obtained are consistent with those reported by Molazemhosseini et al.[45] and Ji et al.[46].

On the other hand, the µ-HB value of the unaged PA-11 was 32.9 MPa, which was reduced to approximately 29.8 MPa (reduction of 9.4%) and 28.8 MPa (reduction of 12.5%) for the materials aged for 1 month in anhydrous and hydrated ethanol at 60 °C, respectively. Meanwhile, the PA-11 aged for 3 months in anhydrous and hydrated ethanol at 60 °C showed µ-HB values of 24.7 MPa (reduction of 24.9%) and 26.1 MPa (reduction of 20.7%), respectively. In this case, the statistical analysis of Student's t-tests also showed significant differences among µ-HB values of the aged and unaged PA-11 samples. These reductions are correlated with chain scion and polymer swelling effects, previously mentioned.

As occurred in the analyses of the E_{it} of the PA-11 after ageing in ethanol at temperatures of 60 and 23 °C, its µ-HB values were distributed in a range of values between the µ-HB of unaged PA-11 and that aged in ethanol at 60 °C (Figure 10). In case of the PA-11 annealed at 60 °C, the µ-HB values showed increases of 24.3% (equivalent to 40.9 MPa) and 24.6% (equivalent to 41.0 MPa) for the samples annealed for 1 and 3 months, respectively. These increases are also well correlated with the X_c increases of Table 1, occurred due to crystal growth, as previously correlated, and explain the higher E_{it} values and again justify the effective influence of the environment on the mechanical properties of the aged PA-11.

4. Conclusions

PEEK showed good chemical resistance to ageing in anhydrous and hydrated ethanol and a mechanical, thermal and structural behavior apparently compatible with this fluid. WAXD and DSC results identified a small plasticizing effect of ethanol on the PEEK surface molecules, but apparently without affecting the volumetric physical-mechanical properties. The PEEK elastic modulus maintained values of approximately 3.4 and 3.7 GPa, obtained on the stress-strain and DMTA/micro-IITs, respectively. In general, the elastic modulus values obtained by these three methods were consistent for the PEEK and PA-11 polymers. The mechanical properties were also well correlated with the crystallinity degree development by samples of PEEK and PA-11 unaged and aged in ethanol (60 and 23 °C), as well as with those obtained from samples annealed at 60 °C. In view of these results, it is safe recommends the use of PEEK for ethanol fuel transport or storage.

PA-11, conversely, had a significant interaction with ethanol, leading to its swelling due to the fluid absorption by its amorphous phase. The final E_{it} and µ-HB of the PA-11 were predominantly governed by this amorphous phase. After the ageing in ethanol at 60 °C, a significant reduction of these mechanical properties was verified due to chemical effect, leading to loss of material performance. On the other hand, annealing purely at 60 °C caused significant increases in E_{it} and µ-HB due the crystallization of this amorphous phase. However, the influence of these X_c increase on the mechanical properties was suppressed by the effect of the swelling. Because of the sensitivity of the PA-11 to ethanol, it was concluded that the use of this polyamide grade in ethanol transport/storage structures at temperature of 60 °C is not indicated, though its application in this work was very helpful as a reference material for comparison with PEEK, indicating that test conditions, although very mild, can lead to important information on materials performance during the ageing evaluation of the both polymers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at home page of Materials Research Ibero-american Journal of Materials (http://www.materialsresearch.org.br).

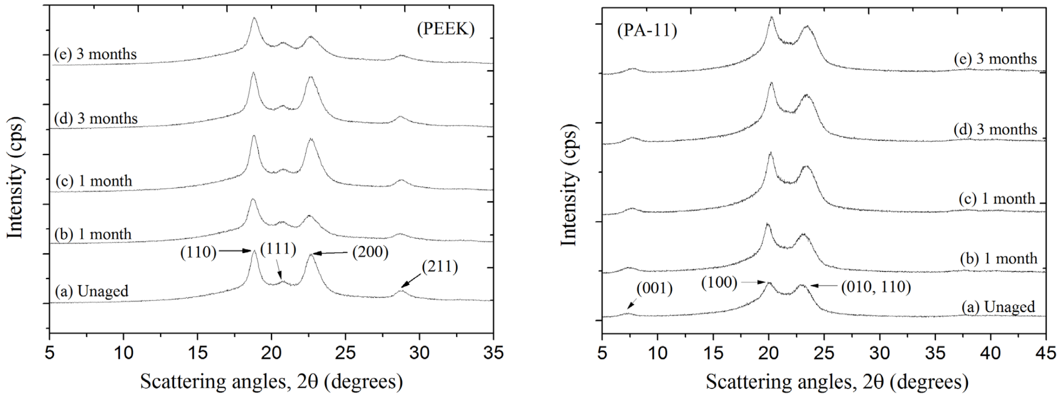

Figure 1A. X-ray diffractograms of the unaged PEEK and PA-11 (curves a) and aged at 60 °C for 1 month in anhydrous ethanol (curves b), 1 month in hydrated ethanol (curves c), 3 months in anhydrous ethanol (curves d), and 3 months in hydrated ethanol (curves e).

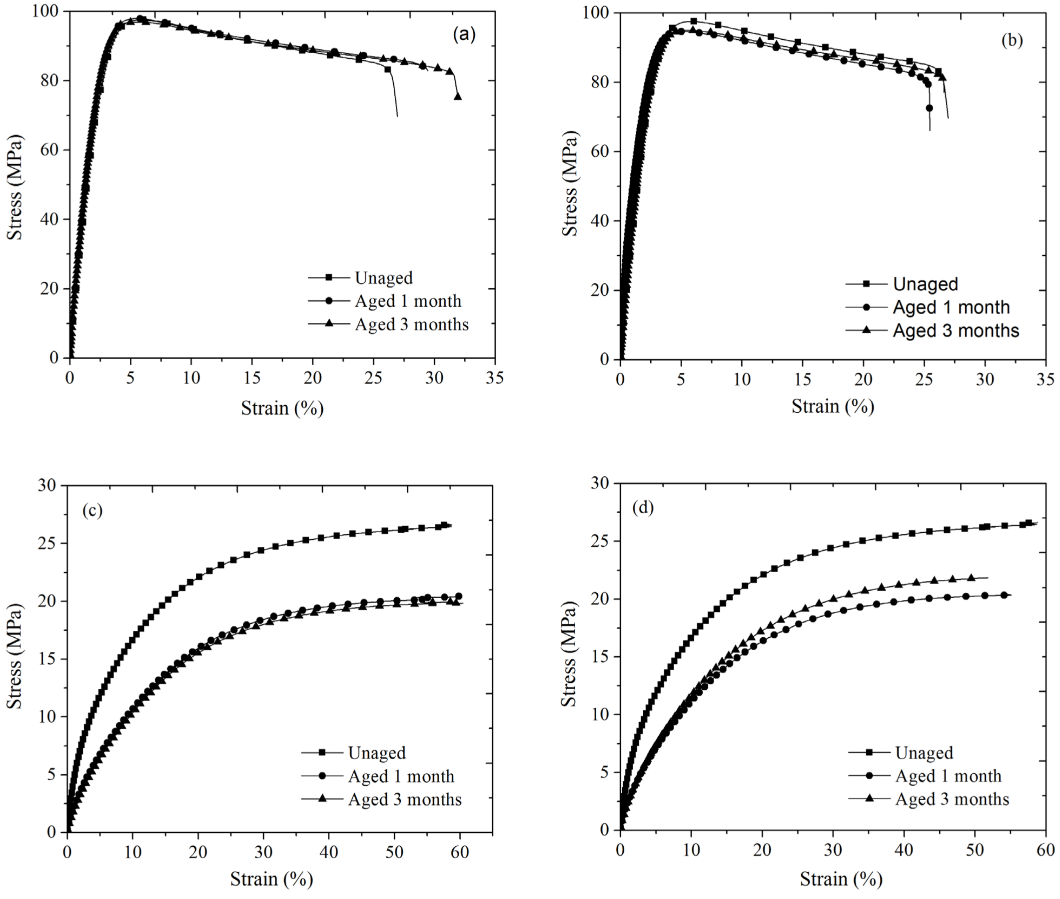

Figure 2A. Stress-strain curves of the polymers aged at 60 °C: a) PEEK in anhydrous ethanol, b) PEEK in hydrated ethanol, c) PA-11 in anhydrous ethanol, and d) PA-11 in hydrated ethanol.

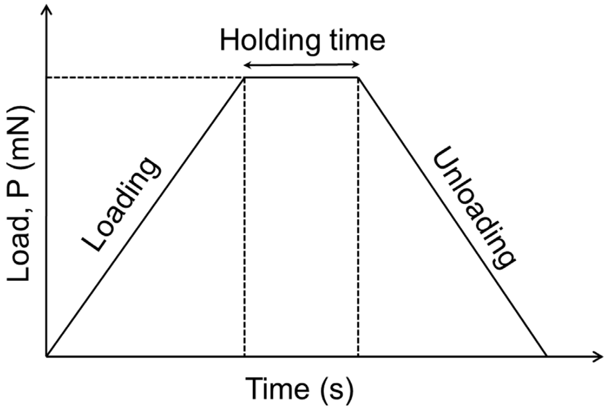

Figure 3A. General representation of a curve of load versus time with three segments during a complete loading-holding-unloading cycle.