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Influence of thermal aging on tensile and creep behavior of thermoplastic polyurethane

A. Boubakri [a,*], N. Haddar [a], K. Elleuch [a], Y. Bienvenu [b]

[a] Unité de recherche de chimie industrielle et matériaux, URCIM – ENIS, BP 1173-3038, Sfax, Tunisia
[b] Centre des matériaux P.M. Fourt, École des Mines de Paris, 91003 Evry cedex, France

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ABSTRACT

Changes in mechanical and physical properties of polyurethane thermoplastic during aging at 70 °C and 90 °C were investigated. The loss weight response was analyzed by gravimetric measurements under these temperatures. Changes in appearance and morphology of TPU after thermal aging were revealed by optical microscopy. The prolongation of the thermal exposure time, up to 270 days, leads to a progressive increase in tensile strength. In fact, elastic modulus and stress at 200% of strain were increased with thermal exposure time. These results can be explained by the increase of thermal stability due to the increase of material rigidity and the decrease in chain mobility. The evolution of the mechanical properties from tensile tests seems to be well correlated to the creep behavior. Finally, Scanning Electron Microscopy (SEM) revealed the modification of TPU morphology fracture surface after thermal aging.

1. Introduction

Thermoplastic elastomers (TPEs) are extensively applied as an anti-vibration material in machinery, transportation and construction. They have replaced vulcanized rubber because of their favourable mechanical properties and recyclability [1]. One advantage of these polymers is that they can be processed by conventional thermoplastic processes such as extrusion and injection molding. The properties of TPEs are similar to vulcanized rubber, e.g., softness, flexibility, extensibility, and resilience [1,2]. Polyurethane thermoplastic is one of the most useful commercial classes of these polymers which are widely used in both industry and in everyday life. It can be used in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, as well as in many biomedical applications [3,4]. In fact, as those materials are subjected to (i) environmental stresses such as high and/or low temperatures, UV exposure, saline atmosphere, moisture/water attack, presence of micro organisms and (ii) long term mechanical stresses.

Different mechanisms may occur simultaneously according to the severity of the exposure conditions and led to a decrease in the polymer durability: (i) physical aging inducing mechanical degradation including plasticization swelling and release of internal stresses, (ii) chemical aging inducing an irreversible chemical degradation such as hydrolysis.

The knowledge of the ultimate stability of polyurethanes after thermal, oxidative and photochemical exposure as well as of methods for properly evaluating the material thus appears to be of great significance. However, their use in a variety of conditions such as aggressive elements (higher temperature) can enormously affects their durability. Several studies were adopted an accelerated thermal aging at higher temperatures [5–7], but this method was criticized by many authors [8,9]. The latter have shown that when the aging temperature is near or even superior than transition temperature (T_g), there is

* Corresponding author.
E-mail address: boubakri_abid@yahoo.fr (A. Boubakri).

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not a linearity change of mechanism with the temperature. Patterson-Jones reported that insignificant mechanism at a given temperature can become very influencing at another temperature [10]. This finding can leads to the complexity of thermal deterioration mechanisms. Gravimetric measurements can give some data to explain certain changes in behavior of this material [11]. Similarly, in order to characterize the evolution of the mechanical properties, tensile tests were usually adopted. Generally, an increase in bulk properties (tensile strength and the elastic modulus) and a decrease of elongation at break were found. In fact, the effect of thermal aging on the behavior of some polymeric materials (polyethylene, polypropylene, etc.) was extensively studied [12–20]. To the author's knowledge, the literature dealing with the study of the influence of thermal aging on mechanical properties of TPU is not voluminous [11,21,22].

The main objective of this work is to present durability evaluation of such TPU under accelerated thermal aging. For this purpose, two temperatures were adopted (70 °C and 90 °C) to check its applicability as a heat resistant material at elevated service temperatures. This can give us an idea of the service temperature range where it can be used in practical purpose without any appreciable loss of properties. Results were substantiated by gravimetric measurements. In order to study effects of thermal aging on mechanical properties of TPU, tensile and creep tests were carried out. Also, SEM studies were retained to expertise the fracture behavior of TPU samples.

2. Experimental procedures

2.1. Materials

The material used in this study was a polycaprolactone copolyester based on thermoplastic polyurethane (translucent and colorless pellets) delivered by the MERQUINSA company under the reference D11T92EM. The main characteristics of the retained material were already described in our previous works [23,24]. This material was obtained by injection molding process. Before injection, the polyurethane pellets were dried in ovens for 2 h at a temperature of 110 °C.

2.2. Accelerated aging experiments

In order to evaluate the durability of the used TPU, an accelerated thermal aging procedure, that simulates severe conditions for climatic aging, was adopted. Samples were isothermally aged for over 270 days at two temperatures (70 °C and 90 °C). The choice of these temperatures is essentially justified by the simulation of severe aging conditions where the service temperature can reach 90 °C. After heating and at a given aged time, samples were removed, cooled in a desiccator to avoid the humidity absorption and immediately experiments were carried out.

2.3. Tests

2.3.1. Gravimetric measurements

The weight loss variation of the samples was recorded versus aging duration. Before aging, samples were dried for 48 hours at 70 °C in order to remove the moisture absorption during storage. The initial weights of specimens were carried out. During aging, samples were periodically removed, cooled in a desiccator and reweighed to measure the weight loss ratio. An electronic balance with 0.1 mg accuracy was used for this purpose.

The weight loss ratio of the sample is achieved as below:

$$M_t(\%) = \frac{W_0 - W_t}{W_0} \times 100$$

where W_0 is the initial sample weight and W_t is the sample weight at a given aged time t.

2.3.2. Tensile testing

The uniaxial tensile tests were conducted using an LLOYD universal testing machine at a constant cross-head speed of 10 mm min^{-1} and at room temperature. The dimensions of tensile test samples were taken according to the NF ISO 527-2 standard [24]. The tests were carried out to show the effect of the aging environment on the mechanical properties of TPU. Young modulus and stress at 200% of strain were determined. The results represented the average of three experiments. The range of variation in the Young modulus and stress at 200% of strain measurements was, respectively, less than 5% and 7%.

2.3.3. Creep testing

In order to understand the effect of thermal aging on the viscoelastic response of TPU, creep tests were performed. All tests were carried out at room temperature. Creep tests were performed using INSTRON 5844 machine equipped with 2kN cell capacity with an imposed stress of 4 MPa.

2.3.4. Surface morphology study

Morphology analysis of TPU fracture surfaces at different conditions was carried out by means of a ZEISS DSM 982 GEMINI scanning electron microscope. The sample surfaces were sputtered with an Au–Pd coating (3 μm) before examination. A 5 kV voltage was employed to image surface features.

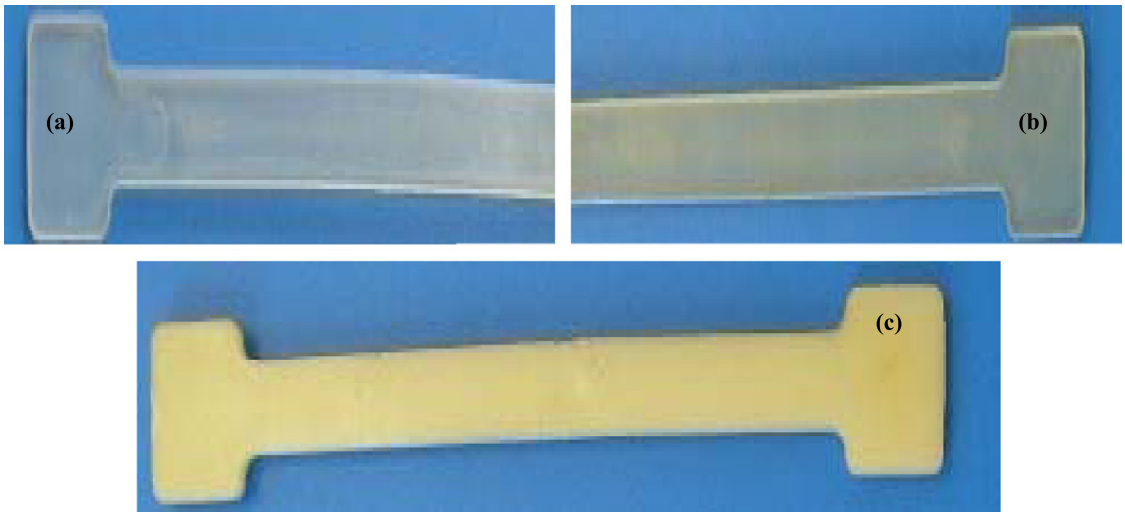

Fig. 1. Color modifications of thermal aging TPU versus temperature: (a) unaged sample, (b) aged TPU after 1 month at 70 °C, (c) aged TPU after 1 month at 90 °C. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Sample discoloration

An optical microscopy photographs were realized in order to determine whether the exposure duration has an effect on the appearance of the tested material. Fig. 1 shows the color variation against temperature of unaged and aged samples. As it can be observed, a change of the samples color from colorless to yellow was noticed during thermal aging. In fact, the color density of the tested samples increases gradually with the temperature. This color shifting can be ascribed to oxidation reactions which lead to the formation of an oxidized layer on the polymer surface. These observations are in good agreement with those found in the literature [25–27]. Flandrin et al. have observed, during thermal aging of polyurethane, that the samples progressively changed color turning from pale yellow to dark brown. This is generally observed when using aromatic isocyanates [28]. Therefore, the yellowing of urethane polymers under UV irradiation was due to oxidation of free-NH_2 groups formed by the photolysis of the urethane groups [29].

3.2. Gravimetric measurements

The gravimetric measurements response is shown in Fig. 2, where the percentage of mass loss is plotted against the aging duration. As it can be seen, both samples TPU aged at 70 °C and 90 °C present approximately the similar tendencies. However the mass loss of aged TPU is higher at 90 °C than 70 °C. Indeed, we can clearly discern two domains:

- first domain: at short aging time, curves show a linear relationship between mass loss rate and aging duration. For the thermal aging at 90 °C, the mass loss after 284 h reaches 0.25%. This behavior corresponds to desorption of the residual water in the material. Considering the initial desorption before aging (drying 48 hours at 70 °C), the water quantity represents approximately 0.71%. The linearity with the duration time is generally associated to a diffusion phenomenon;
- second domain: at long aging time, a relatively deviation corresponds to a drop of mass loss. This change indicates the beginning of volatile matter (plasticizer or products can come from an oxidization due to thermal deterioration process). From Fig. 2, we discern a significant difference of the mass loss between samples aged at 70 °C and 90 °C. In fact, after 2000 hours of aging, the mass loss is about 0.15% and 0.3% at 70 °C and 90 °C, respectively. Marais et al. [27] have shown that it is possible to give explanation of this behavior through three processes:
  - loss of volatile matter (water molecules);
  - oxidization in surface which is accompanied by samples discoloration;
  - loss of molecules due to chain scissions.

The obtained results in terms of mass loss are in accordance with those obtained by Sanchis et al. [30]. They have found that the weight loss of polyurethane film aged in certain condition shows a linear tendency with aging duration and the calculated weight loss rate is about 4.7 $\mu g\,cm^{-2}\,min^{-1}$, which is considerably lower than other polymeric materials subjected to similar conditions. They related this finding to the segmented polyurethane structure.

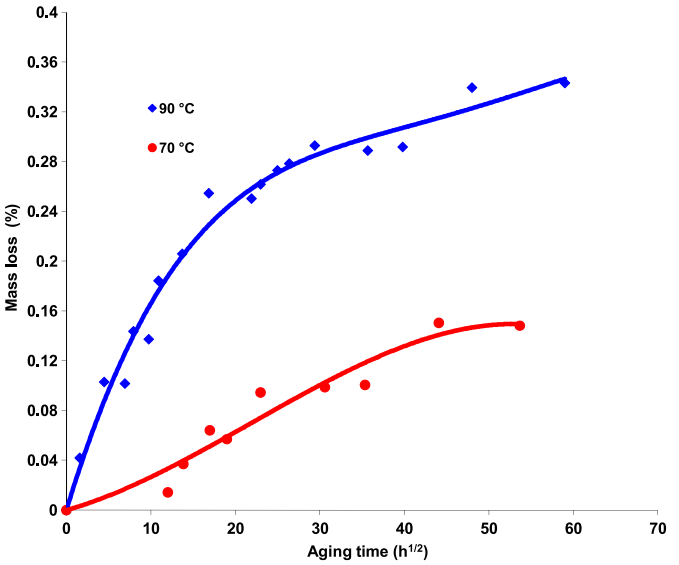

Fig. 2. Evolution of mass loss (%) of aged TPU at 70 °C and 90 °C.

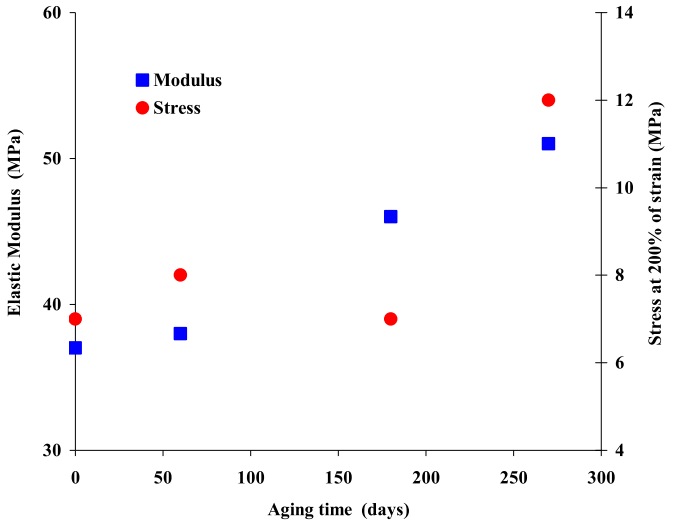

Fig. 3. Variation of elastic modulus and stress at 200% of strain versus aging duration at 70 °C.

3.3. Tensile behavior

In order to know the effect of thermal aging on mechanical behavior of TPU, tensile tests were conducted. The obtained results were plotted in Figs. 3 and 4. These figures display the variation of elastic modulus and stress at 200% of strain versus aging duration at 70 °C and 90 °C, respectively, during 9 months. It can be noticed that mechanical properties increase vs aging duration. For example, at 270 days of thermal aging, the modulus reached 51 MPa at 70 °C compared to unaged (37 MPa). In the same way, the stress at 200% of strain was increased from 7 to 12 MPa. It can be seen from Figs. 3 and 4 that these curves revealed two parts: (i) part 1, short aging time ($\leqslant$ 6 months), presents a moderate improvement of elastic modulus and stress. This improvement of properties proves that the rigidity of the material comes from the loss of volatile matter (water molecules, plasticizer). This volatile matter is known to reduce the plasticity of material; (ii) part 2, long aging time (9 months), shows a significant modification of tensile strength. The increase of properties especially at this stage can be explained by oxidization reactions in polymer which causes a molecular recombination. The thermal aging leads to the formation of free radicals and therefore to an increase in the degree of network reticulation in TPU [31].

Many authors think that this recombination coupled with the molecular rearrangements lead to the formation of a chemical network thermally stable [10,31,32]. The stress–strain properties of polyurethane seem to be very sensitive to thermal aging: elongation at break decreased while tensile strength and initial modulus increased during exposure to heat, mainly due to crosslinking or chain scission, depending on the temperature range [28]. Mathew and De [33] have explained

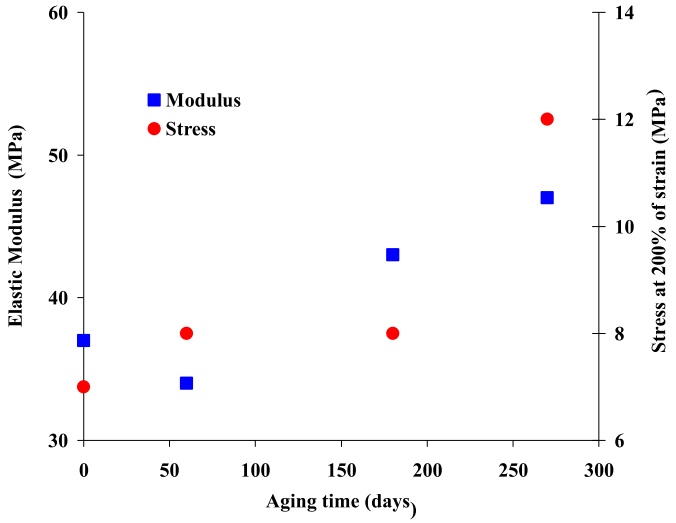

Fig. 4. Variation of elastic modulus and stress at 200% of strain versus aging duration at 90 °C.

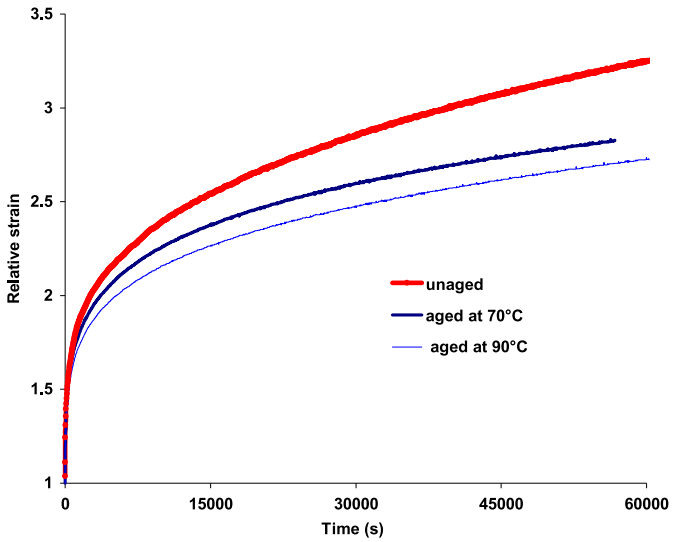

Fig. 5. Relative strain versus time of unaged and aged TPU after 3 months of thermal aging.

the initial increase in tensile strength, modulus and tear resistance during aging of natural rubber by an increase in crosslink density. However when the aging is continued for a longer period, the effect of main chain scission overshadows the effect of an increased crosslink density and as a result the decrease in mechanical properties. Similar finding were reported by Kalidaha and De [34]. They indicated that polychloroprene and its blends with ethylene–propylene–diene rubber become stiff after thermal aging.

From the overall results, it can be concluded that the aging process causes significant changes in mechanical properties. During the measurement period, the thermal aging leads to an enhancement of modulus and tensile stress of TPU.

3.4. Creep behavior

To better explain the observed mechanical modification of TPU, creep tests were equally carried out. Fig. 5 reveals the relative strain against time of unaged and aged TPU for aging duration of 3 months. According to this figure, the thermal aging affects the creep behavior. For example, at creep time of 45 000 s, the relative strain was shifted from 3, for unaged TPU, to 2.7 and 2.6 after 3 months of aging at 70 °C and 90 °C, respectively. The observed decrease of creep strain proves the increase in material rigidity. This finding is correlated with the results found by Vlasveld et al. [35]. They have shown that the reduce of creep compliance is related to the increased modulus. In their study, effect of environmental weathering on flexural creep behavior of long fiber-reinforced thermoplastic composites, Chevali et al. [36] have revealed that the creep compliances of UV-exposed NY66 LFT, decreased. They have shown that UV exposure caused changes in crystallinity due

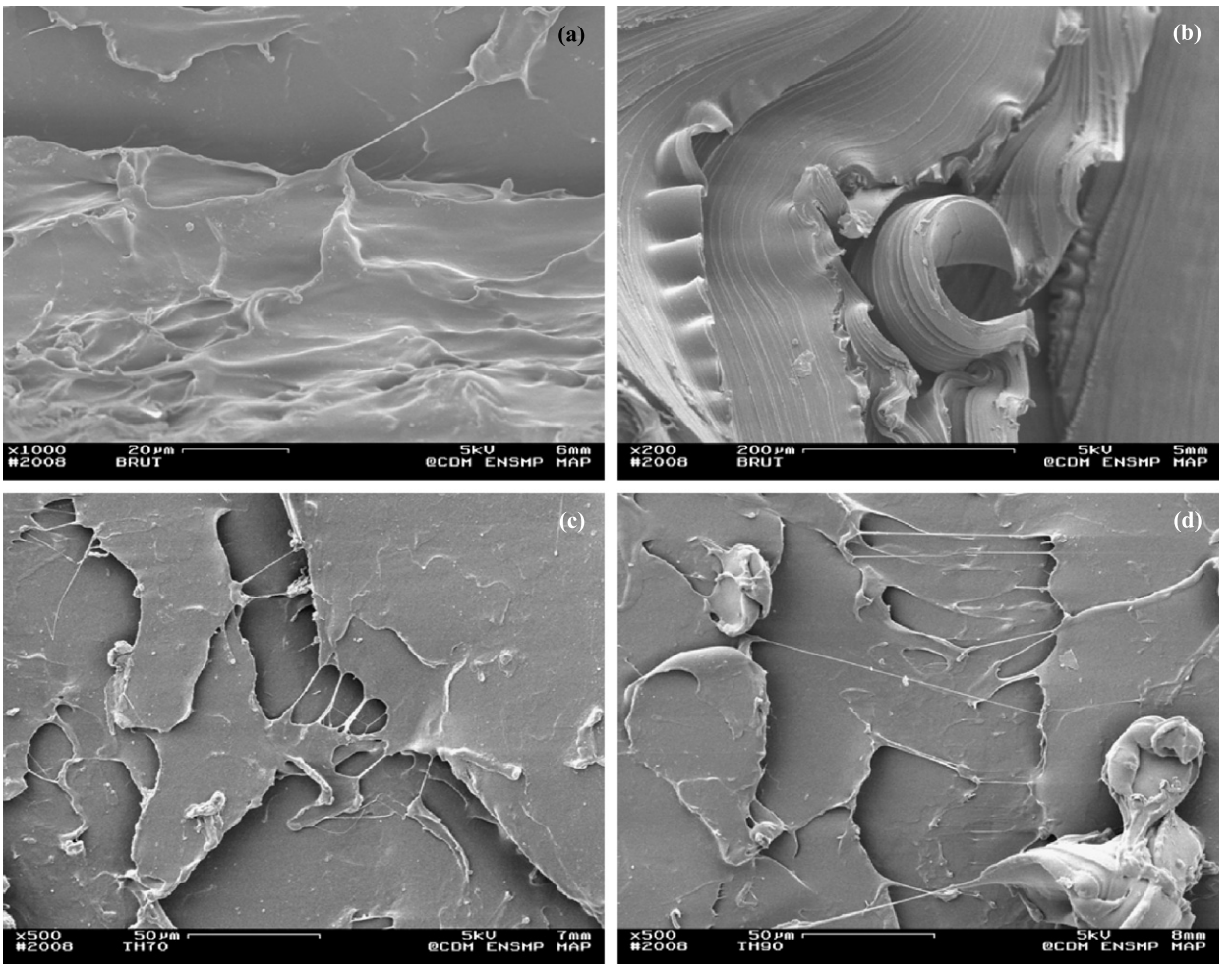

Fig. 6. SEM micrographs of fracture surfaces for TPU material. (a), (b) unaged samples, (c) aged at 70 °C for 3 months, (d) aged at 90 °C for 3 months.

to low oxidation rates and crystallization at the glass fiber interface, and have been reported to cause local resistance to reduce polymeric segmental motion and consequent decrease in deformation. The decrease in the value of creep strain rate with increasing aging time of polyvinylchloride has been explained by the formation of macro-radicals during thermal degradation [37]. Also, Papanicolaou et al. [38] have found that strain response decreased as the number of thermal cycles increased, when studying the effect of thermal shock cycling on the creep behavior of certain composites. Recently, Dean [39] has shown that, the variation of creep behaviour can be attributed to the decrease of the molecular mobility governed by molecular rearrangements.

The observed stiffness in creep tests is in agreement with the tensile response previously founded. Nevertheless, comparing the results at 70 °C and 90 °C, they seem to be similar for tensile strength (Figs. 3 and 4) and different for creep (Fig. 5). The difference, at 45 000 s, is about 3.7%. This dissimilarity can be explained by the viscoelastic behavior of TPU. It is well known that the viscoelastic properties of polymer are significantly influenced by a physical aging process [40]. For this reason the difference in term of creep results is more significant compared to tensile one. Also, it depends on the loading speed. The tensile tests are achieved after about 2000 s with loading speed of 10 mm min^{-1} contrary to the creep tests, which are often achieved during a long time superior than 50 000 s.

3.5. Scanning electron microscopy analysis

In order to confirm the mechanical modifications previously discerned, microscopic observations of the studied materials have been investigated using scanning electron microscopy (SEM). SEM micrographs of fractured surfaces from tensile tests of unaged and aged TPU were depicted in Fig. 6. Apparently, the fracture surface of the unaged TPU samples (Figs. 6a and 6b) was relatively ductile compared with the other samples (Figs. 6c and 6d). Figs. 6a and 6b show a rough surface followed by sinusoidal foldings. These sinusoidal foldings are indicative of high plastic deformation prior to fracture [41]. In addition to the wavy crests, fibrils and oriented bundles of the materials are discernible. All these features are characteristic of ductile

failure. The fracture surfaces of aged TPU at 70 °C and 90 °C for 90 days (Figs. 6c and 6d) show a dramatic change in the fracture topography. The areas show a tufted texture and a rough surface with a broad fracture path accompanied by several tear lines. The sinusoidal foldings are absent in theses micrographs. So it can be deduced that the mentioned modification in fractures surface morphology may be ascribed to the thermal aging. It seems that this aging induces a change in the mode of fracture from ductile to moderate brittle one. These SEM observations are in agreement with the mechanical modification previously founded. The morphology changes due to aging was, equally, observed by some other authors [30,42,43]. In fact, they have reported a modification of the fracture mode from ductile to brittle. Surface roughness changes of polyurethane film were observed by Sanchis et al. [30] when studying the aging effect of nitrogen plasma treatment. Krupicka et al. [42] have found, in their investigation, that the polyurethane was greatly affected by storage, which can reduce the plasticity and increase brittleness. Suarez and Biasi [43] have, equally, revealed a significant modification in the topographic aspects of failure surface and in the fracture mechanisms according to gamma irradiation of ultra-high molecular weight polyethylene.

4. Conclusion

In the current contribution, thermal aging experiments were conducted to determine its effect on mechanical properties of TPU. The following findings were derived from this experimental study: (i) changes in appearance of TPU was observed, (ii) mass loss of TPU due to thermal aging was analyzed by gravimetric measurements, (iii) improvement of TPU rigidity was discerned from tensile and creep tests and (iv) SEM photographs have shown that the thermal aging seems to be modifying TPU mode fracture surface from ductile to brittle.

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