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Thermal Ageing Effect on Mechanical Properties of Polyurethane

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This study concerns the effect of thermal ageing on mechanical properties of polyurethane. The polyurethane samples have been exposed at 85°C and 120°C under inert atmosphere. Mechanical tests were realized on these samples during the time of ageing. Tensile tests were performed to see the effect of ageing on elastic modulus (E), stress (σ_r) and strain (ε_r) at break. It was shown that there are two distinct periods. Because of ageing, E and σ_r increase, in the first period, then they decrease in the second period. ε_r decreases first and then increases. The fatigue tests were performed on unaged and aged samples. It was shown that the fatigue behavior of polyurethane (PU) is improved, the same way during the first stage of aging. In the second step, the number of cycles to failure increases due to aging. The results show that aging has an important effect on mechanical properties of PU. The strain at break decreases during the first step of aging due to post-crosslinking and then increases due to chain scission in the network. Based on these results, the effect of crosslinking and chain scission on the mechanical properties of PU was discussed.

Keywords: Fatigue behaviour; Mechanical properties; Polyurethane; Thermal ageing.

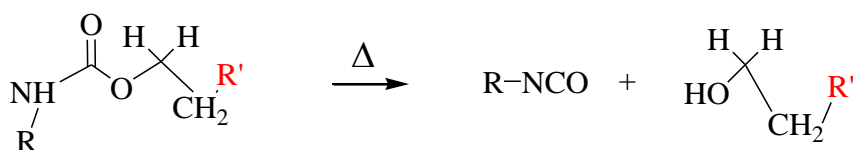
INTRODUCTION

Recently, the polyurethane thermosets are proposed for manufacturing of technical industrial products like the inner layer of the composite tanks for stocking the gases (hydrogen, natural gas...) at high pressure.

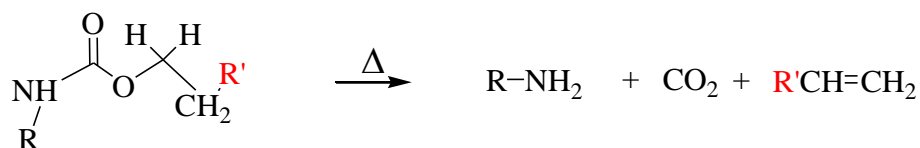
In fact, this type of polymer presents a very high impermeability to different gases. At the same time, as the gas pressure is very high, it should also have appropriate mechanical properties. However, during the manufacturing of the reservoir and also during the loading of the tank by the gas, it is possible that the polymer undergoes degradation due to the rise of temperature. This degradation may affect the properties of the polymer especially mechanical properties.

The literature is not very rich in the field of thermal ageing of polyurethane. Only a few papers are devoted to study this phenomenon. Simon and Agić [1,2], using thermo-gravimetric analysis in an inert atmosphere, have analyzed the products of degradation by gas and gel permeation chromatography. They consider that, in chemical structure of polyurethane, the urethane group has the lowest dissociation energy. Les polyethers and polyesters, in turn, have a similar stability but higher than the urethane group. Other authors have investigated in this field [3-7]. When the polyurethane is synthesized with aromatic isocyanate and polyols like polyether, the degradation may take place at lower temperatures. The following schemas summarize the reactions during the thermal ageing of polyurethanes in absence of oxygen [8]:

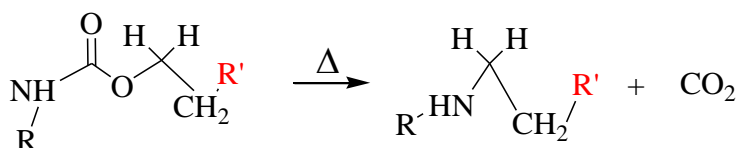
- i) Dissociation to isocyanate and alcohol (Retropolymerization/Depolymerization)



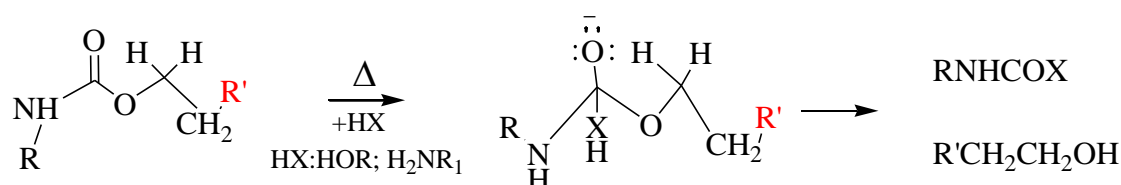
ii) Dissociation to primary amine, olefin and carbon dioxide



iii) Formation of secondary amine



iv) Trans-esterification type bimolecular displacement



At high temperatures, the polyurethane undergoes thermal degradation phenomena. This degradation is a chemical ageing during which an irreversible structural change of the macromolecular network takes place. The effects of thermal degradation depend on the polymer nature and the ageing condition [9].

The thermal ageing leads to a modification of the microstructure of the material. According to Abouzahr et al (1982), the temperature may initiate the chain scission leading to a mixture of the soft and hard segments [10]. However the kinetic of this phenomenon depends on the formulation of polyurethane.

In the field of mechanical properties of polyurethane, several works have been performed [11-17]. Some of these works is devoted to the effect of ageing on mechanical properties of polyurethane. However this effect is not clearly understood particularly, on fatigue behavior of polyurethane.

This paper is essentially interested on influence of thermal degradation on the properties of thermoset PU.

MATERIALS AND METHODS

Materials

The polymer used for this study is polyurethane supplied by RAIGI Company (Rouvray-Saint-Denis, France). This polymer results of the reaction between an isocyanate and a polyol. In our case, the diisocyanate is MDI with functionality more than two. The polyol is polyester called PES4 with molecular weight of 800g/mol. The ratio of NCO/OH is equal to 19.8. This polyol is then mixed with another polyol (PES4) with a molecular weight of 400 g/mol. The catalysts of the type of aluminosilicate and diamine have been used for the reactions.

Ageing conditions

The samples are put for ageing in autoclaves which have been purged a few minutes with Argon, in order to reproduce an inert atmosphere. They are maintained at temperatures of 85 and 120 °C. The temperatures of autoclaves are monitored and recorded during the study, in order to ensure that the temperature remains constant.

Characterization

Fourier transformer infrared spectroscopy:

The spectrum by the transmission is done with a Bruker IFS28 FT-IR spectrometer (Bruker, Karlsruhe, Germany), in the range of 400 to 4000 cm⁻¹.

Differential scanning calorimetric test (DSC):

Measurements are carried out with the DSC Q1000 (TA Instruments, Guyancourt, France). Samples of a mass of between 10 and 20mg are placed in hermetic aluminum capsules. The temperature program suffered by the samples were heated first up to 160°C with a heating rate of 5°C/min, in order to eliminate the thermal history of material. The sample was cooled at -40°C in order to be reheated up to 160 °C with the same temperature rate. Each cycle step is separated by a 5 min isotherm.

Dynamical Mechanical Thermal Analysis (DMTA):

The tests are carried out in 3 point bending using DMA 242 instrument from Netzsch Company (NETZSCH-Gerätebau GmbH Analyses & Tests, Dardilly, France). These test are performed under following conditions: Frequency 1Hz, Temperature range -80 to 160°C, temperature rate 2°C/min, amplitude of deformation 30 µm, proportional factor: 1.1, and dynamic force 1N.

Tensile test:

Tensile tests have been achieved with an Instron 5881 machine (Elancourt, France) using 10 KN load cell and according to the standard NF T51-034. The strain rate is 50mm/min. The dimensions of the samples were 115 mm length, 10 mm width and 4mm thickness.

Fatigue tests

Two different fatigue tests have been performed:

- Tensile-tensile fatigue tests: Using a MTS 831 Elastomer test system (MTS Systems Corporation, Eden Prairie, MN, USA), the conditions of these tests were as follows: Frequency 10Hz and the minimum applied stress was 10% of maximum applied stress.
- Alternative flexural fatigue tests: in this test, the sample is under a sinusoidal strain at room temperature. The frequency is 10Hz.

RESULTS AND DISCUSSION

The evolution of chemical structure of polyurethane during ageing at 85°C and 120°C were followed by ART-FTIR method. The spectra of aged and unaged polymer are

shown in Figure 1.

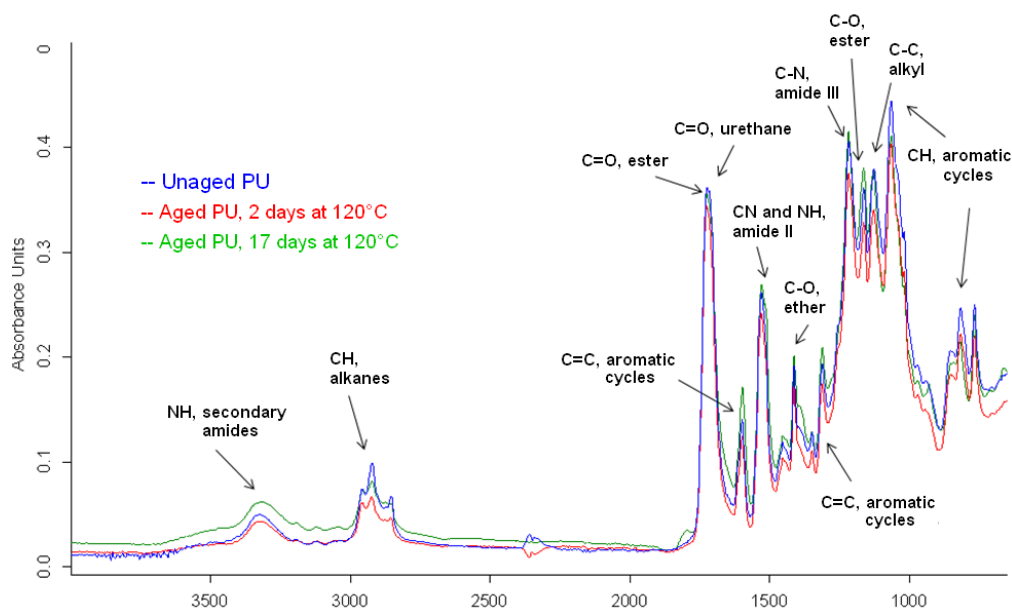


Figure 1: The spectra of the polyurethane during ageing at 120°C.

During aging at 120°C, very small changes especially in the shape of the peak at 1720cm⁻¹ are observed, related to the urethane bonds. The changes at 1800cm⁻¹ and at 1515cm⁻¹ can be attributed to double bonds, responsible for change of color and yellowing of the samples. During ageing at 85°C, these changes in the infrared spectrum are observed only after 52 weeks.

The products extracted from aged PU by Soxhlet were analyzed by infrared spectrometry (Figure 2) and by gel permeation chromatography (GPC). The results show that:

- There are no significant soluble products in unaged polyurethane sample,
- There is a large soluble fraction with a wide distribution of molecular weights extracted from the aged polyurethane. These species absorb UV, so they are aromatic groups or the groups containing double bonds.

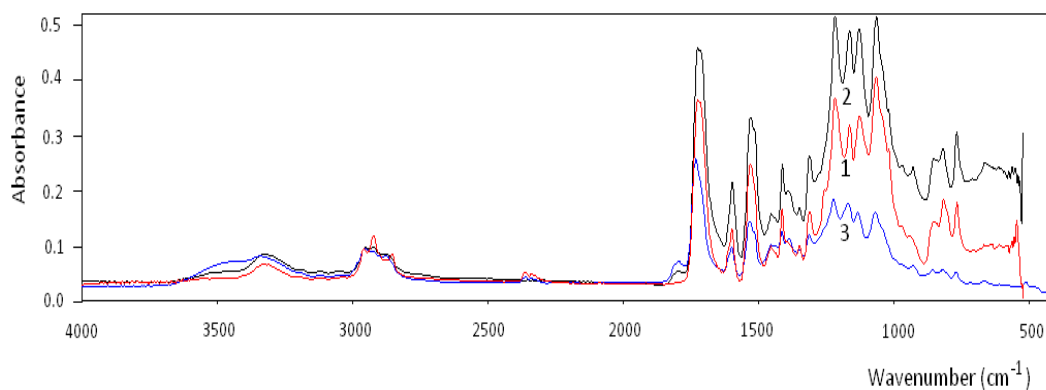


Figure 2: Infrared spectrum of: 1) unaged PU, 2) PU aged at 120°C during 13 weeks and 3) products extracted from PU aged at 120°C during 13 weeks.

Tensile tests

The effect of ageing, on stress-strain curves obtained by tensile tests, is shown in figures 3 and 4.

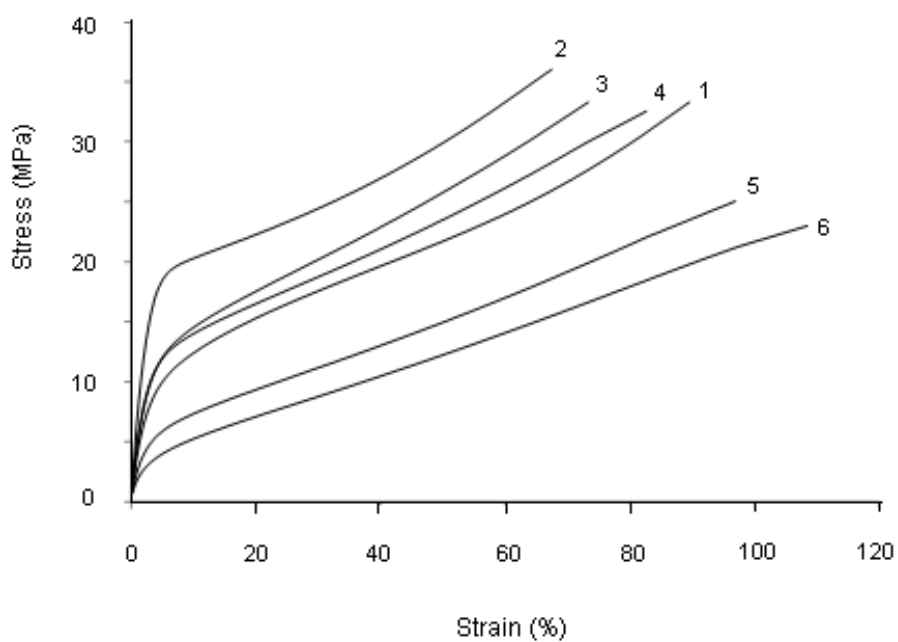


Figure 3: Stress-strain curves of polymer at different stages of ageing at 85°C.

1) unaged, 2) 3 weeks, 3) 9 weeks, 4) 24 weeks, 5) 52 weeks and 6) 62 weeks of ageing.

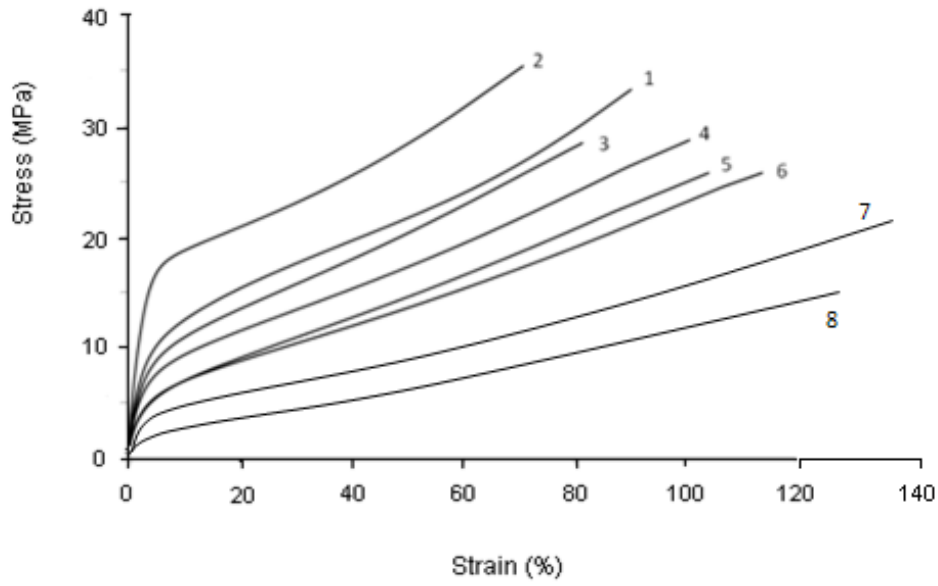


Figure 4: Stress-strain curves of polymer at different stages of ageing at 120°C.

1) unaged, 2) 2 days, 3) 1 week, 4) 2 weeks, 5) 3 weeks, 6) 4 weeks, 7) 9 weeks and 8) 13 weeks of ageing.

From these results, one can follow the variations of Young's modulus and stress at break during ageing (Figures 5 and 6).

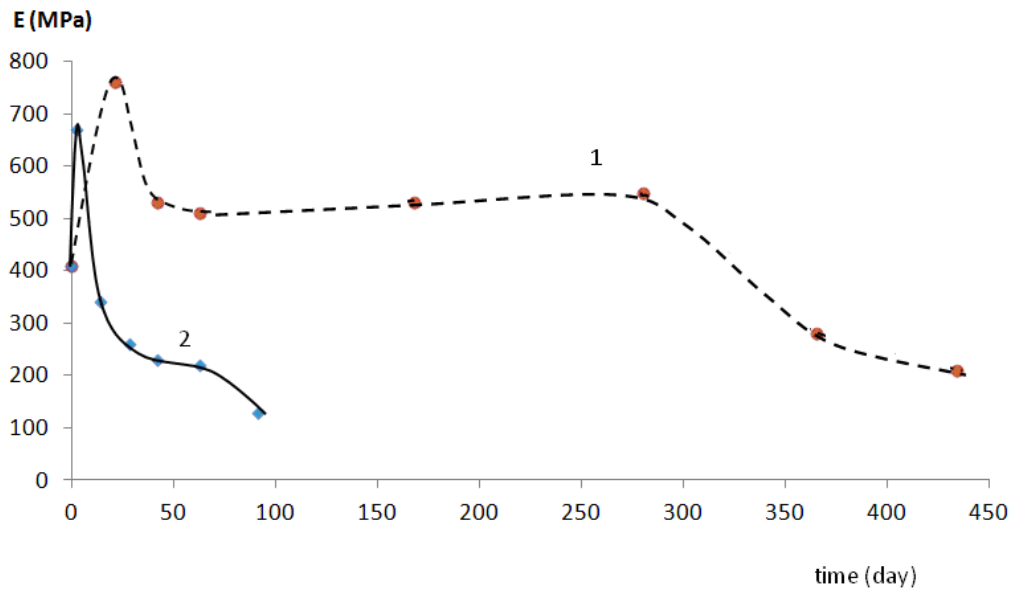


Figure 5: Evolution of Young's modulus during ageing at 85°C (1) and 120°C (2).

These results show that variation of tensile strength is similar to the variation of Young's modulus.

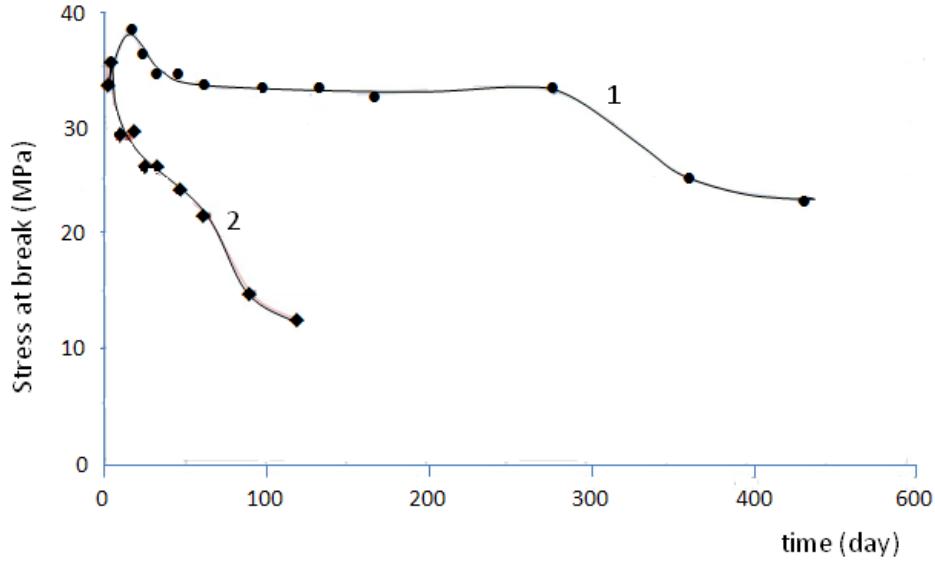


Figure 6: Evolution of stress at break during ageing at 85°C (1) and 120°C (2)

This variation presents three different steps during polymer ageing:

- In the first step, Young's modulus and stress at break increase because of the post cross-linking. Indeed the polymer was not completely cross-linked before ageing.

The stress at break increases slightly from 34 to 36 MPa, during the 3 first weeks of ageing at 85°C; the Young's modulus increases from 410 to 780 MPa.

In this step, the increase rate of the Young's modulus (and the stress at break) is more important when the ageing temperature is higher. After only two days of aging at 120°C, the modulus increases from 410 to 670 MPa.

- In the second step and according to the results of ageing at 85°C, Young's modulus and stress at break decrease during 40 days to reach their initial values, and then remain constant during almost 42 weeks. This phenomenon is essentially due to the increase of critical molecular weight (M_c), and to the decrease of cross-linking density

related to the chain scission in the network. Because of the chain scission, the linear molecules will be formed in the network. These molecules can have a plasticization effect. This effect also can be another reason of the decrease of Young's modulus and tensile strength.

The same effect is observed for ageing at 120°C with a significant higher rate. Young's modulus decreases to a value of 210 MPa during six first weeks and tensile strength changes from 36 to 20 MPa.

- In the third period, during ageing at 85°C, Young's modulus and stress at break decreases again to the low values (210 MPa and 23 MPa respectively) after 62 weeks of ageing.

The same results have been obtained for the samples aged at 120°C with a higher rate. Young's modulus and stress at break decrease respectively to 130 MPa and 13 MPa after only 17 weeks of ageing.

Concerning the change of strain at break, the results are not the same (Figure 7). In the first period and because of cross-linking, it decreases from 90% to 65% and 50% for ageing respectively at 85°C and 120°C. In the second period, the strain at break increases up to 93% and 120% for ageing respectively at 85°C and 120°C. In the period, it continues to increase for sample aged at 85°C and decrease for sample aged at 120°C.

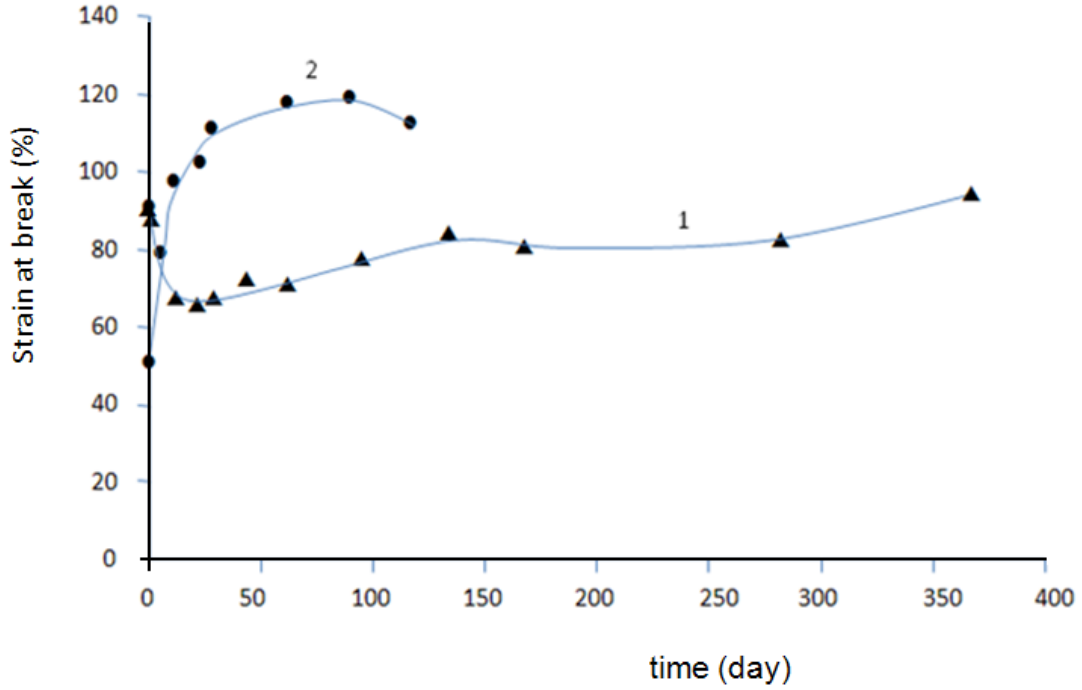


Figure 7: Evolution of strain (%) at break during ageing at 85°C (1) and 120°C (2).

These results call the following comments:

i) The decrease of the module is due to the increase in critical mass according to the elastic theory of rubber [18]:

$$E = \frac{3\rho RT}{M_c} \quad (01)$$

Where E is the Young's modulus at rubbery plateau (MPa), R is the gas constant, ρ is the polymer density (kg. m^{-3}), T is the temperature (K) and M_c is the critical molecular weight between two crosslinking points (kg. mol^{-1});

The results of DMTA tests (Figure 8) let us to evaluate the increase of critical molecular weight (M_c) because of ageing at 85°C (after 62 weeks) and 120°C (after 13 weeks):

$$(M_c)_2 = 1.22 (M_c)_1 \text{ and } (M_c)_3 = 1.34 (M_c)_1$$

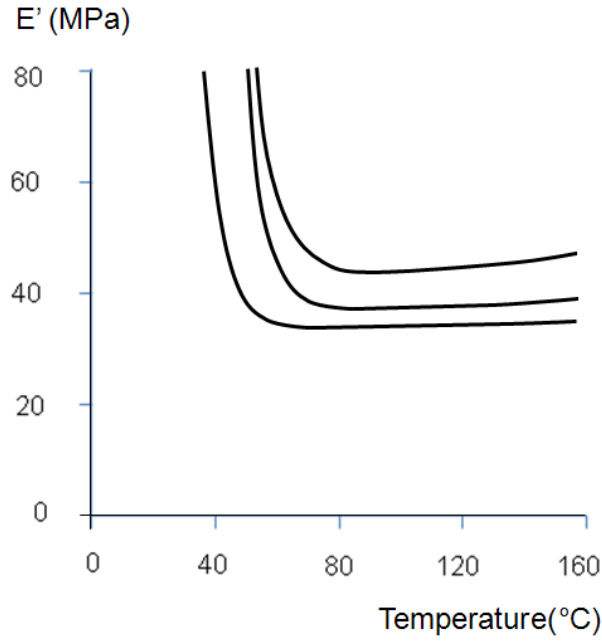


Figure 8: Loss modulus spectrum of 1) unaged, 2) aged 62 weeks at 85°C, 3) aged 13 weeks at 120°C.

ii) The increase of the critical mass and the decrease in cross-linking density are the origins of the decrease of the strength of the polymer during degradation. This may be accentuated by the plasticizing effect of degradation products, accumulated during ageing. Reduction of stress can be expressed by the law of Kambour [19]:

$$\sigma = C(T_g - T) \quad (02)$$

Where T_g is the glass transition temperature and T the test temperature. C is a constant related to the cohesive energy density.

iii) The results of tensile tests, explain well the effect of ageing on mechanical properties of polyurethane. It was shown an improvement of elastic modulus and stress at break during the first stage of ageing. Several authors have been attributed this improvement to the cross-linking, depending on the temperature and the time of exposure [1-6]. In fact, during ageing there is a competition between chain

scission and cross-linking. At the first stage of ageing, the effect of cross-linking overshadows the effect of chain scission and as a result, elastic modulus and the strength of polymer increase. However for the second stage of ageing the effect of chain scission becomes more important and then the polymer loses its resistance and its rigidity.

Concerning the evolution of strain at break, our results for the second period of ageing do not follow the observation of these authors. Indeed, during the first stage of ageing, the strain at break decreases when the cross-linking density increases. But at the second stage, it increases in spite of chain scission. How can we explain this phenomenon?

In the case of thermoplastics, during thermal or thermooxidative ageing, Young's modulus and stress at break do not change significantly. At the same time, it was observed that strain at break decreases and the sample becomes more and more brittle. This decrease of ductility of the sample is understandable. Thermoplastics have linear or branched molecular structure and they become brittle because of chain scission specially when the amorphous phase is at rubbery state and chain mobility is relatively significant.

In the case of thermosets and elastomers (the polyurethane under study), the problem is not the same. They have a network structure and chain scission makes the network more flexible. Indeed, because of chain scission, cross linking density decreases; the result is a decrease of T_g .

In the case of the polyurethane under study, the result is the same. This polyurethane is a thermoset polymer and the same phenomenon has been observed. As it has been previously explained, two steps can be distinguished during ageing. In the first step, the increase of Young's modulus and stress at break and the decrease of strain

at break can be attributed to the different parameters: post cross-linking, cross-linking because of ageing, and loss of volatile matters like water or plasticizer if it exists in the system. In the second step because of chain scission in the network, the sample becomes more flexible but less stiff.

These results can be confirmed by the study of the effect of ageing on glass transition temperature of the polymer. The DSC tests give a T_g of 23°C for unaged polymer. Figure 9 shows that, during ageing at 85°C, T_g increases slightly during 3 week of ageing and then decreases. At 120°C, T_g decreases from 23 to 16°C during 13 weeks. As it is explained before that the decrease of T_g during ageing is related to the chain scission in the network.

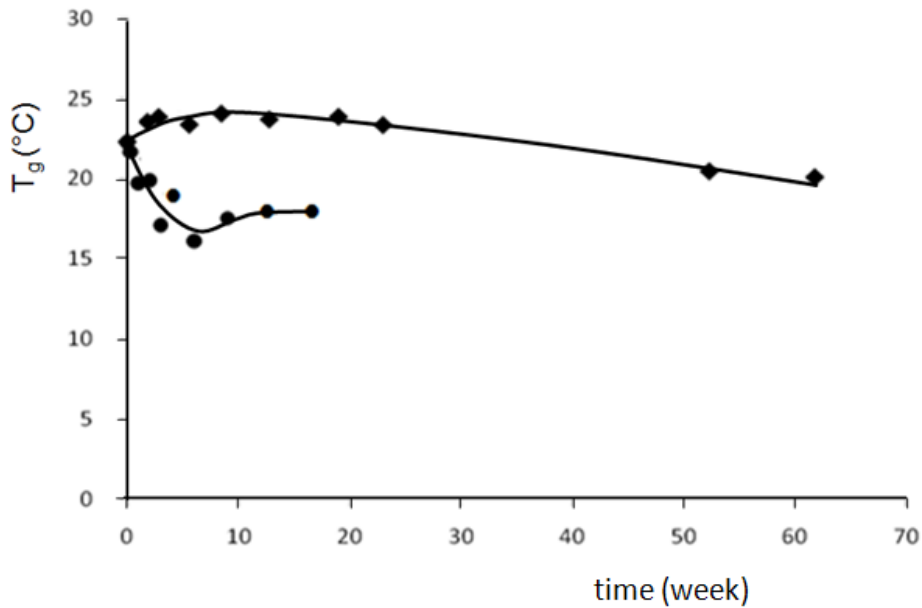


Figure 9: Evolution of T_g during ageing at 85°C (◆) and at 120°C (●)

These phenomena can be schematized by the Figure 10. It is important to mention that at the end of the second step, because of the important degradation, the polymer becomes brittle.

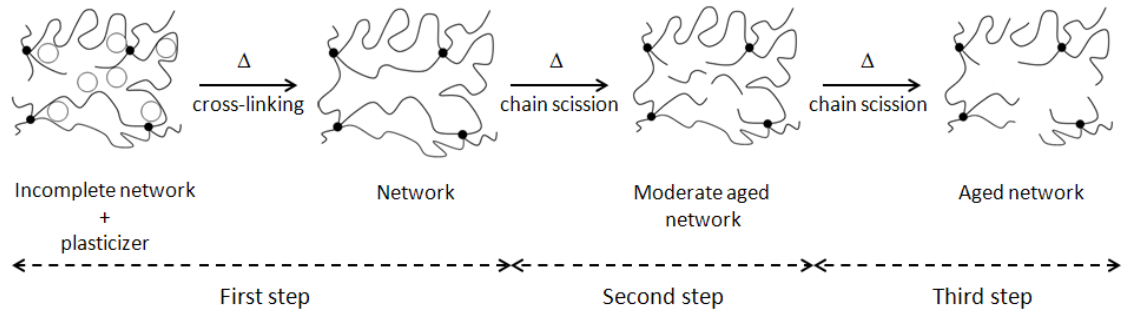


Figure 10: A schematically presentation of two steps during ageing of polyurethane under study.

The validity of these results has been also verified by DMTA experiments. Figure 11 shows the increase of T_α (related to the T_g) during the first 24 weeks of ageing at 85°C; then it decreases. T_α increases from 47°C (unaged) to 53°C after 24 weeks of ageing at 85°C under vacuum and then decreases to 39°C after 52 weeks.

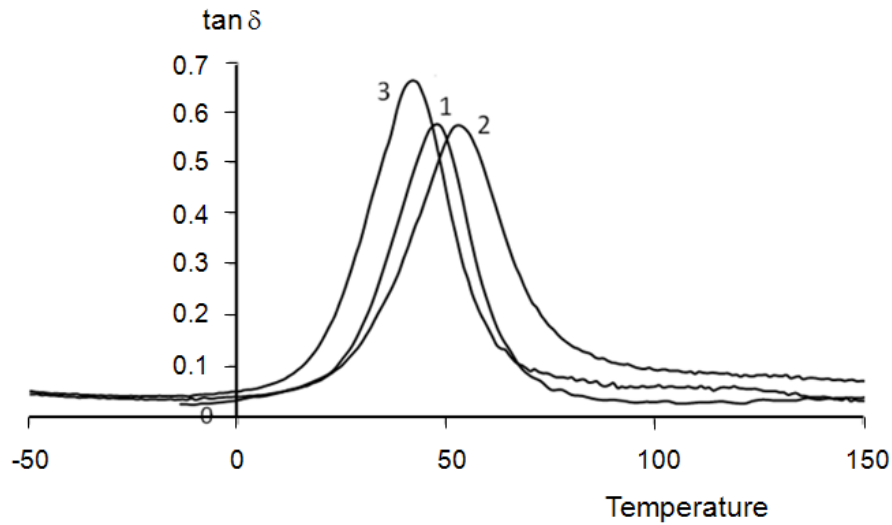


Figure 11: $\tan \delta$ spectrum of non-aged and aged PU at 85°C: 1) unaged, 2) aged 24 weeks, 3) aged 52 weeks.

Coupling of fatigue-ageing

In order to study the effect of ageing on fatigue behavior of polyurethane, tensile-tensile fatigue tests have been realized on non-aged and aged samples (Figure 12). One can see

that the number of cycles at break increases because of ageing.

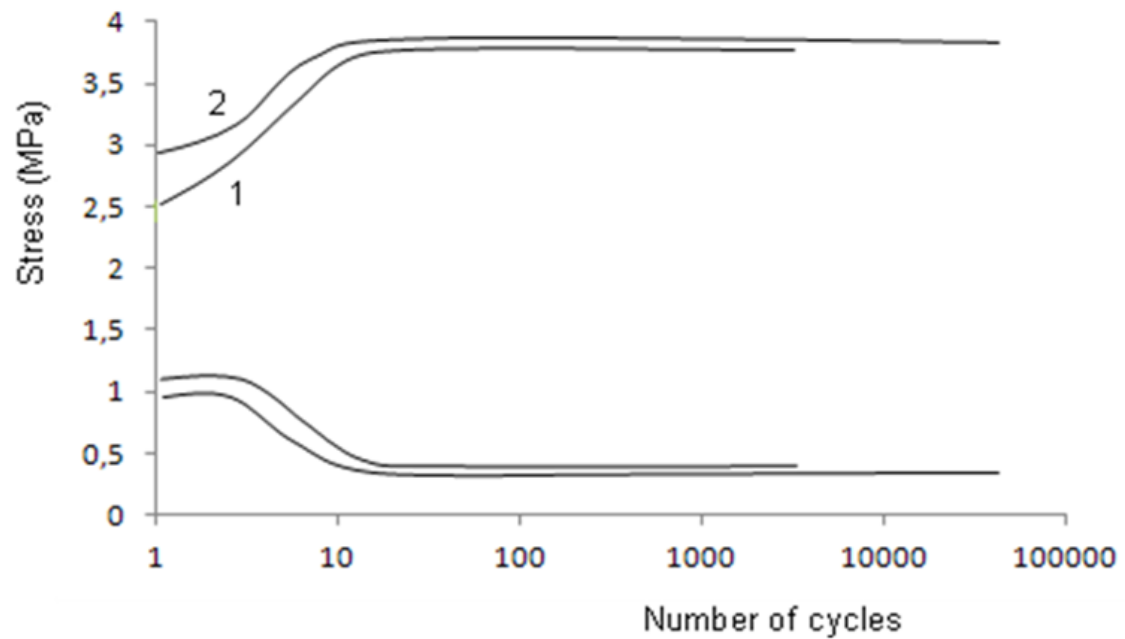


Figure 12: Fatigue curves of unaged (1) and aged (2) PU samples.

The fatigue behavior of PU under cyclic loading can be studied by Wöhler curve which can be established using the results of several fatigue tests. It represents the variation of maximum stress *versus* number of cycles at break for each fatigue test. Figure 13 shows the Wöhler curves of unaged and aged PU after 32 weeks at 85°C.

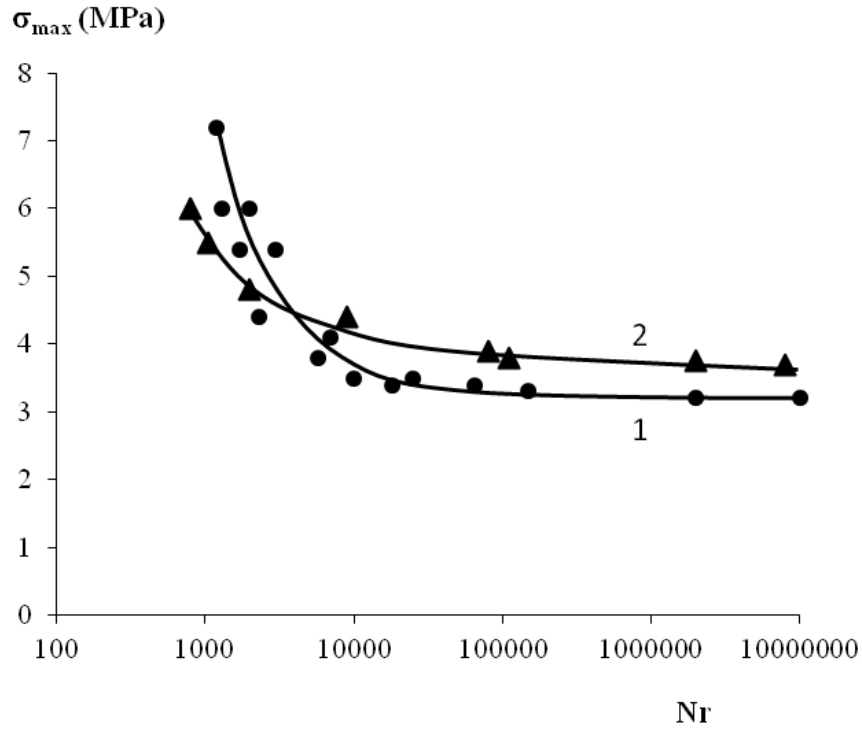


Figure 13: Wöhler curve obtained by fatigue tests on unaged (1) and aged (2) polyurethane samples.

The results show that when the sample is subjected to high fatigue stresses, it breaks quite quickly: in the range between 4 and 7 MPa, the specimen breaks at less than 6000 cycles. It is observed that the lifetime increases as the applied stress decreases. Between 3.4 and 3.2 MPa the lifetime increases significantly. For example, for an applied stress of 3.2 MPa, the lifetime reaches to 10^7 cycles. Nevertheless, in this zone a small variation of stress has a very important effect on lifetime. The curve obtained from the fatigue test on sample aged at 85°C during 32 weeks presents two tendencies: between 4.2 and 6 MPa, the sample breaks after almost 10^5 cycles.

Comparing unaged sample to the aged one, two different domains can be distinguished: high maximum stress and low maximum stress. The results show that when applied stress is high (between 4 and 7 MPa); the lifetime is shorter for aged polymer. In contrary, ageing is the cause of the increase in endurance limit. In fact aged

PU has an endurance limit of 3.1 MPa and PU aged at 85°C for 32 weeks has an endurance limit of 3.3 MPa.

In order to predict the effect of ageing on fatigue behavior of polyurethane, alternative flexural fatigue tests have been performed on samples at 120°C in inert atmosphere during different ageing time. For all of these tests the amplitude of applied sinusoidal strain and the test frequency were respectively 2.2% and 10Hz. The results are shown in figure 14.

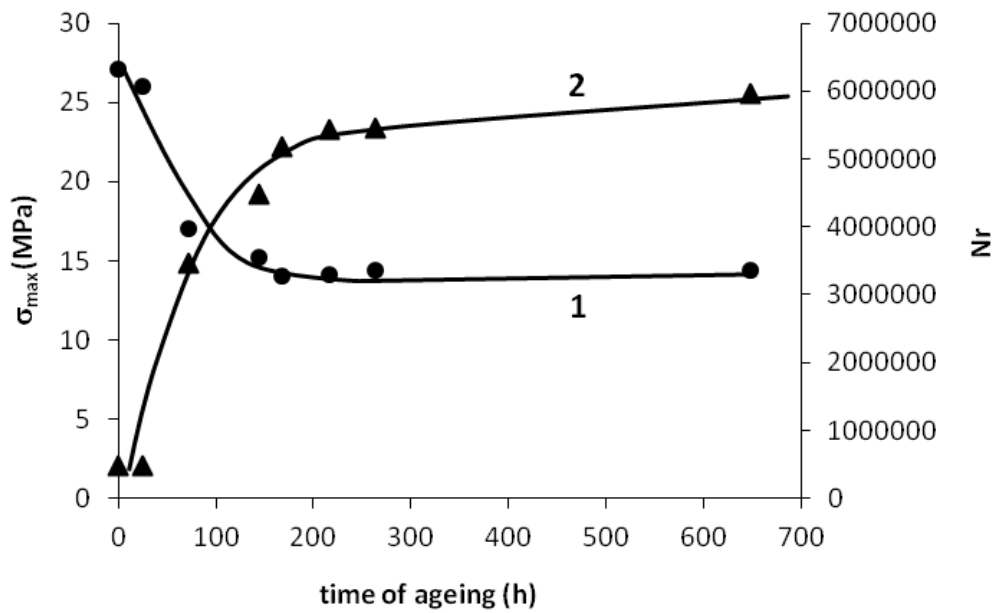


Figure 14: Variation of σ_{max} of fatigue test (1) and number of cycle (2) *versus* time of ageing at break

Rupture-envelope S-N curve of fatigue tests

These results permit to plot the evolution of stress max (σ_{max}) *versus* number of cycles at break (N_r) for the aged samples during the time of ageing (Figure 15). This curve can be considered as rupture-envelope diagram [20] for fatigue tests. Unfortunately we don't have the Wöhler curve to compare with it; however we have verified that the rupture-envelope diagram can be modeled by following equation which is proposed for

the Wöhler curve of certain polymers [21-23]:

$$\sigma_{max} = A \log Nr + B \quad (03)$$

Where A and B are a constants. The regression method gives us the value of these constant: A = -5.1 MPa and B = 93.3 MPa with R^2 (coefficient of linear regression) = 0.994. So this model can predict the evolution of stress of the sample under fatigue load during the time of ageing.

Figure 15: Variation of maximum stress (σ_{max}) of fatigue test *versus* time of ageing.

Conclusions

In conclusion, the thermoset polyurethane is a relatively thermostable polymer. In inert atmosphere and at moderate temperatures, its chemical structure remains the same for a long time without significant modification. At high temperature ($>120^\circ\text{C}$) and after several weeks, the chains scission of urethane bond in its network happens with formation of double bonds. In this case the critical molecular weight increases; the cross-linking density decreases. This phenomenon is responsible of the decrease of glass transition temperature and also the decrease of Young's modulus and strength. However the polymer becomes more ductile because of ageing. It was also shown by fatigue tests that when the applied fatigue force is high, the lifetime of aged polymer is shorter the life time of unaged polymer. On the contrary, for low applied fatigue forces, ageing will increase the lifetime of the polymer. In fact the endurance limit of aged polymer is greater than unaged. These results have been confirmed by the results of DSC and DMTA tests.

Acknowledgment

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