

Study of the ageing of polyurethanes in general applications for UV radiation

Fábio G. Aquino^{1*}, Fernanda M. B. Coutinho², Terry Sheldrake¹, Judimar Clevelario¹, Fábio Pires¹

^{1*} Wellstream International – fabio.aquino@wellstream.com

² Universidade do Estado do Rio de Janeiro - UERJ

Polyurethanes are a class of polymer that present a wide range of mechanical properties. Polyurethane is a versatile material and, depending on the monomers and catalysts, can generate a great variety of materials with dense or cellular texture. Polyurethanes can be produced in three forms: thermoplastic, thermoset and elastomeric. Good abrasion resistance and easy processing are notable properties of this material. The urethane linkages, result from the polyaddition reaction between isocyanate groups and polyol groups, depending on the presence of a catalyst. . Currently, polyurethanes are in service under UV radiation conditions. Studies have been conducted on the durability of polyurethanes when exposed to UV radiation where the most common technique used to accelerate the ageing of materials involves performing tests in ovens that simulate UV rays. The influence of ageing is related to the mechanical properties of the material and is easily monitored by tensile tests.

Keywords: degradation; polyurethanes; mechanical properties; variation; UV radiation.

Introduction

The demands of modern life have spurred the need for more durable materials for daily use. The discovery of polymers has been pivotal, as the material is suitable for a wide range of applications due to its properties, versatility and price [1]. Polyurethanes, developed by Otto Bayer, Germany, in 1937 [2], are among the classes and types of polymers studied. Initially, this class of polymer was intended to compete with polyamide (nylon) discovered by Du Pont CAROTHERS, USA [3]. Saunders, et al. [4], at the end of the 1930s in Germany, began the commercialization of polyurethanes to manufacture adhesives, paints, bristles, fibres, and rigid foams.

Polyurethane elastomers appeared in England and Germany during the 1940s and were advanced commercially with the development of flexible foam in the mid 1950s. In the 1960s, the use of chlorofluorocarbons (CFCs), an expanding agent in the production of rigid foam, resulted in the extensive application of this material in thermal insulation.

The development of another polyurethane product in the 1970s, semi-rigid foam coated with thermoplastic material, was used in the automotive industry. Reaction injection moulding (RIM) experienced significant commercial growth during the 1980s; however the knowledge of its

environmental impact during the 1990s initiated research into replacing CFCs, which were found to be harmful to the ozone layer. Currently, the emphasis is on RIM applications and related research into the molecular structure and properties of polyurethanes. Polyurethane technology has become a great success story resulting in billions of dollars' worth of business [5].

Polyurethanes are a versatile class of polymer that exhibit a wide range of mechanical properties and, depending on the catalyst and monomers used, can generate a wide variety of materials with solid or cellular structure. They can be produced in three forms: thermoplastic, thermoset and elastomeric. Good abrasion resistance and easy processing are notable properties of this material [2].

The urethane linkages, resulting from the polyaddition reaction between isocyanate groups and polyol groups, depend on whether they are in the presence of a catalyst or not, as illustrated in Figure 1.

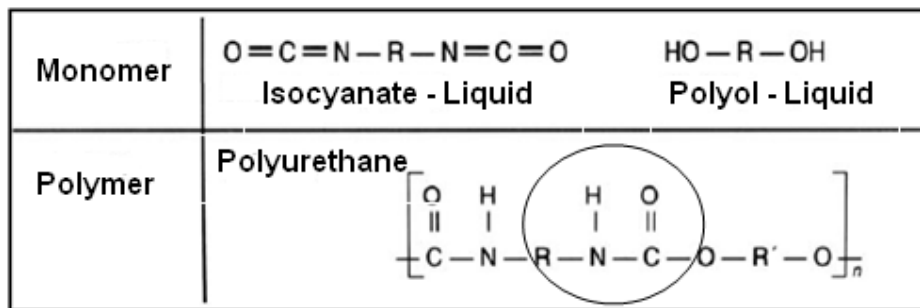


Figure 1 - Details of the urethane links

When designing with polyurethane, one must consider all possible failure modes during its service conditions; a comprehensive knowledge of its mechanical behaviour is also pertinent. The following aspects can be taken into consideration: mechanical resistance, creep behaviour, impact strength, fatigue behaviour and abrasion characteristics for example. When compared with other polymers, some specific polyurethanes present the possibility of combining high resistance with an increased hardness and high elasticity modulus [6]. Currently, polyurethanes are applied in services under UV radiation conditions.

Studies have been conducted into the durability of polyurethane when exposed to UV radiation. Many of these studies are related to ageing in air, where photodegradation is the main focus. A recent review of elastomers used in the offshore industry describes different types of degradation including mechanical degradation, chemical changes and link breakage due to the reaction catalyzed by UV action [7].

The most common technique used to accelerate the ageing of materials involves performing tests in ovens that simulate UV radiation. The influence of ageing is related to the mechanical properties of the material and can be easily monitored by tensile, compression, and sealing resistance tests [8]. Other methods that can be used in parallel with mechanical tests are spectroscopy in the infrared region (FTIR), weight variation and permeability data, as well as size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR).

Experimental

The materials used in this work are described as follows:

- Polyurethane (PTMEG/TDI) identified as PU – 1, Origin: Company A. Details of the formulation of polyurethane used are confidential.
- Polyurethane (PTMEG/TDI) identified as PU – 2, Origin: Company B. Details of the formulation of polyurethane used are confidential.

Mechanical Properties

Tensile Strength in Virgin Polyurethanes

Tensile strength test was performed in accordance with the ASTM D638-09 standard. Continuous measurement of the resistance developed by the polymeric material was performed under a constant rate of elongation.

The tensile properties were measured in a universal testing machine, Instron model 5569, with a load cell of 2 KN. The tests were performed at 10, 20, 50 and 70°C to monitor the behaviour of polyurethanes as the temperature varies. 10 specimens per temperature level were used in the tests, each specimen being moulded by method ASTM D638 - 03 - Type 4. The analyses were determined by applying an extension rate of 50mm/min. Figure 2 shows the universal testing

machine Instron model 5569 and Figure 3 shows the specimens. The samples were placed in the chamber and the tests commenced after 50 min of stabilization at the test temperature.

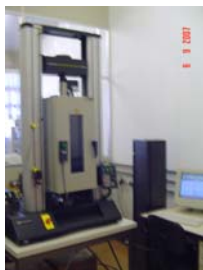


Figure 2 - Testing machine used to determine the mechanical properties.



Figure 3 –The specimens moulded by Type 4 – ASTM D638-03

Exposure to UV Radiation

Exposure to UV radiation was performed according to the ISO 37 standard to evaluate any degradation tendency in polyurethane samples by UV radiation. Three sheets of polyurethane with 4.0 mm of thickness were assembled in an oven to evaluate the effect of the direct and indirect radiation, as shown in Figure 4.

The polyurethane sheets were exposed using the specific equipment brand Weather-Ometer Atlas, Model CI 35 with a 6500 w lamp.

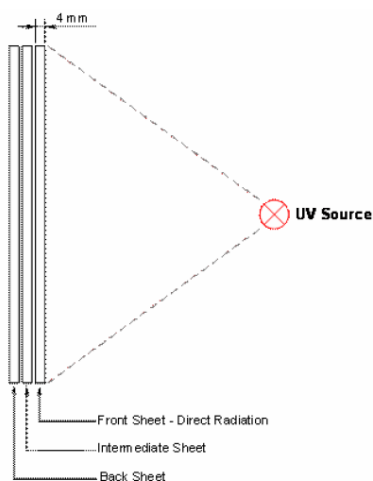


Figure 4 – Details of the sheets assembled in the oven for exposure to UV rays.

10 specimens were taken from each sheet (taken out of the oven) and their mechanical properties were measured in the universal testing machine Instron model 5569 after each period of exposure, as detailed below. The tests were performed at room temperature after 250, 500, 1000, 2000, 3000, 4000 and 5000h of exposure respectively.

Tensile tests were performed according to the ASTM D638-09 standard to evaluate the mechanical behaviour of the polyurethane before and after each period of exposure. The polyurethane's mechanical properties were also determined by applying an extension rate of 50mm/min. The specimens were moulded after each period of exposure as per ASTM D638 standard – Type 4.

Results and Discussion

Tensile Strength in Virgin Polyurethanes

The tensile properties of the polyurethane were evaluated as described above. The tests were performed at 10, 20, 50 and 70°C respectively, to verify the behaviour of the material as the temperature varies. Figures 5 and 6 present the average results of elongation at break and tensile strength in the rupture obtained during the tests, as shown below.

The analysis of the mechanical behaviour of a polymeric material is based on the study of the deformation caused by the application of external forces. The final application of a polymeric material is mainly dictated by its mechanical properties. In turn, these properties are strongly

dependent on the level of homogeneity, compatibility and adhesion between the system components [9].

The tensile strength and elongation at break can be quantitatively correlated to the polymer structure. Materials with high crosslink content, such as those used in rigid foams, are strong and hard but otherwise brittle. Elastomers and flexible foams have a higher elongation at break. Another way of studying the mechanical behaviour of polyurethanes is related to the synthesis of the polymer since the increase of rigid segments in polymerization, in other words the increase of isocyanate content in the formulation of the material, leads to the increase of the modulus and reduction of the elongation at break of the same [6].

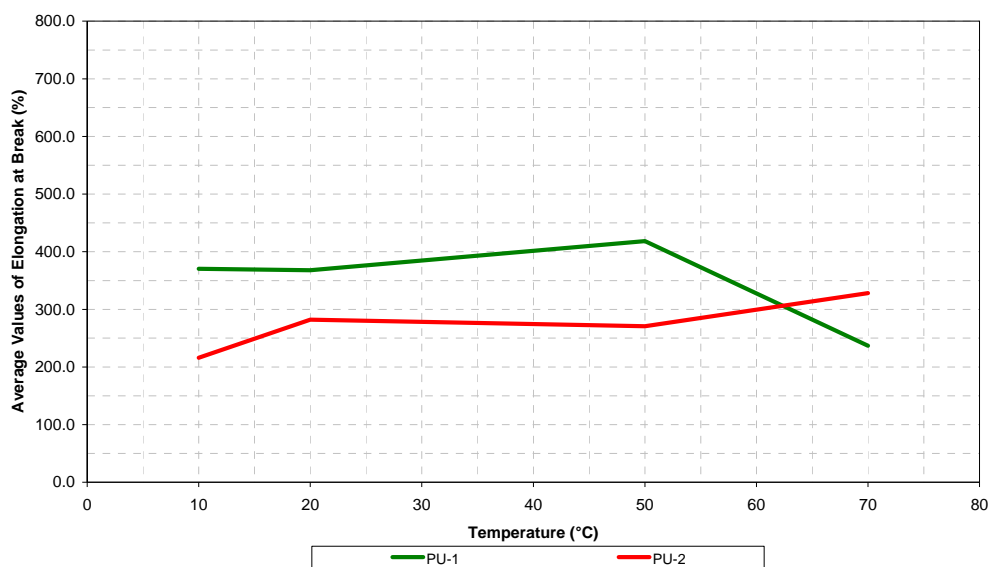


Figure 5 – Average results of elongation at break

In general from the elongation at break results, the polyurethane identified as PU – 1 tended to stabilize until it reached a temperature of 50°C. With the increase of the test temperature to 70°C the results show a reduction of approximately 134%. The results show that the polymer identified as PU – 2 tended to elongate as the test temperature increased and in general, exhibited greater stability in the properties of elongation when compared to PU – 1. The higher values of elongation at break for PU – 1 when compared to PU – 2– may be correlated with the lowest content of rigid segments in the structure of the polyurethane. This behaviour is confirmed by the tensile strength results in the tests at 20, 50 and 70 ° C, as the values of tensile strength were higher for PU – 2.

The crosslink content is another factor that can explain the mechanical behaviour of polyurethanes as the higher the number of crosslinks in the polymer structure, the higher the tensile modulus of rupture of the same will be.

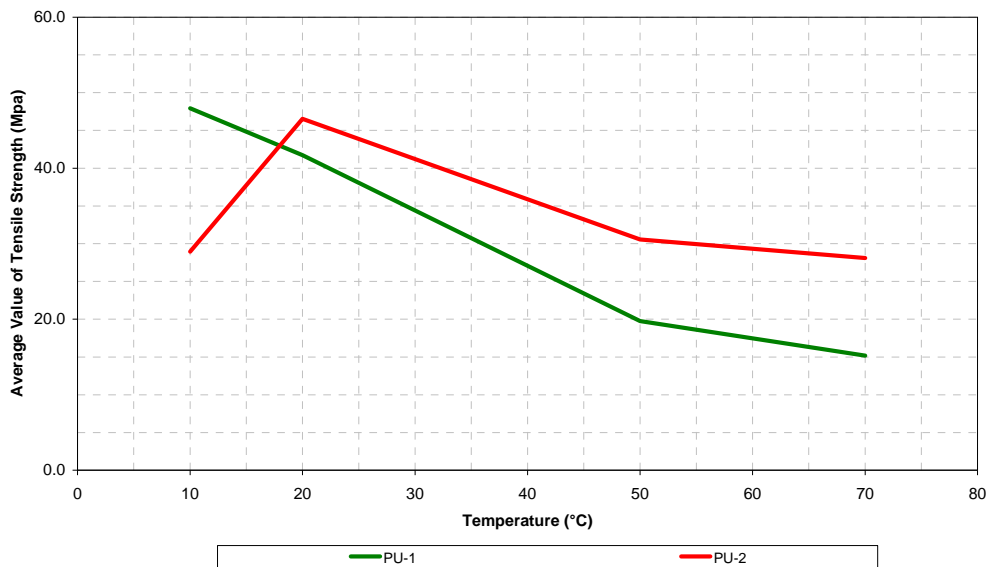


Figure 6 – Average results of tensile strength

In terms of the average tensile strength results, PU – 1 tended to reduce as the test temperature increased, while the results verify that at 20°C PU – 2 elongated, followed by a reduction in the tensile strength value as the test temperature increased. The results at 10 and 70°C for PU – 2 were similar, meaning that PU – 2 was more stable with temperature variation. PU – 1 experienced a reduction in stress properties as the temperature increased, proving that the material is limited in applications at high temperatures.

Exposure to UV Radiation

Exposure to UV radiation was performed on the polyurethane specimens as previously described. The specimens were exposed in an oven for up to 5000h and their mechanical properties evaluated after each period of exposure. The reference point for the beginning of the ageing test was the tensile test result performed on the specimen at 20°C.

Figures 7 and 8 present the average elongation at break results and tensile strength in the rupture obtained for the polyurethanes PU – 1 and PU – 2 respectively. It is important to note that

the results taken are related to the arrangement of the sheets in the oven, as already detailed above. In general, the elongation at break results for PU – 1 were higher than the results for PU – 2 during the exposure period. For the average tensile strength values, the values for PU – 1 are higher than the values observed for PU – 2 after 250h of exposure and remained so until the end of the tests.

In general for the average elongation at break results, PU – 1 tended to stabilize, demonstrating a higher stability of this property when exposed to UV radiation. The same can be observed for PU – 2, since the average values of elongation at break present a slight tendency toward stabilization for all sheets.

In terms of the average tensile strength data, PU – 2 showed a significant tendency toward reduction in this property. This can be better assessed with the increase of exposure time. The results of tensile strength for PU – 1 showed a higher tendency toward stability when compared with the results of PU – 2. This reduction in the tensile properties of PU – 2 can be related to the polyurethane’s degradation by formation of hydroperoxides in the presence of oxygen and such process can be accelerated in the presence of water [10]. A further observation is that the three sheets of PU – 2 presented a reduction in tensile strength. This behaviour may be related to surface degradation, as well as degradation in the internal layers of the polyurethane. Both polyurethanes present a tendency toward reduction in the tensile properties of the sheets that were directly exposed to UV radiation, as presented in Figure 8.

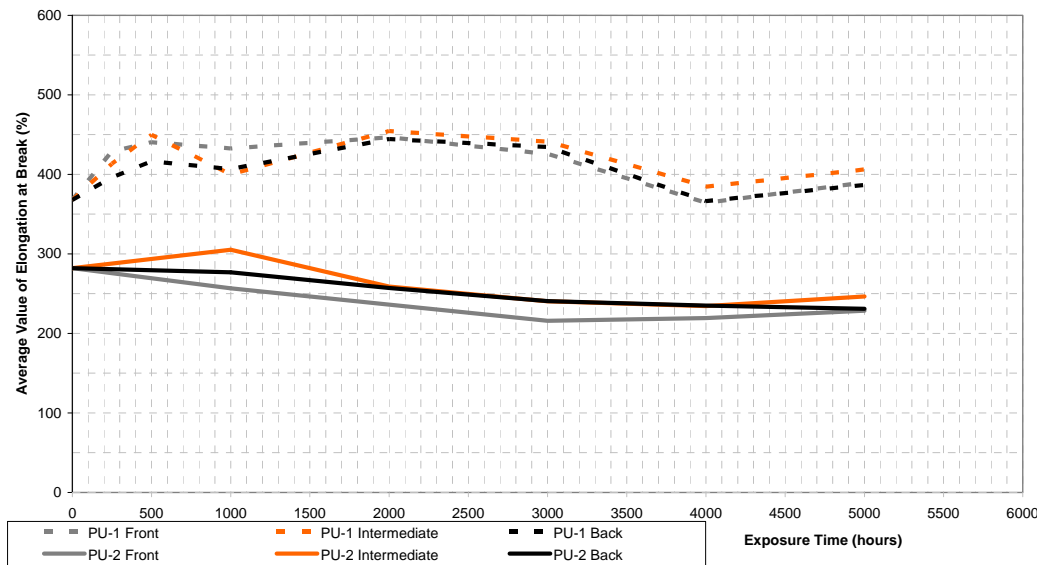


Figure 7 – Average results of elongation at break after exposure to UV radiation action

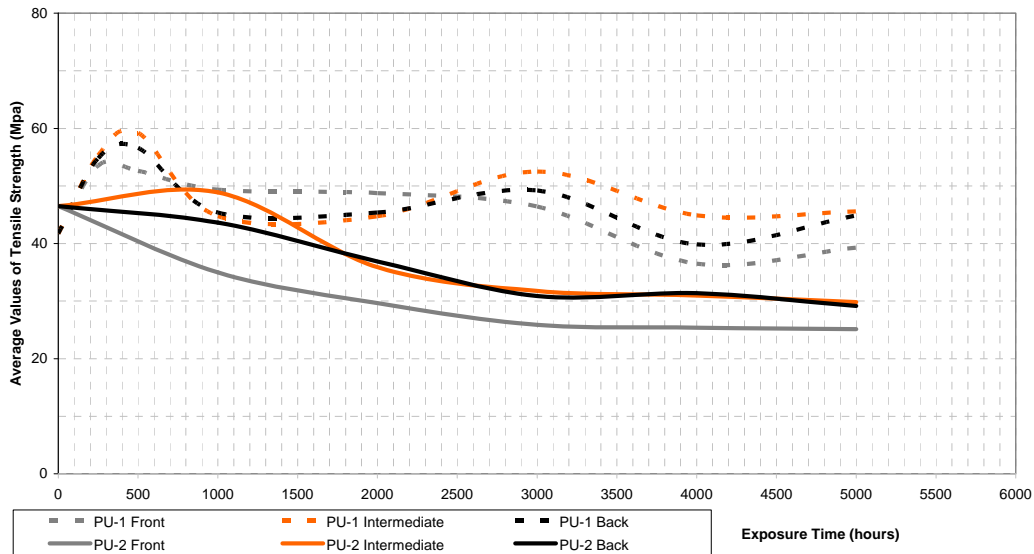


Figure 8 – Average results of tensile strength after exposure to UV radiation action

Conclusions

- ❖ PU – 2 presents a higher crosslink content and/or rigid segments than PU – 1.
- ❖ PU – 2 shows greater stability in the property of elongation at break with the increase of temperature.
- ❖ The average tensile values for PU – 1 and PU – 2 presented a tendency to reduce with the increase of test temperature.
- ❖ PU – 2 presented a reduction in the mechanical properties with exposure to UV radiation both on surface and internal layers.

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