Relationship between network structure and ultimate properties in polyurethane during a chain scission process

Sabrina Taourit [a,b,c], Pierre-Yves Le Gac [a,*], Bruno Fayolle [c]

[a] Ifremer, Marine Structures Laboratory, Centre de Brest, BP 70, 29280 Plouzané, France
[b] Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands
[c] PIMM, Arts et Metiers Institute of Technology, CNRS, Cnam, HESAM University, 151 Boulevard de l'Hopital 75013 Paris, France

ABSTRACT

To investigate the impact of chain scission on the tensile properties of elastomers, a polyester-based polyurethane was aged in seawater at several temperatures ranging from 40 °C to 90 °C. Before the hydrolysis process, water diffusion was first characterized and described by Fickian behaviour. In terms of temperature dependence, both mass at saturation and water diffusivity followed Arrhenius behaviour. For ageing durations that exceed saturation time, ester bond hydrolysis occurs and leads to chain scission within the polymer network. This chain scission rate could be described using a first-order reaction and followed Arrhenius behaviour with an activation energy of 71 kJ/mol. From a mechanical point of view, hydrolysis leads to large changes in both stress and strain at break. A gradual decrease in stress at break was observed for all ageing temperatures. Nevertheless, strain at break first increases during ageing and then drops off when the crosslink density is below a critical value of 1.25 kg/mol. After considering more than 30 ageing conditions, relationships between the average crosslink density and these ultimate properties were proposed and discussed here.

1. Introduction

Polyurethane (PU) elastomers are widely used in marine environments due to their properties such as their simple fabrication, affordable cost and good thermal properties [1–3]. In terms of PU durability, the nature of the polyol plays a major role [4]. When PUs are made with polyether, the material exhibits good hydrolysis resistance (even if the urethane bonds undergo hydrolysis at a high temperature) but poor resistance to oxidation. On the contrary, when PU are made with polyester, they are sensitive to hydrolysis [5] but have good oxidation resistance [6]. Polybutadiene can also be used for the polyol in very specific cases to reduce water absorption in PU, although it is highly sensitive to oxidation due to the presence of a double bond [7]. Therefore, the choice of PU depends on the use of the material in service conditions. Here we will focus on polyester urethane.

When used in a marine environment, PU based on polyester absorbs water according to Fickian behaviour [8]. The amount of water is about 2.5% at 80 °C with the water diffusion coefficient close to 1.3×10^{-10} m^2. s^{-1}. The presence of water within the material does not greatly change the mechanical properties of the PU [9], as mobility between macromolecular chains is already very high even without water. PU based on polyester is composed of a succession of urethane and ester functions. Due to the presence of the ester group in the backbone of the polymer, hydrolysis occurs when PU is in contact with water [10]. It has been observed that ester groups hydrolyse faster than urethane linkages [11]. This reaction between the ester group and water leads to a chain scission process that results in the formation of two chain ends: one with a hydroxyl group and the other with a carboxyl group (COOH) [10]. The latter is an acid group that becomes a catalyst and thus accelerates the degradation process [12], with carbodiimide being used to avoid this acceleration of hydrolysis [9]. This hydrolysis reaction has been widely studied in the literature and depends largely on the nature of the polyester polyol. Hydrolysis kinetic studies on polyester-based PU give activation energies ranging from 68 to 83 kJ.mol^{-1} [12–14]. These differences are explained by the wide range of existing polyester polyols as well as the many possible combinations in the chemistry of polyurethanes [15]. Murata et al. showed that the hydrolytic stability of a polyester-based PU can be changed by varying the total carbon number of the polyol [16]. Regarding the macroscopic impact, chain scissions produced by hydrolysis are one of the parameters that largely affects the mechanical behaviour of PU and especially stress and strain at break [8,13,17].

---

* Corresponding author.
  E-mail address: pierre.yves.le.gac@ifremer.fr (P.-Y. Le Gac).
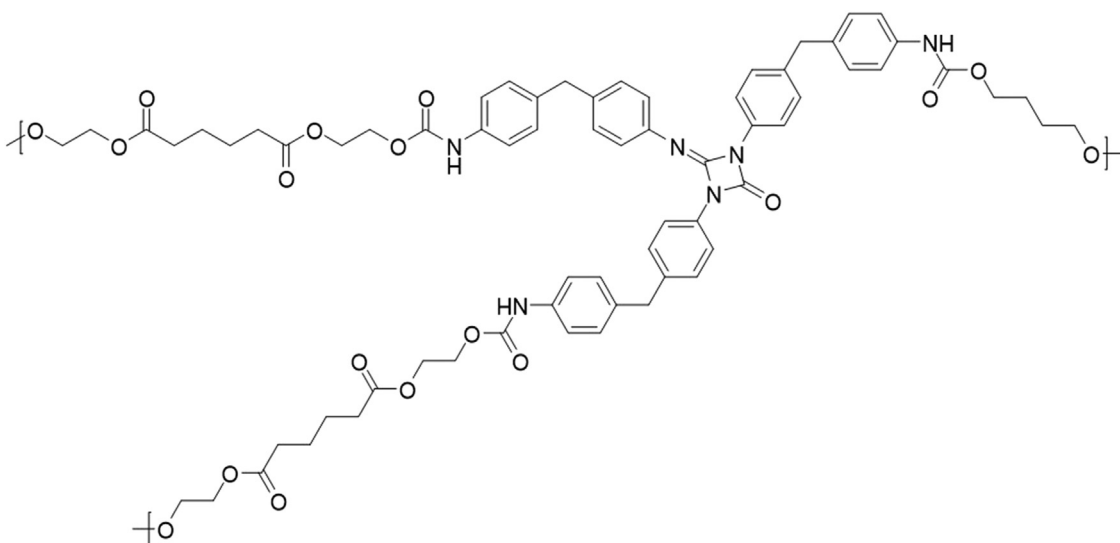
Fig. 1. PU based on polyester chemical structure.

Property	Value
Glass transition temperature	−30 °C
Density	1.23
Reinforcing fillers	None
Hardness	80 Shore A

Despite the existence of studies with a qualitative description of the ultimate properties of PU during hydrolysis, to our knowledge, the relationship between network properties and mechanical behaviour is not described in the literature for crosslinked PU. This type of relationship is needed to perform a reliable prediction of the ultimate tensile properties during ageing and thus ensure that the material is suitable for application. This study aims to set up and discuss such relationships between the PU network and its mechanical behaviour. In this study, a polyester-based PU is aged in seawater at temperatures ranging from 40 °C to 90 °C. First, water absorption is characterized, and then chemical degradation is considered at the macroscopic scale with both soluble fraction and chain scission measurements. In the meantime, tensile results are presented as a function of the degradation degree. Finally, these results are discussed to highlight the relationships between the concentration of elastically active chains and mechanical properties.

2. Materials and methods

2.1. Materials

The material considered in this study is a polyester-based polyurethane. Two types of polyols are used in the formulation: poly (ethylene adipate) with a molar mass of 2000 g/mol as the main polyol and butanediol as a chain extender. The chemical structure involved in the polyurethane network is shown in Fig. 1. In addition, a mixture of 2,4 and 4,4′-diphenylmethane di-isocyanate (MDI) was used as the hardener. Samples were produced in a 2 mm-thick sheet and post-cured at 120 °C for 5 h under inert atmosphere prior to ageing. The main properties of the studied material are summarized in Table 1. Carbodiimides were sufficiently added to avoid the catalytic effects of the degradation

product such as carboxylic acids. The hydrolysis rate is thus not expected to be accelerated.

2.2. Ageing

Samples were immersed in natural seawater from Brest Bay, France, at temperatures ranging from 40 °C to 90+/−2 °C in 50 L tanks. Water was continually renewed to avoid any water contamination during ageing. Afterwards, ageing samples were removed from the ageing tank, dried at 40 °C in a desiccator for 24 h, and characterized according to the following protocol.

2.3. Mass changes

During immersion, square samples are periodically weighed using a Sartorius LA 310 S balance with an accuracy of 0.1 mg. The sample size is 50 mm*50 mm, with a thickness of 2 mm; three samples are tested for each condition. Samples are dried at 40 °C in a desiccator for at least 24 h prior to immersion. The mass change (w) is calculated as follows:

$$w\ (\%) = \frac{m(t) - m_0}{m_0} \times 100 \tag{1}$$

Where m(t) is the sample mass after immersion at time t in grams, and m_0 is the initial mass of the sample in grams.

2.4. Swelling in solvent

Swelling measurements are carried out by immersing the samples in toluene at room temperature according to the standard ISO1817. Sample mass before immersion (m_b), after saturation by toluene (m_s), and after drying at 80 °C in an oven until the mass reaches an equilibrium (m_d) are made using a Sartorius LA 310 S balance with an accuracy of 0.1 mg. Soluble fractions (F_S) and the volume fraction of rubber (Φ_r) are calculated using the following equations:

$$F_S(\%) = \frac{m_b - m_d}{m_b} \times 100 \tag{2}$$

$$\Phi_r = \frac{(m_d/\rho_p)}{(m_d/\rho_p) + (m_s - m_d)/\rho_s} \tag{3}$$

ρ_s and ρ_p are respectively the density of the solvent and polymer. The molecular weight between crosslinks (M_c) for a tetra functional network is expressed (Eq. (4)) according to the Flory-Rehner

$$M_c = \frac{-\rho_p V s \Phi_r^{\frac{1}{3}}}{\left[\frac{\chi \Phi_r^2}{2+ln(1-\Phi_r)+\Phi_r}\right]} \qquad (4)$$

In the case of a network with a functionality f, this equation can be written as follows:

$$\ln(1-\phi_r) + \phi_r + \chi \phi_r^2 = -\frac{\rho_p}{M_c} V_s \left(\phi_r^{1/3} - \frac{2\phi_r}{f}\right) \qquad (5)$$

Where V_S is the molar volume of the solvent and χ is the interaction parameter between the solvent and the polymer. Here, χ is calculated by the Bristow and Watson semi-empirical equation [19] (Eq. (6)) according to the literature [20]:

$$\chi \approx 0.34 + \frac{Vs}{RT} \times (\delta_s - \delta_p)^2 \qquad (6)$$

Where R is the universal gas constant equal to 8.314 J.K^{-1} mol^{-1} and T the temperature equal to 298 K. δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively [20,21]. For the polyurethane-toluene system, χ is equal to 0.56.

In this paper, even if two types of polyols are used in the PU, the polyurethane network is considered trifunctional ($f = 3$) as shown in Fig. 1. Thus, the concentration of elastically active network chains $v(t)$ can be expressed by the following equation [22]:

$$v(t) = \frac{2}{3M_C} \qquad (7)$$

2.5. Tensile tests

Tensile tests are performed according to the ISO 37 standard [23] using dried samples. Type 3 dumbbell samples are tested at 10 mm/min using a 10 kN tensile machine from Instron. Load is measured using a 10 kN load cell. Strain is measured using an AVE2 optical extensor directly linked to the tensile machine; the strain presented here is thus the "true" strain. At least three samples are tested for all conditions considered in this study, and the results are averaged.

3. Results

3.1. Water absorption

Fig. 2 represents mass changes (w) corresponding to water uptake as a function of normalized immersion time. For all temperatures considered here, Fickian behaviour is first observed with a linear increase of mass before reaching a plateau at w$_\infty$. The lines represent the identified Fickian law (Eq. (8)) and symbols the experimental data.

$$\frac{dw}{dt} = D\frac{\partial^2 w}{\partial x^2} \qquad (8)$$

Considering the samples as thin sheets of thickness l, the relative mass uptake $\frac{w(t)}{w_\infty}$ can be simulated using the expression below (Eq. (9)) according to the literature [24].

$$\frac{w(t)}{w_\infty} = 1 - \frac{8}{\pi^2} \sum_{n}^{\infty} \times \frac{1}{(2n+1)^2} \times exp\left[\frac{-D(2n+1)^2\pi^2 t}{l^2}\right] \qquad (9)$$

It is thus possible to determine the water diffusion coefficient D and the water solubility S assuming Henry's law (Eq. 10) for temperatures ranging from 25 °C to 90 °C.

$$S = \frac{w_\infty \times \rho_p}{M_{water} \times P_V} \qquad (10)$$

P_V is the vapour pressure of water (bar) that depends on temperature and M_{water} is the molar mass of water equal to 18 g.mol^{-1}.
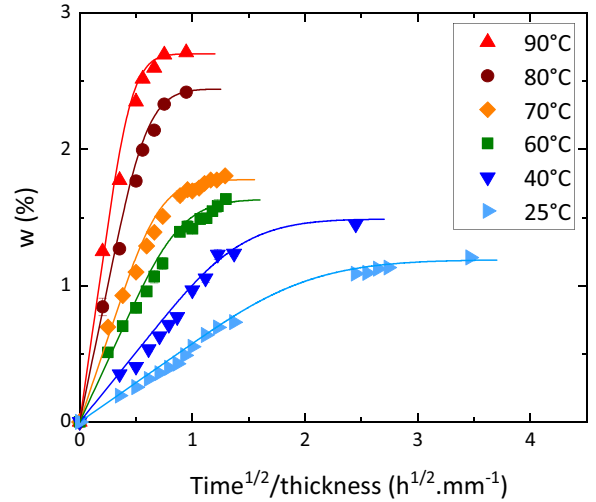

Fig. 2. Mass changes (w) of a polyurethane ester in immersion in seawater at different temperatures, continuous lines correspond to fickian behaviour.

These two parameters are plotted as a function of water temperature in Fig. 3a and 3b. As expected, an increase in water temperature leads to an increase in water diffusivity [25]. Moreover, it appears that the temperature dependence of the water diffusion coefficient can be described with Arrhenius behaviour and activation energy of 44 kJ/mol. This value is in accordance with existing knowledge in the literature about water diffusion in polymers [13,26]. Fig. 3b focuses on the impact of testing temperatures on water solubility in the PU considered here, with the calculation made using Henry's law with water activity equal to 0.98 [27]. Once again, it is possible to describe the temperature dependence using an Arrhenius law with an activation energy of 32 kJ/mol. Based on these results, one can predict water absorption in this material in all conditions when knowing the sample size, temperature, and humidity level.

3.2. Hydrolysis leading to chain scissions

The soluble fraction (F$_S$) is a direct measurement of the polymer weight that is not linked to the initial polymer network. It is well known that when polyester-based PU is exposed to a humid environment, chain scission occurs within the polymer network through a hydrolysis reaction [12]. This increase in soluble fraction as a function of ageing time in seawater (Fig. 4) clearly shows that chemical degradation occurs within the material. It is worth noting that water diffusion is much faster than chemical degradation, meaning that the degradation is homogenous through sample thickness. As an example, at 60 °C in seawater, water saturation is reached after 7 h, whereas no chemical degradation is measured after several days. It appears the soluble fraction is a sensitive indicator of chain scission, but it is not straightforward when assessing a quantitative value. For this purpose, the assessment of numbers of elastically active chains though swelling is preferred (see next section).

The concentration of elastically active network chains (v) can be determined through swelling tests using the Flory-Rehner theory [18]. As expected during hydrolysis, a decrease in v is observed regardless of the ageing temperature (Fig. 5). However, for the lowest exposure temperature (40 °C), a slight induction period can be noticed. By increasing the ageing temperature, a faster decrease in the concentration of elastically active chains occurs.
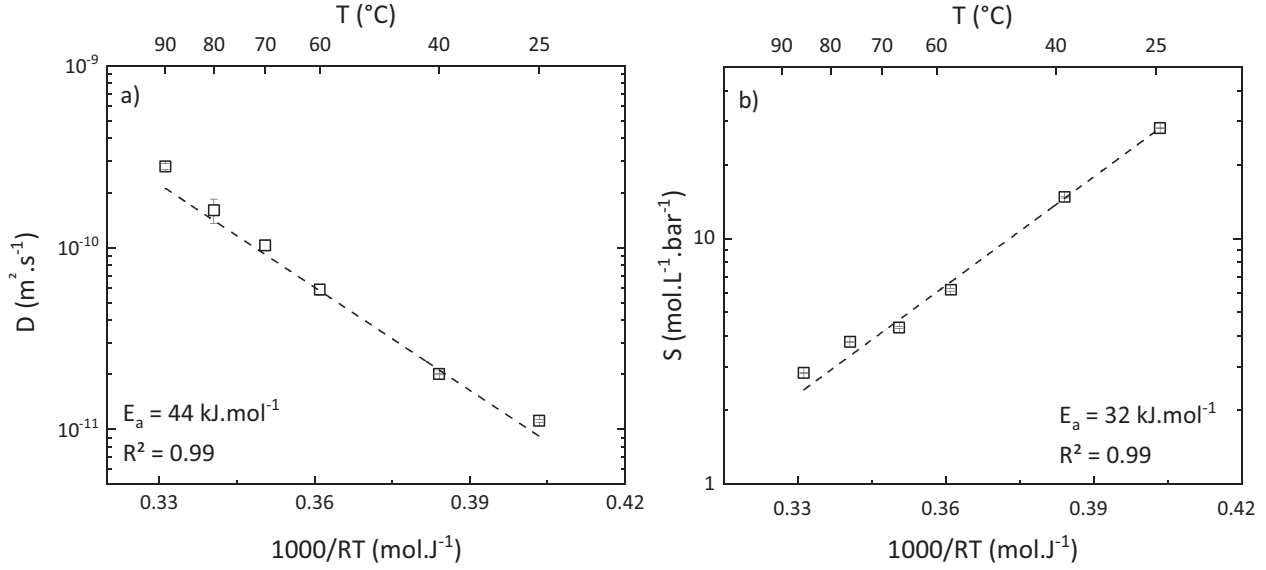
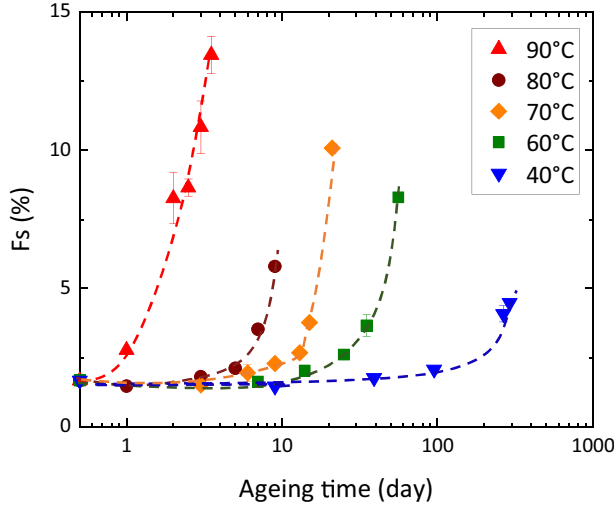**Fig. 3.** Effect of temperature on water diffusion D (a) and solubility S (b).

Fig. 4. Soluble fraction (Fs) as a function of ageing time for all ageing temperatures. The dotted lines are a guide for eyes.
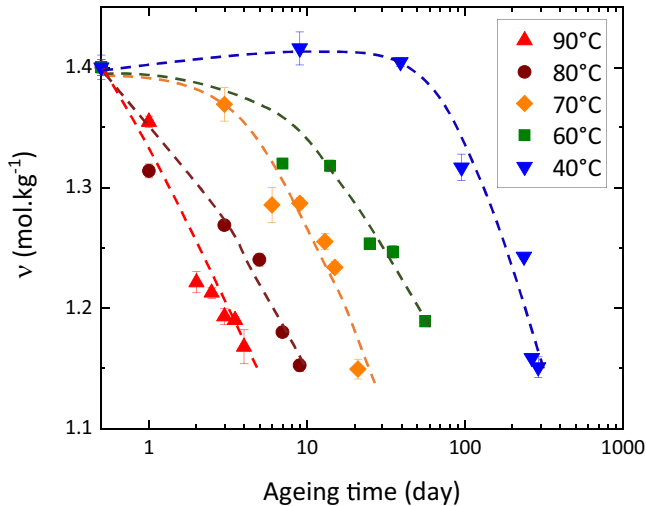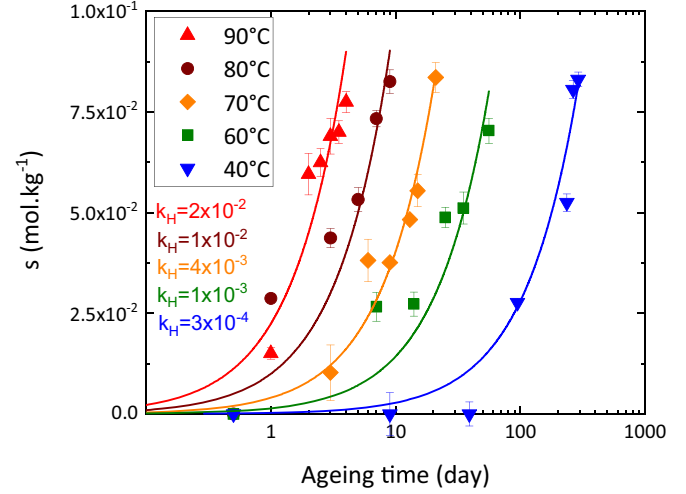

Fig. 6. Chain scission (s) as a function of ageing time for each ageing temperature, continuous curves correspond to constant chain scission rate model.

3.3. Hydrolysis kinetic study

Let us now focus on the hydrolysis rate in a quantitative way using the chain scission (s) that is considered by Eq. (11) [28] even if 2 types of polyols are used in the PU.

$$s(t) = \frac{1}{3}(\nu_0 - \nu(t)) \tag{11}$$

Where s is the number of chain scissions (in kg/mol), ν_0 and $\nu(t)$ are the initial concentration of elastically active network chains equal to 1.40 kg/mol determined using Eq. (7) before immersion and after ageing respectively.

Following this approach, chain scission as a function of ageing time is plotted in Fig. 6 on a log scale for all ageing temperatures. Curve fitting according to Eq. (11) was used to assess the hydrolysis rate as a function of ageing temperature.

$$ds/dt = k_H[H_2O] \tag{12}$$

As a result, we can propose in a first approach that the chain scission rate (ds/dt) is related to the water content in the polymer for a given temperature as follows (Eq. 12). This equation
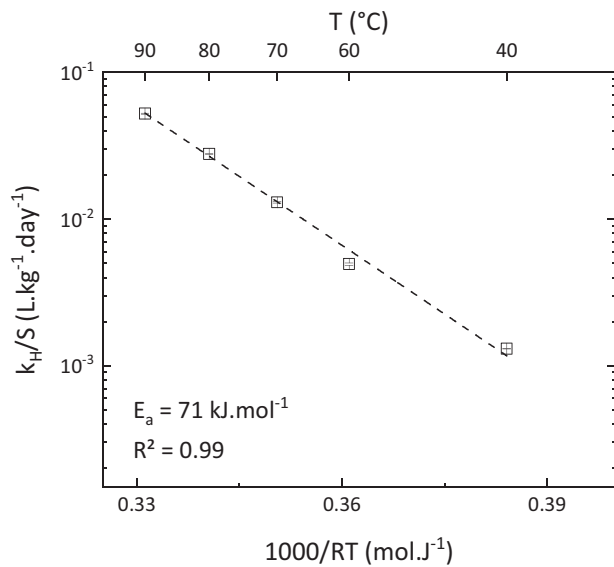

Fig. 5. Concentration of elastically active network chains (ν) as a function of ageing time. The dotted lines are a guide for eyes.

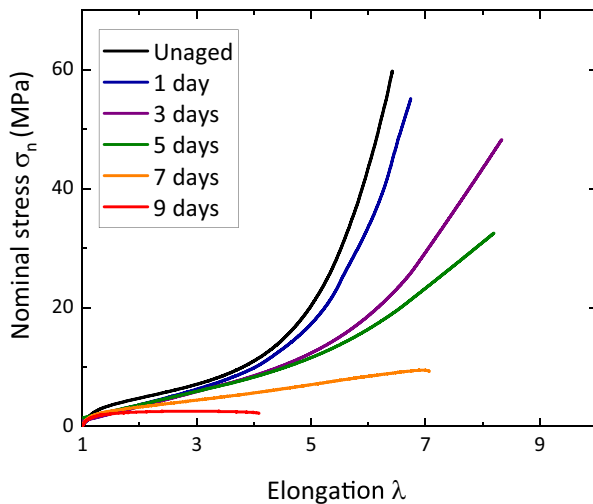**Fig. 7.** Effect of temperature on hydrolysis kinetic.

Fig. 8. Tensile curves of samples aged in seawater at 80 °C.

(Eq. (12)) can be used here thanks to the fact that PU undergoes only one type of chemical degradation (i.e. hydrolysis), the degradation is not auto accelerated because of the presence of carbodiimide within the formulation and the hydrolysis reaction is not limited by water diffusion (see above). Where k_H is the hydrolysis constant, and $[H_2O]$ the water content.

This hydrolysis rate k_H is then normalized by water solubility (because water content within the polymer depends on the testing temperature) and plotted as a function of temperature in Fig. 7. We observed that the degradation rate follows Arrhenius behaviour, which can easily be used to evaluate the chain scission rate as a function of ageing conditions in practice. The activation energy is here equal to 71 kJ/mol, which is in accordance with existing data where activation energy varies from 68 to 81 kJ/mol depending on the nature of the PU [12]. Let us now focus on the impact of chain scission on the tensile behaviour of the polymer.

3.4. Impact of chain scissions on tensile properties

Tensile behaviour has been characterized at 21 °C for all ageing conditions. Fig. 8 plots the stress/strain curves obtained before and after ageing at 80 °C. The unaged material, in black, shows typ-

ical non-linear behaviour for rubber with a low modulus (several MPa) and large extensibility up to $\lambda = 6$. It is worth noting that the stress increases significantly for an elongation above 4 due to the formation of crystallites within the rubber using the strain-induced crystallization process [6,29]. During ageing, an increase in maximal elongation is first observed (up to 5 days at 80 °C), and then a drop occurs. In the meantime, a gradual decrease in both maximal stress and modulus is observed. The same behaviour is observed for all ageing temperatures as shown in Fig. 9a and 9b. Other studies on polyester-based thermoplastic PU highlighted the same mechanical behaviour when materials undergo a chain scission process [13,30]. In 2010, the results of Neffe et al. on polyester-based PU elastomers showed an increase in elongation at break and then a decrease during hydrolysis. However, the sudden drop in this elongation at break was not discussed [31]. This point will be considered below. Similar maximal elongation changes as a function of chain scission have been observed in the case of ethylene propylene diene monomer under irradiation [32].

4. Discussion

This discussion considers the potential relationships between the types of network through the concentration of elastically active chains (ν) and the ultimate properties measured during tensile tests. In fact, based on Fig. 6, it is thus possible to determine ν within the polymer as a function of the environment. However, the most interesting properties in practice are the ultimate properties, namely maximal elongation and stress. It is thus necessary to study the relationships between these parameters.

First let us consider stress at break. During ageing, for all temperatures considered here, a gradual decrease in stress a break is observed. Moreover, Fig. 10 shows a general trend between maximal stress and ν regardless of the ageing temperature. Thanks to this curve, it is possible to directly link the concentration of elastically active chains using a simple linear relationship. To the best of our knowledge, this kind of relationship is highlighted for the first time in crosslinked elastomers. However, it has already been observed in thermoplastic elastomers [33] and attributed to changes in strain-induced crystallization: as chain scission occurs within the polymer, the crystallization process becomes harder to initiate.

In the same way, a general trend between the elongation at break and the concentration of elastically active chains is evidenced in Fig. 11 whatever is the ageing temperature. Here again, the general behaviour is independent of ageing temperature. However, two trends are observed depending on the ν value. When ν is between 1.25 and 1.4 kg/mol, an increase in elongation at break is observed with the chain scission process. On the contrary, when ν is below 1.25 kg/mol, a drop-off occurs in maximal strain due to embrittlement in the PU. A critical value of elastically active chains can thus be defined here for the first time for crosslinked elastomers. This value is named ν_{crit} and is equal to 1.25 kg/mol.

Let us first consider the increase in elongation at break with chain scission when ν is above the critical value. Based on the rubber elasticity theory, the maximal elongation is related to the maximal extension of the macromolecular chain within the network, meaning that $\lambda_b \, \alpha \, \nu^{-1/2}$ [34]. Fig. 11 plots λ_b as a function of $\nu^{-1/2}$ for the 30 ageing conditions considered in this study, clearly highlighting a general trend between these two values. This means that the increase in elongation at break can be described based on theoretical considerations. This point has been already observed but only when crosslinking is predominant overs chain scission. For instance, Le Gac et al. showed that λ_b is proportional to $\nu^{-1/2}$ in the case of an unfilled polychloroprene rubber [35]. For filled natural rubbers where crosslinking is dominant during oxidation, Ahagon et al. [36] point out a relationship equal to $\lambda_b \, \alpha \, \nu^{-3/4}$. This power law was also found by Grasland et al. [37] on
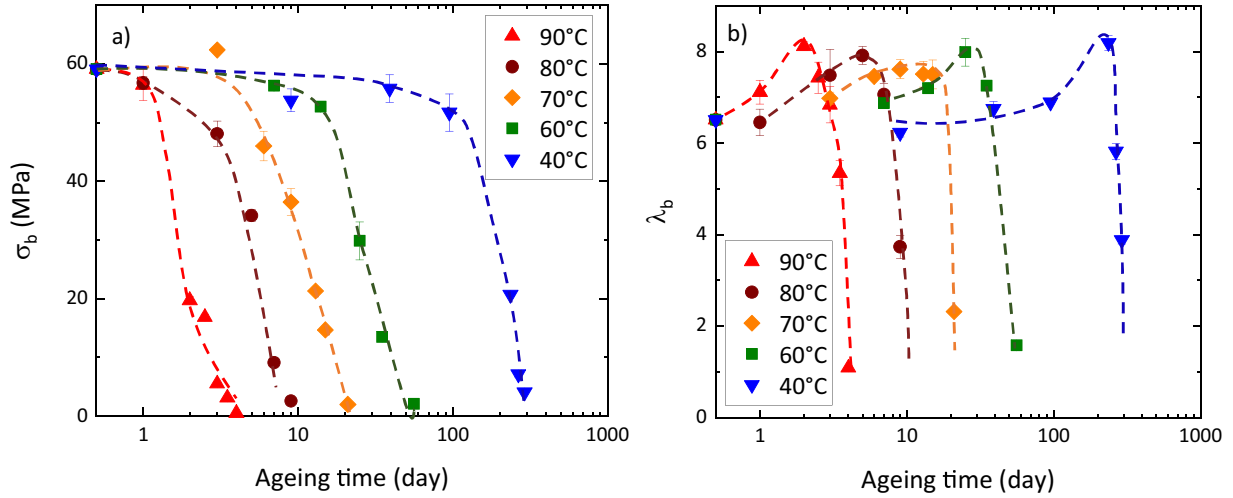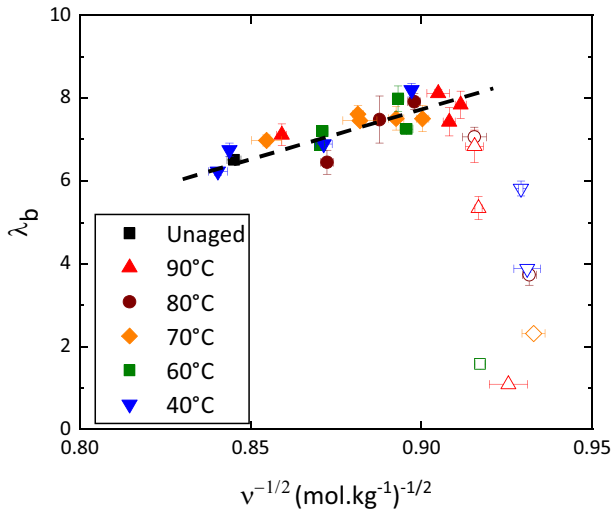
Fig. 9. Stress at break (a) and elongation at break (b) of polyurethane as a function of ageing time for all the temperatures considered here. The dotted lines are a guide for eyes.
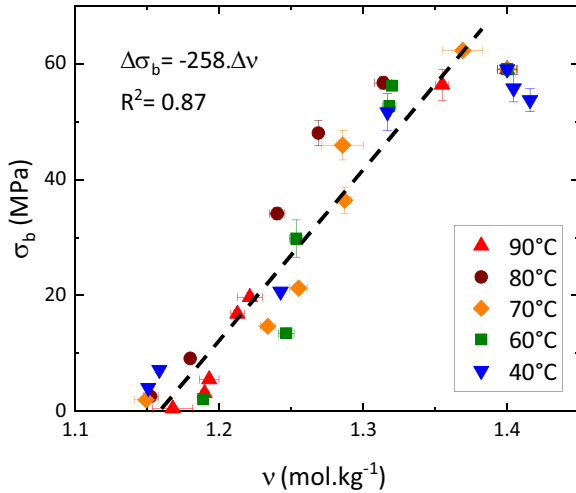
Fig. 10. Relationship between stress at break (σ_b) and concentration of elastically active chains (ν).

Fig. 11. Relationship between elongation at break and elastically active chains, with the dotted line corresponding to ν values above ν_{crit}.

unfilled natural rubbers. This means that for $\lambda_b \, \alpha \, \nu^{-n}$, the value of n is close to 0.5 independently of the nature of the rubber.

For high degradation levels, namely ν below ν_{crit}, a drop in elongation at break occurs, meaning that changes in elongation at break with ageing can no longer be described using rubber elasticity theory (empty dots in Fig. 11). The exact origin of this drop remains unclear. However, based on the tensile curves presented in Fig. 8, we can observe a change in the tensile behaviour of the material for samples aged for 7 and 9 days at 80 °C (i.e., $\nu < \nu_{crit}$); the upturn observed for λ above 4 and attributed to strain-induced crystallization is no longer observed further investigations are need to conclude here. This observation suggests that the crystallization process during the tensile test does not occur when the concentration of elastically active chains is below 1.25 kg/mol. The origin of embrittlement needs further attention such as suppression of strain-induced crystallization or bimodal structure of the network (before and/or after chain scission). For the first mechanism, X-Rays in situ experiments are underway on the same networks as mentioned. For the second mechanism, multiple quantum proton NMR experiments on the network are also in progress.

5. Conclusions

Polyester-based polyurethane was aged in seawater for a year at five different temperatures ranging from 40 °C to 90 °C. Rapid water absorption occurs when the PU is placed in water, which can be described using a Fickian model. Both the water diffusion coefficient and water solubility are affected by the testing temperature. The impact of the water temperature can be described using the Arrhenius law for these two parameters.

The presence of water within the polymer leads to hydrolysis of the ester bond, and thus chain scission occurs within the elastomer network. This chain scission process results in an increase in the soluble fraction and a decrease in elastically active chains. It is worth noting that the hydrolysis process here is not autocatalyzed due to the presence of carbodiimide, and thus the chain scission rate and the associated kinetic constant can be easily estimated based on our results.

Chain scission leads to large changes in the mechanical behaviour of the PU, especially ultimate properties. A gradual decrease in maximal stress is observed here for all ageing temperatures under consideration. A linear relationship is found between the concentration of the elastically active chains of the PU and its stress at break; this relationship can be useful

to predict the long-term behaviour of polymers. Chain scission first leads to an increase in elongation at break, and then a drop-off occurs. A critical elastically active chain value is introduced to describe this behaviour: when $\nu > \nu_{crit}$, the material is ductile and λ_{max} increases with the chain scission process, whereas when $\nu < \nu_{crit}$, the material is brittle; here ν_{crit} is equal to 1.25 kg/mol. The increase in λ_{max} with chain scission can be described based on the rubber elasticity theory, allowing the prediction of the ultimate properties of PU during hydrolysis.

Declaration of Competing Interest

None.

CRediT authorship contribution statement

Sabrina Taourit: Investigation, Data curation, Writing – original draft, Writing – review & editing. **Pierre-Yves Le Gac:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision. **Bruno Fayolle:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision.

Acknowledgements

References

[1] P.Y. Le Gac, D. Choqueuse, D. Melot, Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions, Polym. Test 32 (8) (2013) 1588–1593.

[2] P. Davies, G. Evrard, Accelerated ageing of polyurethanes for marine applications, Polym. Degrad. Stab. 92 (8) (2007) 1455–1464.

[3] T. Ramotowski, K. Jenne, NUWC XP-1 polyurethane-urea: a new," acoustically transparent" encapsulant for underwater transducers and hydrophones, *Oceans 2003. Celebrating the Past... Teaming Toward the Future (IEEE Cat. No. 03CH37492)* (Vol. 1, pp. 227-230), IEEE, 2003.

[4] M. Szycher, Structure–property relations in polyurethanes, *Szycher's Handbook of Polyurethanes, 2nd ed.; Szycher, M., Ed*, 37-86, 2012.

[5] I.R. Clemitson, Chemistry of polyurethanes, in: Castable Polyurethane Elastomers, 2nd ed., CRC Press, 2015, pp. 13–44.

[6] C. Prisacariu, Chemistry of polyurethane elastomers, Polyurethane Elastomers: from Morphology to Mechanical Aspects, Springer Science & Business Media, 2011.

[7] M. Celina, A.C. Graham, K.T. Gillen, R.A. Assink, L.M. Minier, Thermal degradation studies of a polyurethane propellant binder, Rubber Chem. Technol. 73 (4) (2000) 678–693.

[8] T. Pretsch, I. Jakob, W. Müller, Hydrolytic degradation and functional stability of a segmented shape memory poly (ester urethane), Polym. Degrad. Stab. 94 (1) (2009) 61–73.

[9] F. Xie, T. Zhang, P. Bryant, V. Kurusingal, J.M. Colwell, B. Laycock, Degradation and stabilization of polyurethane elastomers, Prog. Polym. Sci. 90 (2019) 211–268.

[10] C.S. Schollenberger, F.D. Stewart, Thermoplastic polyurethane hydrolysis stability, J. Elastoplast. 3 (1) (1971) 28–56.

[11] J.V. Cauich-Rodríguez, L.H. Chan-Chan, F. Hernandez-Sánchez, J.M. Cervantes-Uc, Degradation of polyurethanes for cardiovascular applications, Adv. Biomater. Sci. Biomed. Appl. (2013) 51–82.

[12] D.W. Brown, R.E. Lowry, L.E. Smith, Kinetics of hydrolytic aging of polyester urethane elastomers, Macromolecules 13 (2) (1980) 248–252.

[13] A. Bardin, P.Y. Le Gac, S. Cérantola, G. Simon, H. Bindi, B. Fayolle, Hydrolytic kinetic model predicting embrittlement in thermoplastic elastomers, Polym. Degrad. Stab. 171 (2020) 109002.

[14] M.R. Salazar, J.M. Lightfoot, B.G. Russell, W.A. Rodin, M. McCarty, D.A. Wrobleski, … R.T. Pack, Degradation of a poly (ester urethane) elastomer. III. Estane 5703 hydrolysis: experiments and modeling, J. Poly. Sci. Part A 41 (8) (2003) 1136–1151.

[15] J.P. Santerre, K. Woodhouse, G. Laroche, R.S. Labow, Understanding the biodegradation of polyurethanes: from classical implants to tissue engineering materials, Biomaterials 26 (35) (2005) 7457–7470.

[16] S. Murata, T. Nakajima, N. Tsuzaki, M. Yasuda, T. Kato, Synthesis and hydrolysis resistance of polyurethane derived from 2, 4-diethyl-1, 5-pentanediol, Polym. Degrad. Stab. 61 (3) (1998) 527–534.

[17] A. Pegoretti, J. Kolarik, A. Penati, Hydrolytic stability and mechanical properties of poly (ester urethanes), Die Angewan. Makromol. Chem.: Appl. Macromol. Chem. Phys. 220 (1) (1994) 49–60.

[18] P.J. Flory, J. Rehner Jr,, Statistical mechanics of cross-linked polymer networks II. Swelling, J. Chem. Phys. 11 (11) (1943) 521–526.

[19] G.M. Bristow, W.F. Watson, Cohesive energy densities of polymers. Part 1.—Cohesive energy densities of rubbers by swelling measurements, Trans. Faraday Soc. 54 (1958) 1731–1741.

[20] M. Barlkani, C. Hepburn, Determination of crosslink density by swelling in the castable polyurethane elastomer based on 1/4-cyclohexane diisocyanate and para-phenylene diisocyanate, Iran. J. Poly. Sci. Technol. 1 (1) (1992) 1–5.

[21] D.W. Van Krevelen, K. Te Nijenhuis, Properties of polymers: Their Correlation With Chemical structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Elsevier, 2009.

[22] J.P. Pascault, H. Sautereau, J. Verdu, R.J. Williams, Thermosetting Polymers, CRC Press, 2002.

[23] ISO, Rubber, Vulcanized or Thermoplastic – Determination of Tensile Stress-strain Properties, ISO/TC 45/SC 2-Rubber and Rubber Products, 2011.

[24] J. Crank, The Mathematics of Diffusion, Oxford University Press, 1979.

[25] C. Slater, C. Davis, M. Strangwood, Compression set of thermoplastic polyurethane under different thermal–mechanical-moisture conditions, Polym. Degrad. Stab. 96 (12) (2011) 2139–2144.

[26] J.A. Barrie, A. Nunn, A. Sheer, The sorption and diffusion of water in polyurethane elastomers, in: Permeability of Plastic Films and Coatings, Springer, Boston, MA, 1974, pp. 167–182.

[27] P.Y. Le Gac, G. Roux, P. Davies, B. Fayolle, J Verdu, Water clustering in polychloroprene, Polymer (Guildf) 55 (12) (2014) 2861–2866.

[28] E. Richaud, P. Gilormini, M. Coquillat, J. Verdu, Crosslink density changes during the hydrolysis of tridimensional polyesters, Macromol. Theory Simul. 23 (5) (2014) 320–330.

[29] C. Hepburn, Polyurethane Elastomers, 2nd ed., Springer Science & Business Media, 2012.

[30] D.G. Thompson, J.C. Osborn, E.M. Kober, J.R. Schoonover, Effects of hydrolysis-induced molecular weight changes on the phase separation of a polyester polyurethane, Polym. Degrad. Stab. 91 (12) (2006) 3360–3370.

[31] A.T. Neffe, G. Tronci, A. Alteheld, A. Lendlein, Controlled change of mechanical properties during hydrolytic degradation of polyester urethane networks, Macromol. Chem. Phys. 211 (2) (2010) 182–194.

[32] A. De Almeida, L. Chazeau, G. Vigier, G. Marque, Y. Goutille, Ultimate and toughness properties of γ-irradiated EPDM, Eur. Polym. J. 97 (2017) 178–187.

[33] A. Bardin, P.Y. Le Gac, H. Bindi, B. Fayolle, Relationships between molar mass and fracture properties of segmented urethane and amide copolymers modified by chemical degradation, J. Polym. Sci. 58 (22) (2020) 3170–3182.

[34] Treloar, L.R.G. (1975). *The physics of rubber elasticity*.

[35] P.Y. Le Gac, P.A. Albouy, B. Fayolle, J Verdu, Relationship between macromolecular network and fatigue properties of unfilled polychloroprene rubber, Polym. Degrad. Stab. 192 (2021) 109669.

[36] A. Ahagon, Extensibility of black filled elastomers, Rubber Chem. Technol. 59 (2) (1986) 187–203.

[37] F. Grasland, L. Chazeau, J.M. Chenal, J. Caillard, R. Schach, About the elongation at break of unfilled natural rubber elastomers, Polymer (Guildf) 169 (2019) 195–206.