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# EFFECT OF THERMAL AGING ABOVE THE GLASS TRANSITION TEMPERATURE ON THE MECHANICAL PROPERTIES OF RIGID PVC TUBE

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## Abstract

Thermal aging of standard samples of rigid PVC (u-PVC) taken from plastic tubes near and above the glass transition temperature (Tg) was used to investigate the effect of elevated temperatures on the mechanical properties of rigid (u-PVC) tubes used in industrial areas. Three aging protocols were used, each lasting 90 days at 80 °C, 100 °C, and 120 °C. Crosslinking and chain scission reactions changed the tensile properties, either increasing them or decreasing them. For all three aging protocols, it was discovered that Young's modulus increased with aging time. Furthermore, the rate of increase of the modulus was observed to increase with aging temperature. The Yield stress showed the same pattern. Their increase in both cases is due to material stiffening caused by a crosslinking process. This last one was revealed by DSC, where Tg increased as a result of the chemical process. The decrease in elongation at break, which occurred progressively in all aging protocols and more precisely at temperatures above Tg, on the other hand, demonstrated the relationship between chain scissions and temperature. The material becomes more brittle as the temperature rises. Brittleness is caused by a high activity of chain scissions on the surface sample, which allows micro-cracks to form. When subjected to tensile forces, cracks propagate from the surface toward the sample's thickness.

**Keywords**: (u-PVC) tube; thermal aging; glass transition temperature; tensile properties; crosslinking; chain scissions.

## Introduction

Most thermoplastic pipes with sufficient Ultra Violet screens and heat stabilizers are weather resistant. This resistance is affected by the temperature, humidity, and geographical location [1]. PVC tubes are used in a variety of industries (industrial,

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agricultural, etc.) and are exposed to a wide range of environmental factors. One of the most significant is most likely high service temperature.

According to several studies, the thermal aging of poly (vinyl chloride) is frequently accompanied by various processes such as dehydrochlorination, color change, crosslinking between the main chains, and chain scission reactions. All of this has a significant impact on the material's microstructure and mechanical properties [1-5].

The final section of this study was carried out at temperatures lower than the glass transition temperature, which is approximately (Tg =80 °C) [6, 7]. The aging temperature was shown to increase the rate of oxidation reactions while negatively affecting the microstructure due to chain scission and crosslinking reactions.

To fully encompass the role of aging temperature, the present study aims to highlight the effects of thermal aging at temperatures near or above glass transition on the structural and mechanical properties of rigid poly (vinyl chloride) tubes stabilized with a lead stabilizer system and used for either water transportation for irrigation or in industrial areas.

Dumbbell-shaped test pieces cut from the original PVC tube were exposed to temperatures of 80, 100, and 120 °C in thermo-regulated ovens that were left open to the atmosphere. Tensile tests were used to determine mechanical properties such as Young's modulus (E), yield stress ($\sigma_y$), stress at break ($\sigma_b$), and elongation at break ($\varepsilon_b$). Differential Scanning Calorimeter (DSC) was used to measure the change in thermal properties (glass transition temperature Tg, dehydrochlorination peak d'HCl).

## Experimental

*Material*

The material used in this study is a rigid (u-PVC) unplasticized polyvinyl chloride tube (Outside diameter = 63 mm, thickness = 3 mm ± 0.3, nominal pressure = 10 bars) produced by PLASTUB-society (Ghardaïa, Algeria) according to the ISO: EN-1452-2 standard.

The composition in weight of the dry-blend used for the tube production is 86% of PVC powder; 2% of the as-received stabilizer systems (tribasic lead sulfate/lubricant; Chemson-Polymer-Additive AG, Austria); 5% Calcium carbonate filler (OMYALITE-95T, Omya-SAS, Paris, France); and 7% Carbon black.

*Sampling and aging protocol*

Before aging, a number of specimens are picked up from the original rigid PVC tube and cut out by a mill cutter as dumbbell-shaped test pieces according to the ISO 6259-2 standard. The test pieces’ aspect and dimensions are indicated in Fig. 1. Three thermal aging protocols were performed on the test pieces at 80 °C, 100 °C and 120 °C in thermo-regulated ovens open to the atmosphere. Sampling was done monthly throughout the 90 day aging protocols.

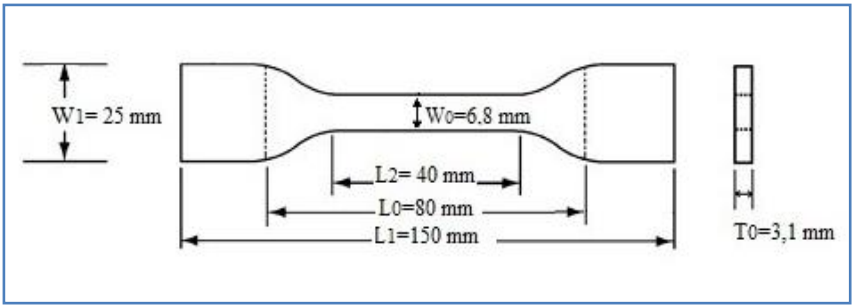


*Fig. 1. Tensile test piece of rigid PVC [6].*

### *Characterization techniques*

#### a) Tensile Test

The mechanical tests were carried out using a tensile test machine, Rochdale model 500-50AT (England). They were performed according to the ISO 6259-2 standard at room temperature (T = 23 °C ± 2 °C) and a relative humidity (RH ≈ 30% ± 5%). The strain rate was fixed at a low value to the yield point ($d\varepsilon/dt = 1 \times 10^{-3}$ $s^{-1}$) and maintained until a fracture occurred [8].

The tensile test results are presented in terms of the nominal stress (Eq. 1) and nominal strain (Eq. 2).

$$\sigma = \frac{F}{(W_0 \times T_0)} \tag{1}$$

Where:
$W_0$: Width of the narrow section.
$T_0$: Thickness sample.

$$\varepsilon = \left(\frac{L}{L_0}\right) - 1 \tag{2}$$

Where:
$L_0$: Initial distance between grips.
$L$: Current distance between grips.

Young's modulus E, is obtained by measuring the slope of the axial stress-strain curve in the elastic region. The yield stress ($\sigma_y$) appears as a change over from elastic state to a plastic state.

The stress and strain at break ($\sigma_b$, $\varepsilon_b$) were measured while the sample reached its ultimate elongation before ductile or semi-brittle failure occurred. The average values of the different mechanical greatnesses ($E$, $\sigma_y$, $\sigma_b$, $\varepsilon_b$) were computed on the basis of five test pieces by measurement point.

#### b) Thermal Analysis

The thermal analyses were performed employing a Thermogravimetric Analyzer (TG) and Differential Scanning Calorimeter (DSC) – TA Instruments DSC SDT Q600 (USA). It provides simultaneous measurement of weight change (TG) and accurate differential heat flow (DSC) on the same sample; it is controlled by the Thermal Advantage TM software (USA), allowing as such an analysis in true time.

On samples of around 30 mg, the DSC-TG tests were carried out in an inert gaseous environment ($N_2$) and in a temperature range (50-600 °C), with a rate of temperature rise of 10 °C/min. On the DSC thermogram, the glass transition temperature (*Tg*) characteristic temperature of an amorphous polymer was taken as the midpoint of the transition [3, 9, 10].

The thermogravimetric analysis was performed to assess the effectiveness of the stabilization systems on the rate of dehydrochlorination of the rigid PVC (u-PVC). From the thermogravimetric curve, it can be deduced the value of weight loss ($\Delta W$%) which corresponds to the difference between the initial weight ($W_i$%) and the final weight ($W_f$%) measured at the end of the step [10].

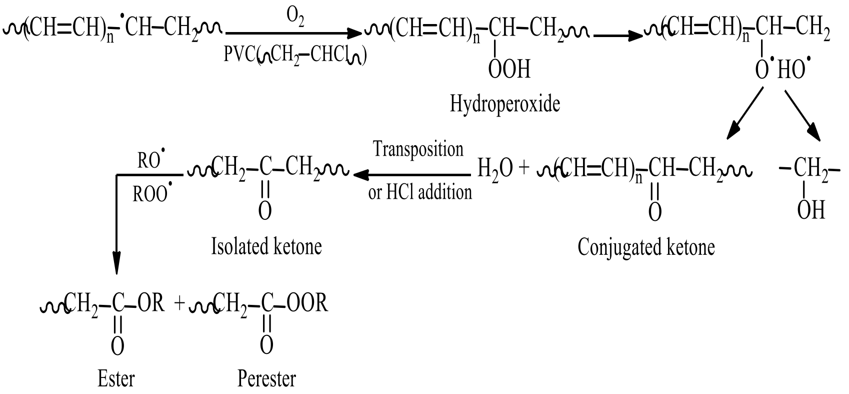
## Results and discussion

*Aging effect on the tensile properties*

The variations of Young's modulus (E), yield stress ($\sigma_y$), stress at break ($\sigma_b$), and elongation at break ($\varepsilon_b$) as a function of time of (u-PVC) thermally aged at temperatures of 80 °C, 100 °C, and 120 °C are shown in Figs. 2, 3, and 4.

The Young's modulus increases with aging time in Fig. 2, which is more pronounced for the sample aged at 120 °C. Indeed, the abrupt departure of the curve after 30 days of exposure corresponds with the sudden embrittlement visible in Fig. 3.

At the end of this aging protocol, the modulus increase rate is 51.84%. Unlike the other two protocols, the modulus of the sample aged at 100 °C decreased slightly after the first 30 days of exposure. (*Hadj amar et al.* 2022), using FTIR-ATR analysis on the same sample aged at 100 °C, demonstrated that the conjugated double bonds increased during the first 30 days, while the esters increased to a significant value during the first 60 days, owing to oxidation reactions of a critical concentration of double bonds reached during the first step of the aging protocol and occurring as described in the following mechanism [5].



*Scheme 1. Oxidation reactions of the polyene sequences [5].*

According to Fig. 3, the general trend of yield stress increases with aging time in all cases. It increased at a rate of 32.15%, 36.8%, and 34.8% over the first 30 days for the following temperatures (80, 100, and 120 °C). The sample aged at 120 °C became so stiff after 30 days that the yield point in the curve began to progressively disappear, indicating that it had lost its viscous aspect. Yield stress ($\sigma_y$) decreased significantly until the end of the aging protocol for the two others at 80 °C and 100 °C. The increase in yield stress and Young's modulus is primarily due to material stiffening caused by the thermal treatment's crosslinking process [1, 4, 6]. This process causes polyene sequences to propagate, resulting in the formation of chemical double bonds within the material structure [5].

The stress at break ($\sigma_b$) evolved differently depending on the aging temperature (Fig. 3). The sample aged at 80 °C showed no significant changes. Others aged at 100 °C and 120 °C saw a decrease of about 17% for the first and 46% for the second. This mechanical greatness provides a good indication of the material's ability to withstand the effect of increasing stress up to rupture. Temperature appeared to significantly reduce this capability [11].

The elongation at break (Fig. 4) for the samples exposed to the three different temperatures (80, 100, and 120 °C) decreased significantly throughout the aging period. At the end of the aging protocols, the rate of decrease reached 66%, 82.5%, and 99.75%, respectively. This rapid decrease in ($\varepsilon_b$) demonstrates the significant impact of temperatures above Tg on the material's mechanical resistance at the break. This is due to an increasing chain scission process with temperature, which results in the formation of a significant amount of oxidation products (conjugates, isolated ketones, and esters) [5, 6] on the sample surface (see Scheme 1), making it more brittle and lowering its toughness significantly [1, 4, 6].

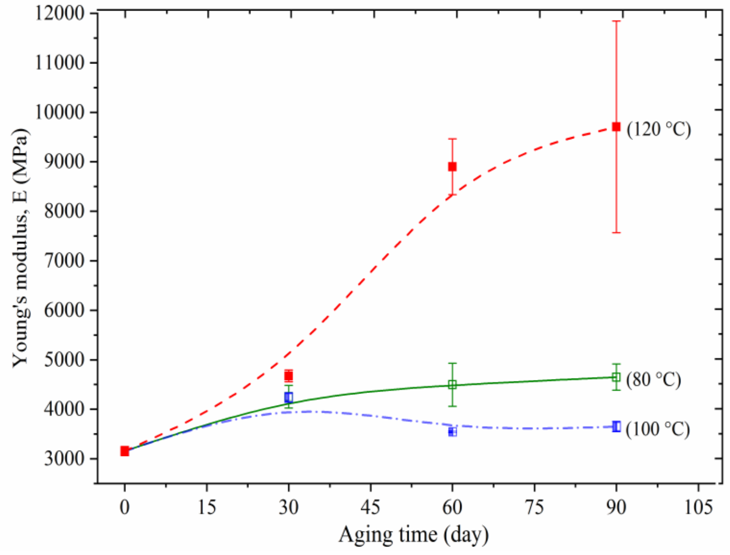


*Fig. 2. Evolution of Young's modulus of (u-PVC) aged at (80, 100 and 120 °C) versus aging time.*

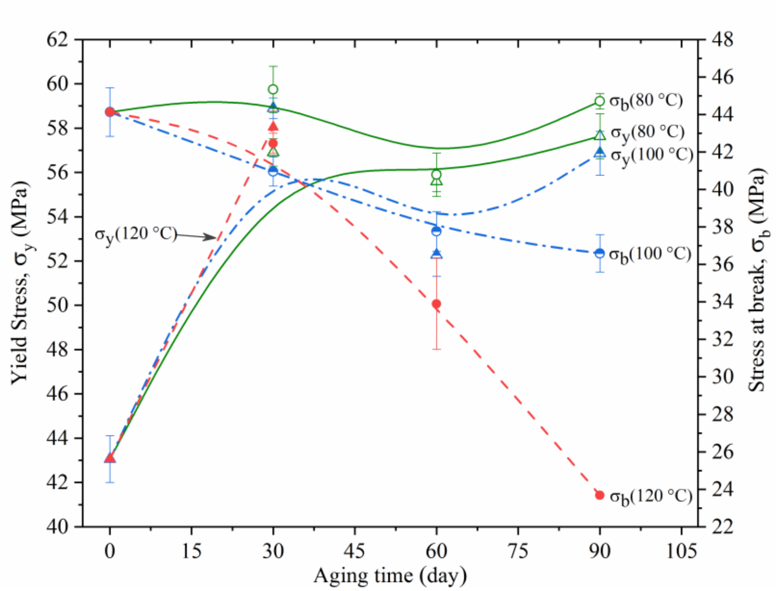


*Fig. 3. Evolution of stress at yield and stress at break of (u-PVC) aged at (80, 100 and 120 °C) versus aging time.*

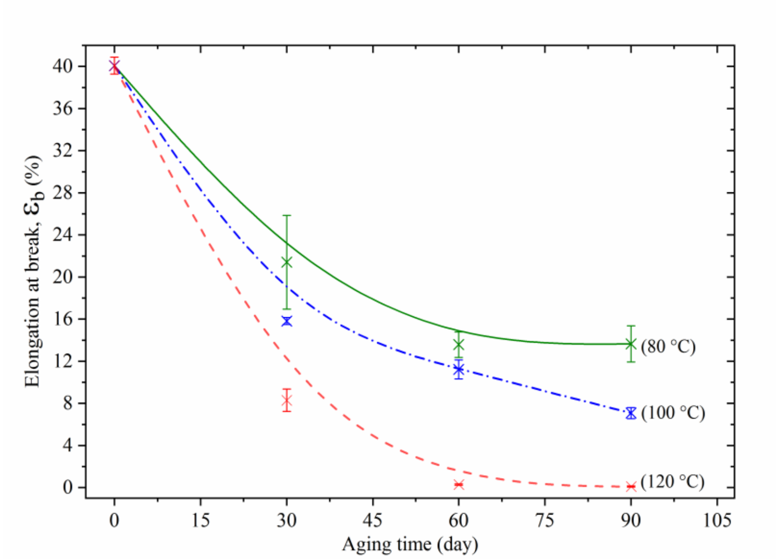


*Fig. 4. Variation of the elongation at break of (u-PVC) aged at (80, 100 and 120 °C) versus aging time.*

*Aging effect on the thermal properties*

(*Hadj amar et al. 2021*) discovered two transitions in the DSC thermogram of unaged rigid PVC. The first was observed in the temperature range (65-95 °C), and it corresponded to the glass transition temperature (Tg) of PVC's amorphous phase [6, 11]. The second, much larger transition appeared as a broad endothermic peak in the temperature range (236-360 °C), with a maximum (T peak) corresponding to the maximum rate of the dehydrochlorination process (d'HCl) caused by chlorine atom release [7, 13].

The values of the Tg and the dehydrochlorination (d'HCl) enthalpy peak versus aging time for samples aged at 80 °C and 100 °C are shown in Fig. 5. They were both determined using DSC thermograms for each aging time.

These two greatnesses varied only slightly with aging time for the sample aged at 80 °C, with a minimum at 30 days; this irregular but slight change indicated that the thermal properties are not adversely affected by aging [7].

Tg shifted from 79 to 82 °C (an increase of 3 °C) for samples aged at 100 °C. Tg has shifted to higher values as a result of structural changes related to crosslinking reactions [10, 12]. Similarly, the d'HCl enthalpy decreased noticeably with aging time, falling from 182 j/g to 142 j/g (a 40 j/g decrease). This enthalpy decrease can be attributed to the number of chlorine atoms already released during thermal aging, implying that the stabilizer was consumed and became less efficient in scavenging HCl during aging.

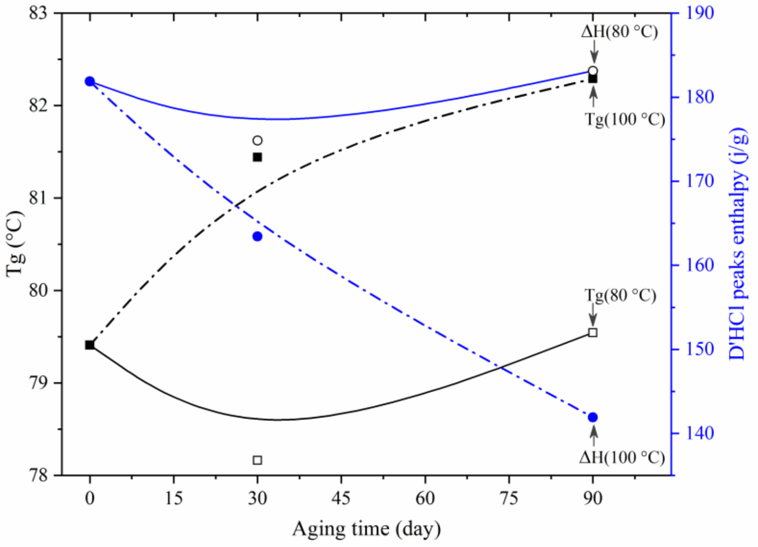
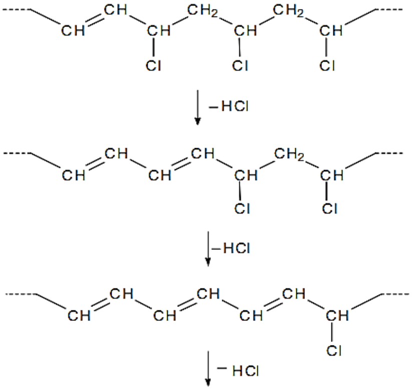


*Fig. 5. Evolution of the glass transition temperature and dehydrochlorination peak enthalpy of (u-PVC) aged at 80 °C and at 100 °C versus aging time.*

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the same samples are shown in Figs. 6 and 7. In both cases, the difference in total weight loss percentage between the oldest and youngest samples is not statistically significant. However, for the sample aged at 80 °C, the temperature at which weight loss begins (baseline dropout) decreases from 202 °C for the unaged sample to 186 °C after 30 days and to 86 °C after 90 days, respectively.

While the weight loss process began much earlier for the samples aged at 100 °C, it occurred at 58 °C for 30 days of exposure and at 52 °C for 90 days. This demonstrates the effect of higher aging temperatures not only on the increase of the oxidation reaction kinetics, but also on the progressive consumption of stabilizers with exposure time. Of course, the use of stabilizers contributes to the deterioration of material resistance. As a result, it is unable to maintain labile chlorides, which are more easily released via zip-elimination (scheme 2), and the resulting polyenes and radicals allow crosslinking, which tends to increase the Young's modulus [5, 7].



*Scheme 2. Zip-elimination of HCl [5].*

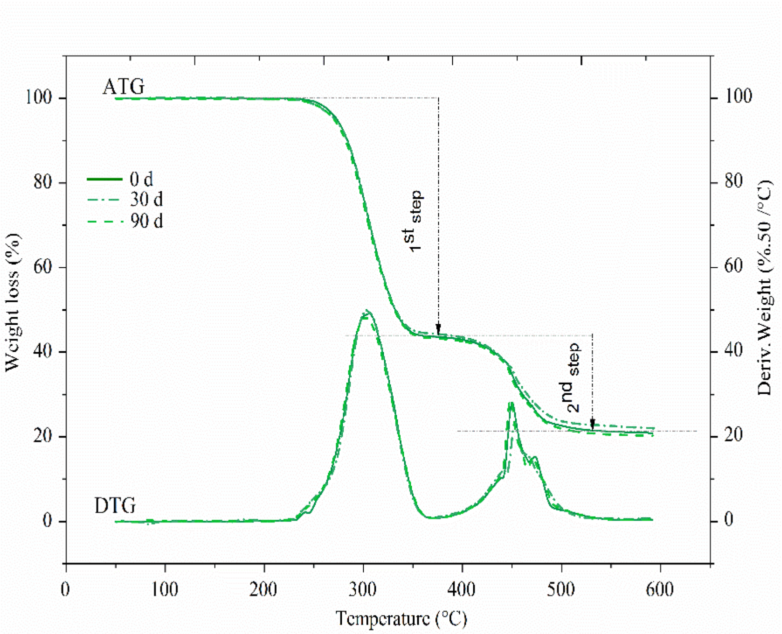


*Fig. 6. Thermogravimetric and differential thermogravimetric (TG, DTG) curves of (u-PVC) aged at 80 °C for three aging stages (0, 30 and 90 days).*

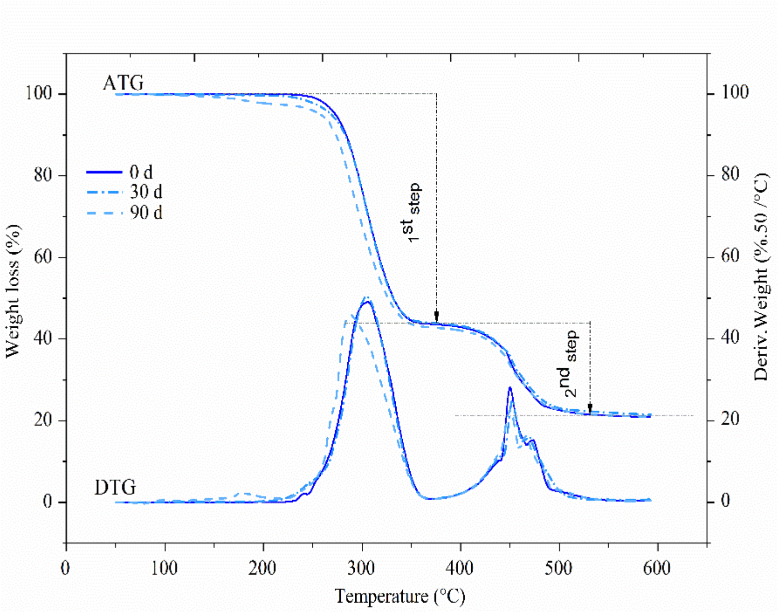


*Fig. 7. Thermogravimetric and differential thermogravimetric (TG, DTG) curves of (u-PVC) aged at 100 °C for three aging stages (0, 30 and 90 days).*

## Conclusion

The effects of thermal aging on rigid PVC tubes were studied at three different temperatures (80 °C, 100 °C, and 120 °C). For the first, these temperatures were chosen near the glass transition temperature and above for the other two. The mechanical properties of the rigid (u-PVC) were significantly affected by structural changes. During the entire duration of the aging protocols, chain scission and crosslinking reactions competed. The temperature had the greatest effect on the samples aged at 120 °C. Young's modulus (51.84%) and yield stress (34.8%) increased. This was due to the material stiffening globally as a result of an important crosslinking process known to reduce the viscous character of the material. In contrast to crosslinking, chain scissions that cause material embrittlement became more important near the end of the aging protocol. They caused a catastrophic drop in elongation at break of approximately (99.75%). As a result, the material transitioned from ductile to very brittle fracture mode.

The two processes of chain scissions and crosslinking become increasingly important for the sample aged at 100 °C over time. Furthermore, the increase in Young's modulus and yield stress during the first and last 30 days of the aging protocol indicates that crosslinking reactions are predominant during these two time periods. This also aided in raising the glass transition temperature at the end of the aging protocol. Young's modulus decreased significantly at the halfway point of the aging protocol, indicating that chain scissions became more prevalent.

Chain scission reactions are more effective in the first 30 days of aging at an aging temperature of around 80 °C. After 30 days, when Young's modulus reaches a significant value, crosslinking reactions become more important.

A comparison of the three aging protocols reveals that raising the aging temperature reduces elongation at break. This happened more frequently during the first 30 days of the aging protocol, indicating that chain scission reactions are more common. At higher temperatures, the stress at break is also affected by the stabilizer system consumption, affecting the material thermal resistance.

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