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ABSTRACT

Study of the Thermal, Hydrolytic, and Mechanical Aging Mechanisms of PDMS Through a Multi-Scale Experimental Approach

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Polydimethylsiloxane (PDMS) is a polymer widely used as a synthetic oil and as an additive in the cosmetics industry. In its crosslinked form, this polymer is used as a replacement for natural rubber in protective sheaths for electrical and electronic applications, and due to its biocompatibility, it is also found in contact lenses, valves, and catheters. The chemistry of this polymer is well-documented in the literature, which makes it possible to obtain PDMS with specific thermo-mechanical properties through precise control of the crosslinking density in these materials. Given its broad range of applications, PDMS is often exposed to various environments that cause material aging under different types of media. In this context, studies on thermal and hydrolytic aging have been reported in the literature. However, these studies have not focused on describing the physical and chemical changes in PDMS network under these aging conditions. Specifically, the chain scission mechanism, as well as the production and nature of dangling and free chains, and the effect of these structural changes on the durability of PDMS throughout its functional lifetime, remain poorly understood.

Moreover, the effect of mechanical fatigue on the structure of PDMS has not yet been studied. This work aims to fill these gaps through a comprehensive multi-scale physico-chemical investigation. To achieve this, three PDMS samples representative of industrial applications, each with different crosslinking densities, were aged according to three different mechanisms: thermal aging, accelerated hydrolytic aging, and mechanical fatigue under dynamic stress.

The evolution of the network structure (crosslinking node density, percentage of dangling and free chains) in both aged and unaged PDMS was characterized using Dynamic Mechanical Analysis (DMA, macroscopic scale) and solid-state NMR, which has previously been used to characterize the intrinsic structure of unaged PDMS. Swelling measurements and Differential Scanning Calorimetry (DSC) further complemented these investigations.

Through this approach, a direct relationship was established between the crosslinking node density, the percentage of dangling and free chains, the relaxation times of crossliked chains and the thermo-

mechanical properties of both aged and unaged materials. Indeed it was observed that thermal aging lead to an increase of crosslink density, resulting in higher mechanical moduli after aging, whereas mechanical and chemical ageing As a result, this work provided an original analysis recently published which was not available in the literature for PDMS before and which could be of interest to the industrial community. Additionally, the academic community may be drawn to this multi-scale approach as a means to better understand other functional crosslinked polymers, such as elastomers and thermosetting resins.

[1] Khaled, T., Rios de Anda, A., Richaud, E., Macromolecular and mechanical changes in aged silicones, Polymer Degradation and Stability (2025), p. 111211. doi: 10.1016/j.polymdegradstab.2025.111211