STUDY OF RATCHETING PHENOMENON AND INTERNAL STRESSES IN A HIGH-DENSITY POLYETHYLENE THANKS TO FLUORESCENCE SPECTROSCOPY

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High-Density Polyethylene (HDPE) is one of most used polymers in industry thanks to its beneficial properties, and its processing's low cost. That's why HDPE is employed in new industrial sectors, involving new mechanical solicitations and so new degradation mechanisms. One of them is ratcheting phenomenon, taking place during asymmetrical cyclic loading. This phenomenon generally results to stress-strain redistribution at different scales. The aim of this work is to measure internal stress thanks to fluorescent spectroscopy during these asymmetrical cyclic loads in the case of a semi-crystalline polymer. The internal stresses evolution is considered to discuss ratcheting behaviour and proposed physical base on cyclic behaviour.

The polymer adopted in this study is HDPE with crystallinity rate equal to 70 %. To allow extrinsic fluorescence, we select the Rhodamine 101 laser dye (Rh101). This laser dye insert preferentially in amorphous phase, between macromolecular chains, without reaction with them.

Ratcheting experiments were conducted at room temperature with a micro-tensile testing coupled with a fluorescence spectrometer, enabling to perform *in-situ* fluorescence spectroscopy during mechanical testing. All specimens were subjected to cyclic test at the same loading rate during the same time with $[\sigma_m ; \sigma_a]$, where σ_m is the mean stress and σ_a is the stress amplitude defined like $(\sigma_{max} - \sigma_{min})/2$. Simultaneously, fluorescent emission wavelength of Rh101 is recorded. As a matter of fact, the extrinsic fluorescence is function of the environment around the dye molecule. So, stress state modifications involve changes in polymer microstructure, changing the emission wavelength of Rhodamine. A link between this evolution of fluorescence emission wavelength and mechanical behaviour has been established, more particularly between emission wavelength and internal stresses developed during cyclic test in HDPE amorphous phase.

During tests, sinusoidal strain evolution with time is recorded, varying between ε_{max} and ε_{min}. So, ratcheting strain and strain amplitude can be determined respectively from $(\sigma_{max} + \sigma_{min})/2$ and $(\sigma_{max} - \sigma_{min})/2$. Strain amplitude doesn't vary very much according to time. However an increase of ε_a with increase of parameters values is observed whatsoever cyclic test conditions (σ_a or σ_m constant). Concerning ratcheting strain, two regimes of evolution can be distinguished. Similarly, an increase of ε_r with increase of parameters values is shown under σ_m constant or σ_a constant.

Moreover, internal stress in amorphous phase present two regimes, like ratcheting strain during time whatsoever cyclic test conditions (σ_m or σ_a constant). It is worth noting that internal stress and ratcheting strain present the same evolution as well as their respective rate. In order to compare internal stress evolution with ratcheting strain, $d\sigma_{ia}/d\varepsilon_r$ versus ε_r is calculated for all couples $[\sigma_m ; \sigma_a]$. The presence of one or two peaks can be observed which highlight a change in regime. Moreover, for each couples, critical ratcheting strain ε_{rc} can be determined which is the maximum of the first peak. We can join up ε_{rc} to change in regime observed on ratcheting strain experiment.

Ratcheting tests, using *in situ* extrinsic fluorescence spectroscopy, have provided information concerning relationship between ratcheting phenomena and internal stresses evolution in amorphous phase. Moreover the predominance of mean stress parameter on amplitude stress parameter in ratcheting strain has shown, even if σ_a play a sizeable function. It is worth noting that extrinsic fluorescence spectroscopy seems to be a very sensitive method to investigate the internal stresses developed in semi crystalline materials during fatigue test.