

## Streszczenie w języku angielskim

The unique physical and mechanical properties of semicrystalline polymers are derived from their equally unique structure. Indeed, during the solidification of most such materials, lamellar crystals are formed, separated by amorphous layers. The structural heterogeneity of the amorphous phase and the relatively limited number of experimental techniques allowing for direct analysis of disordered regions significantly restrict the possibilities of learning about the role of this component in the properties of semicrystalline polymers. At the same time, the contribution of the amorphous phase, typically ranging from 10 to nearly 100 wt%, means that the influence of this component on the properties or the deformation process of crystallizable polymers cannot be marginalized. The dissertation discusses the issue of micromechanisms activated during the plastic deformation of semicrystalline polymers at small strains, with particular emphasis on changes occurring in the amorphous component region.

In the present work, positron annihilation lifetime spectroscopy (PALS) was used for the first time in the plastic deformation analysis of semicrystalline polymers. During the course of the work, an adaptation of the PALS technique was carried out to enable the analysis of strain-induced structural changes in both crystalline and amorphous components. The study of the plastic deformation of high-density polyethylene (HDPE) and low-density polyethylene (LDPE), as well as polypropylene (PP), due to the relatively long time required for a single PALS measurement, was conducted in a "pseudo in situ" method using frames that allow the preservation of the stress state in the samples after deformation. Clamping conditions of the specimens in the designed frames were optimized. The mechanical response of the polymer samples was analyzed within the range of local strains (LS) of 0-0.25 (HDPE/LDPE) and 0-0.20 (PP). Studies using PALS and small angle X-ray diffraction (SAXS) techniques for HDPE and PP samples showed that the initial evolution of free volume pore size is mainly caused by changes in the thickness of amorphous layers. The normalized free volume pore size distributions provided evidence that the average "packing" density of the amorphous regions increases in the analyzed LS range. This, in turn, meant that the average pore size located in disordered regions (average lifetime of the ortho-positronium,  $\tau_3$ ) in the studied LS range is reduced compared to the non-deformed sample, even after the initiation of the cavitation phenomenon (the process of nano/micro-pore formation in the material). This effect was associated with the strongly anisotropic, ellipsoidal shape of cavitation pores at the time of their initiation-by the complementary use of PALS and SAXS techniques, it was possible to determine the aspect ratio of cavitation pores for selected LS values. It was also shown that the increase in the ortho-positronium lifetime dispersion ( $\sigma_3$ ) was caused by a significant reduction in the size of free volume pores existing in the material before deformation and the formation of cavitation pores. Based on the analysis of annihilation spectrum

parameters related to the crystalline phase, it was found that in the investigated range of strains the average positron lifetime ( $\tau_2$ ) did not undergo measurable changes, even after the activation of micromechanisms of plastic deformation of crystals, and the decrease in positron lifetime dispersion ( $\sigma_2$ ) was associated with the "homogenization" of the structure of crystallites due to the relative displacement ("slips") of crystal fragments within individual lamellae.

Next, the PALS technique was employed to study the influence of PP microstructure on its deformation process. The results of PALS and volume strain measurements provided evidence that within the examined LS range, the decrease in  $\tau_3$  values, coupled with an increase in value of volume strain, was caused by a change in the shape of the free volume pores in the amorphous phase from isotropic (spherical) to anisotropic (ellipsoidal). It was also confirmed that the  $\sigma_3$  parameter is an extremely "sensitive" to the presence/intensity of the cavitation phenomenon. In the case of a non-cavitating system (nonadecane-modified PP), there were no changes in  $\sigma_3$  values due to the deformation process, whereas for cavitating materials with different thermal history/microstructure, the  $\sigma_3$  parameter for deformed samples appropriately increased.

The final stage of work carried out within the doctoral dissertation focused on analyzing the evolution of free volume of the amorphous phase during the plastic deformation process of HDPE and LDPE as a function of temperature (-30-70°C) and strain rate ( $3.3 \times 10^{-2}$ - $3.3 \times 10^{-4} \text{ s}^{-1}$ ). In the case of non-deformed samples, it was shown that both the average size and free volume pore size distribution in the amorphous component of LDPE were significantly higher than in HDPE, which indicated a significant difference in the molecular packing density of the interlamellar layers. In the case of HDPE, an increase in strain rate or a decrease in temperature was found to contribute to an increase in the cavitation phenomenon with a decrease and increase in the values of the parameters  $\tau_3$  and  $\sigma_3$ , respectively. These results confirmed the previously presented concept of the anisotropic shape of cavitation pores at the time of their initiation/formation. Reducing the strain rate or increasing the temperature during HDPE deformation, on the other hand, led to the complete suppression of cavitation phenomena, accompanied by corresponding changes in parameters determined from annihilation spectra. On the basis of measurements of volume strain, SAXS and PALS, it was shown that in the case of LDPE, deformation conditions have no significant effect on structural changes occurring in disordered regions.

