Currently, over 400 million tons of polymers are produced worldwide, and the production systematically increases each year. The production of polymeric materials (by volume) has substantially exceeded the production of steel. If we analyze which kind of polymers are in the greatest demand, we will see that the first three positions on the list are occupied by the semicrystalline polymers: polypropylene, low density polyethylene, high density polyethylene. During the solidification of most of these materials, lamellar crystals and spherulites are being created. Between lamellae/spherulites there are non-crystalline, disordered regions called **the amorphous phase**. Semicrystalline polymers are lightweight, cheap and food contact approved, which makes them the materials of choice for packaging applications (≈40% of the produced polymers). For these types of applications, the barrier properties are usually critical. It is commonly accepted that the crystals are impermeable for even the smallest molecules of gas. Thus, the transport of gases through semicrystalline polymers takes place preferentially through the amorphous regions. The nanostructure of disordered regions seems to be a key parameter determining the barrier properties of a given polymeric material.

Accordingly, three main research activities have been selected that aim to better understand the correlation between the nanostructure of amorphous regions and the barrier properties of semicrystalline polymers. The project will involve conducting complex studies related to the **influence of the initial density of entanglements of macromolecules on the nanostructure of amorphous regions and, thus on the barrier properties of semicrystalline polymers (Objective I)**. Recent experimental studies have shown the non-negligible influence of the density of entanglements of macromolecules on the rheological and mechanical properties, as well as the course of crystallization and melting of polymers. However, the influence of the density of entanglements of macromolecules on the nanostructure of the amorphous regions, and thus the barrier properties of semicrystalline polymers, has never been analyzed. The model samples of selected semicrystalline polymers (polypropylene (PP), polylactide (PLA), poly(ethylene oxide) (PEO)) with a similar structure of the crystalline component and different entanglement density of macromolecules in amorphous regions will be prepared and analyzed.
The project will involve conducting systematic studies related to the **influence of the content and nanostructure of rigid amorphous fraction (RAF) on the barrier properties of semicrystalline polymers.** Additionally, it is planned **to find an effective method of modifying the rigid amorphous phase regions leading to an improvement of barrier properties (Objective (II)).** The influence of the RAF on the selected, especially mechanical properties of polymeric materials was studied in the past. However, the influence of the content and nanostructure of rigid amorphous fraction on the barrier properties of semicrystalline polymers, has never been systematically analyzed. The model samples of selected semicrystalline polymers (poly(ethylene terephthalate) (PET), poly(ether ether ketone) (PEEK) and PLA) with different content of rigid amorphous component will be prepared and analyzed. In the final stage of this objective, the modification of the rigid amorphous component was planned, leading to an effective increase of its “molecular packing”, resulting in reduction of average size of free volume pores and significant improvement of the barrier properties.
The project will involve conducting complex studies related to the **influence of the free volume size distribution (pore size distribution) of amorphous regions on the barrier properties of semicrystalline polymers (Objective (III)).** In many papers, the samples with close average free volume size exhibit completely different gas separation capabilities. Therefore, the model samples of selected semicrystalline polymers (high density polyethylene (HDPE), PP, PLA) with a similar structure of the crystalline component/average size of free volume pores but different free volume size distribution will be prepared and analyzed.

The comprehensive characterization of the structure/properties of model samples with the desired nanostructure of amorphous regions (as planned above) will be carried out using: positron annihilation lifetime spectroscopy (PALS), density gradient column (DGC), high-resolution microscopy (AFM, SEM, TEM), quasi-static mechanical measurements in uniaxial stretching mode; thermal and thermomechanical techniques (TGA, DMTA, DSC), x-ray scattering techniques (WAXS, SAXS), apparatus for barrier properties measurements. In the final stage of each task, the correlation between the nanostructure of amorphous regions and barrier properties will be determined and discussed.

The above presented objectives (related to the nanostructure and properties of the amorphous phase and its influence on barrier properties of crystallizing polymers) have been identified based on detailed analysis of literature data and on the potential influence of the results obtained as an effect of the accomplishment of the project on the development of widely understood materials engineering.