Changes of morphology during plastic deformation of cavitating semicrystalline polymers

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The mechanical properties of plastics determine their possible application. Although the deformation of polymers was studied for many years some aspects are still poorly recognized and understood. An example is the plastic deformation of uniaxially stretched semicrystalline polymers. It is known that existing spherulitic structure is in this process reorganized into fibrillar structure. Often the beginning of crystal deformation is accompanied by the formation of numerous voids inside the polymer. The cavitation process is usually detected by X-ray scattering technique or by optical observation of light scattering on voids. The voids are formed inside the amorphous phase, between crystalline elements, so the shape and size of voids depends on the changes of the surrounding polymer. The internal morphology at various deformation steps may be studied by the scanning electron microscopy. Samples for such studies are usually prepared by a frozen fracture followed by the permanganic etching. The etching procedure unravels the details of morphology.

Our previous studies of commercial polymers - polyethylene and polypropylene showed that the process of cavitation does not occur if the crystalline elements are small and defected [1,2]. The strength of crystalline phase is then lower than the strength of amorphous matrix. The relation between strengths may be changed by controlling of crystallization process. Fig. 1 presents the example of a mechanical response of the same material, polyethylene, crystallized quickly or slowly. In the first case, the small angle X-ray scattering (SAXS) studies shows that voids are not formed, in the second case the cavities are generated. The formation of cavities at the beginning of plastic deformation is seen on Fig. 1 as a rapid increase of X-ray scattering intensity. The change of pattern shape with deformation shows that the voids that were initially elongated perpendicularly to the deformation direction are at larger strains elongated in the deformation direction.

The occurrence of cavitation depends also on the deformation conditions, among them on the temperature. Slowly crystallized polypropylene usually cavitates at the room temperature and the evolution of X-ray scattering patterns for this polymer is similar to that presented in Figure 1b. However, when the temperature is 70 °C or more the X-ray scattering is observed only from periodic crystalline structure, which means that voids are not formed in this material near the yield point. The morphological changes in polypropylene samples deformed at selected temperatures are presented in Fig. 2. Initially, for small strains the circular lamellar aggregates - spherulites- are clearly visible. At the strain of 0.3 some voids are visible in polar regions of spherulites if the temperature is 25 or 40 °C. The number of voids and elongation of spherulites increases with deformation. Some new voids are visible at the strain of 0.7. The highly transformed structure appears for the deformation of 1.2. Strongly elongated fibrillar structures are accompanied by a large number of micrometer size voids. In the samples deformed at 70 or 100 °C the morphological changes are different. The cavities are not visible even at large strains. 1. Pawlak A., Polymer 2007, 48, 1397-1409

2. Pawlak A., Galeski A., Macromolecules **2008**, 41(8), 2839-2851



Figure 1. The example of transition from non cavitational to cavitational behavior in uniaxially deformed polyethylene. Stress-strain dependences and related SAXS patterns are presented for polyethylene prepared by rapid cooling from melt (a) and for the same material after slow cooling in the air (b). The increases of scattering intensities in Fig. 1b is results of cavitation for strains larger than 15%.



Figure 2. Evolution of internal structure of PP samples deformed at different temperatures. Morphology at different strain is presented: initial, 0.3, 0.7, 1.2. Deformation direction is horizontal.