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Cavitation during deformation of semicrystalline polymers

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ABSTRACT

Cavitation phenomenon is observed during deformation in many semicrystalline polymers above their glass transition temperature. Numerous voids (cavities) both nanometer and micrometer size are formed inside amorphous phase between lamellae during deformation of a polymer. The cavitation is observed only in tension, never during compression or shearing. Most often used methods of voids detection are: microscopies (SEM, TEM, AFM and light microscopy), small angle X-ray scattering and measurements of density. Usually the voids are detected close to yielding or at yielding, strongly suggesting that yielding is often caused by cavitation. However, there is a competition between two processes: breaking of amorphous phase leading to cavitation and plastic deformation of lamellar crystals. Which process occurs first depends on the relation between compliances of those two phases. If the crystals are weak and defected their deformation occurs (mostly by chain slips mechanism) without cavitation. If the crystals in a polymer are thick and more perfect then the barrier for their deformation, represented by shear yielding stress, is increased and the cavitation sets in first and yielding is determined by the stress needed for cavitation. Further deformation involves deformation of crystals due to rapid local change of stress around voids. The influence of different morphological factors: crystal thickness, crystallinity degree, arrangement of crystalline elements (e.g. in spherulites), morphology of amorphous phase (free volume, entanglements, tie molecules) were analyzed. Experimental factors, such as temperature of deformation and rate of deformation influence remarkably the formation of cavities. Cavitation is generated at points where a high local triaxial state of stress is developed. Triaxiality of stress can be amplified by a notch, even very mild notch with large radius of curvature stimulates generation of cavities. Evolution of nano-cavities into micro-cavities and change of their shapes with increasing deformation were evidenced by SAXS. Initially voids are oriented perpendicularly to deformation direction, however, with increasing elongation they become oriented along deformation direction. Stress whitening is visual sign of cavitation and is caused be light scattering either by microvoids or by assemblies of nanovoids.

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1. Introduction

A cavitation phenomenon, meaning the formation of numerous voids (cavities) in a solidified material is observed in many semicrystalline polymers deformed at temperatures above their glass transition. Many observations confirm that cavities develop when a polymer is stretched (uni- or bi-axially), but do not form in compression or shear. It means that a local three-dimensional tensile stress is important for voiding.

Plastic deformation of semicrystalline polymers is a complicated process, which is based not only on simple shear or crazing schema [1–4]. It includes the events in both phases: amorphous and crystalline. When the external force is applied to a polymer then initially the elastic response occur, by straining of molecular chains of the interlamellar amorphous phase. Amorphous phase above its glass transition temperature, has relatively low modulus and it is easy to initiate its deformation. Crystallities (lamellae) in the semicrystalline polymers are linked with amorphous phase and with other crystallities by entangled molecules and tie molecules. The crystals are stiffer than the amorphous phase, so they passively participate in deformation of the amorphous phase as internal, non-deforming objects. The deformation of amorphous phase leads to the interlamellar shear, rotation of lamellar stacks or separation of lamellae, depending on the local stress field [5]. The constraints imposed by the lamellae imply that only limited deformation can be accommodated by the amorphous phase. With an increase of force the stress-strain dependence becomes nonlinear and inelastic deformation occurs (e.g. Peterlin [6], Patlazhan and Remond [7]). When the limit is reached, a further deformation proceeds by the plastic deformation of crystals. The beginning of massive plastic deformation of lamellae is identified with macroscopic yield phenomenon.

Two distinctly different mechanisms have been suggested for yielding of semicrystalline polymers in the past. Historically first mechanism was initially proposed by Peterson [8,9]: crystallographic slips caused by an emission of dislocations from the edges of the lamellae and their travel across crystals resulting in crystal deformation. That idea that was explored further by Shadrake and Guiu [10] and more rigorously by Young [11]. There are two kinds of possible chain slips: coarse and fine. Both occur in planes containing macromolecular chains by generation and propagation of dislocations. Coarse slips are responsible for the formation of block structures from continuous lamellae and their fragmentation, fine slips change the orientation of lamellar planes in relation to the direction of macromolecular chains in crystals. Fine crystallographic slips causing lamellae rotation and thinning as well as coarse crystallographic slips leading to lamellae fragmentation were observed in numerous studies [2,3,12]. Rigorous theoretical considerations of dislocation generation and travel across crystals first by Young [11] and later by Argon et al. [13] led to the yield stress dependences on lamellae thickness, temperature and rate of deformation that were validated in several independent studies. Many evidences for correctness of that mechanism were found in the past (Wilhelm et al. [14]; Lin and Argon [2]; Seguela [15]; Kazmierczak et al. [16]; Young [1]). The model of thermal nucleation of screw dislocations [8,11,17] was demonstrated to account fairly well for the plastic behavior of polyethylene (PE) [18,19] and polypropylene (PP) [20] and for the yield stress dependency on the crystal thickness [16,21,22]. Dislocation theory predicts the correct order of magnitude of the yield stress that agrees best for the Burgers vector of dislocations equal to the crystallographic unit cell dimension along macromolecular chains [23].

Second mechanism for yielding connected with non-crystallographic changes, related to destroying crystals and resulting in a new crystalline ordering of the material, irrespective of the original structure but characteristic for the temperature of deformation was proposed later (e.g. [24–26]). It was suggested that during deformation an adiabatic heating occurs [27–29] when accompanied by the applied stress, partial melting and recrystallization takes place. It was also suggested that raising the temperature is not a necessary condition for partial melting and